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Photothermal imaging of optical polymers, polymer metal interfaces and photodegradation of polyvinyl chloride.

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by

Marc C. Prystay

A thesis submitted to the

Faculty of Graduate Studies and Research, McGill University In partial fulfillment of the requirements for the degree of

Doctorate of Science.

Department of Chemistry McGill University

Montreal, Canada

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Photothermal imaging of polymers

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## Abstract

Photopyroelectric spectroscopy (PPES) is a relatively new nondestructive photothermal technique that uses a pyroelectric sensor placed in intimate contact with thin film samples to record the photogenerated thermal waves transmitted by the sample. In this thesis it is demonstrated that photopyroelectric spectroscopy is capable of recovering profiles of optical absorptivity in micron scale thick polymer laminates with submicron depth resolution. The pyroelectric method has also been used to characterize adhesion at polymer/metal interfaces from the photothermal impulse response using both the transmission and inverse detection geometries. The PPES technique can also map the distribution of polyene bands created during photodegradation of polyvinyl chloride. Results are obtained in the frequency and time domains using conventional lock-in detection, excitation with wideband time domain sweep waveforms and wideband homodyne techniques. The experimental photothermal results can be modeled using the linear properties of heat conduction to obtain quantitative values of the optical and thermal properties of the samples.

## Résumé

La spectroscopie photopyroelectrique est une méthode d'analayse photothermique nondestructive relativement récente qui emploie un capteur pyroelectrique placé en contact érroit avec une mince pellicule d'échantillon dans le but d'enregistrer les ondes thermiques photogénérées transmises par l'échantillon. Cette thèse démontre qu'il est possible de distinguer les differentes zones d'absorptivité interne d'un échantillon de polymère lamine d'une épaisseur de l'ordre de quelques micromètres avec une resolution en profondeur inférieure à 1 µm. Cette methode a aussi été employée avec succés pour caracteriser l'adhesion à l'interface polymer/métal à partir des résponses aux pulsation photothermiques en employant taut la géometrie de transmission directe que celle de detection inversée. Il est aussi possible de determiner la distribution des polyène générés par la photodégradation du PVC par l'emploi de cette méthode. Les resultats sont obtenus en domaine de fréquence et de temp par la méthode d'une détection verrouillée conventionelle, d'une exitation en employant une envelope de balayage du domaine temps à bande passante large de même que la technique homodyne à bande passante large. Un modèle correspondant aux resultats expérimentaux peut être obtenu en employant les propriétés lineaires de la conduction thermique pour quantifier les proprietés thermo-optiques des échantillons.

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Many of the results presented in this thesis have been published in the following articles.

Chapter 2 has been presented as:

M.C. Prystay and J.F. Power, Spatial depth profiling of chromophores in thin polymer films using frequency domain photopyroelectric spectroscopy. Polym. Eng. Sci., 33(1) 43 (1993).

Chapter 3 has been presented as:

J.F. Power and M.C. Prystay, Rapid recovery of wide-bandwidth photothermal signals via photothermal spectrometry: theory and methodology. Appl. Spect., 47(4) 489 (1993).

Chapter 4 has been presented as:

M.C. Prystay and J.F. Power, Thermophysical measurements and interfacial adhesion studies in ultrathin polymer films using homodyne photothermal spectrometry. Appl. Spect., 47(4) 501 (1993).

#### Manuscripts and Authorship:

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Candidates have the option, subject to the approval of their Department, of including, as part of their thesis, copies of the text of a paper(s) submitted for publication, or the clearly-duplicated text of a published paper(s), provided that these copies are bound as an integral part of the thesis. -If this option is chosen, connecting texts, providing logical bridges between the different papers, are mandatory.

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- Additional material (procedural and design data as well as descriptions of equipment used) must be provided where appropriate and sufficient detail(eg. in appendices) to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.

- In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis of who contributed to such work and to what extent: supervisors must attest to the accuracy of such claims at the Ph.D. Oral Defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of the different authors of co-authored papers.

### Declaration of contributions to research.

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All work in this thesis has been done under the direction of the author's Ph.D. thesis supervisor, Prof. J.F. Power. Prof. Power outlined the studies to be completed for completion of this thesis when the author's research was first started. Specific contributions to work presented in this thesis are listed below.

Prof. Power has contributed significantly to the results of Chapter 3. The concept, theory and electronic circuitry of homodyne photothermal spectrometry was developed by Prof. Power. The author's contribution is in the areas of methodology and applications of the homodyne technique.

Prof. Power introduced the author to the concept of inversion of the photothermal signal developed in Chapter 5 and posed the problem in the integral Green's Function form. The Monte Carlo solution method was jointly developed but it was the author who characterized the inversion problem and put forward solutions to the problem.

Prof. Power wrote all Assembly Language routines used to interface the computers.

## Claims to originality

The contributions of this work to original knowledge are listed below:

1. The phase of the photopyroelectric frequency domain signal is able to detect the spatial distribution of optical absorption with submicron resolution in polymer films up to 100  $\mu$ m thick. Photothermal interference can be used as a tool to enhance the sensitivity of the magnitude of the frequency response to the distribution of chromophores.

2. Wideband homodyne photopyroelectric spectrometry is capable of studying ultrathin polymer films of thickness 80 nm to 1500 nm. The technique is limited to the study of polymer films thicker than 80nm by a 400 nm depoled layer at the surface of commercially supplied PVDF films which effectively filters the thermal response. The technique is limited to a maximum thickness of 1500 nm by the electronic high pass filter which must be kept above 1000 Hz to prevent corruption of the downshifted signal by low frequencies of the upshifted signal.

3. Photopyroelectric interfacial adhesion studies made with thin polymer films spin coated onto the PVDF film will be able to only detect large thermal mismatches due to the thermal filtering effect of the 400 nm depoled layer in the PVDF films.

4. Photothermal impulse response signals generated in thermally continuous samples can be inverted to recover the thermal flux profile by posing the problem as a solution to the free space Green's Function. The problem is ill posed as written due to the matrix being rank deficient and ill conditioned; however, by adding small amounts of noise to the Green's Function matrix the matrix becomes full rank and the conditioning is greatly improved. By averaging of a large number of inversions, each seeded independently and randomly, the thermal flux profile can be accurately reconstructed.

5. Polyvinyl chloride degraded under high optical flux will generate local spot degradation that exhibits optical birefringence. The lightly degraded features can be studied with photopyroelectric spectroscopy and the distribution of specific polyene bands can be mapped. Photothermal impulse responses can be inverted to recover the thermal flux profiles and the thermal flux profiles can then be used to reconstruct the optical profiles in the polyvinyl chloride films.

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### Acknowledgments

The author wishes to express his sincere gratitude to Dr. J.F. Power for her supervision and direction in the course of his studies. The author also thanks her for the time spent teaching the theoretical aspects of photothermal sciences and signal processing techniques.

A special thanks goes out to the technical support staff of the department of chemistry at McGill University. Mr. Roland Gaulin helped in modifications of the lock-in amplifier and rechecked the wiring of the xy translator for safety. Mr. Rick Rossi was invaluable in his help maintaining the lasers. Mr. Fred Kluck and Mr. Bill Bastian are thanked for their work in custom fabrication of the pyroelectric sensor holder and other small devices needed in the course of the research.

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Chapter 1:

Introduction

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The work presented in this thesis is an advancement in the development of photothermal spectroscopy as a tool for the study of the optical and thermal properties of solid phase polymer films. The photothermal method, as applied in this work, is based on the understanding that light is absorbed in homogeneous media according to Beers Law and molecules excited by the incident light decay non-radiatively, generating heat. The change in temperature can be monitored with appropriate transducers and using the linear properties of heat conduction the optical and thermal properties of the sample can then be reconstructed. The best known of the photothermal techniques is photoacoustics which records acoustic emission in the gas phase due to heating of the sample. However, photoacoustics is only one technique in a wide range of photothermal methods which will be discussed in this thesis.

This thesis is separated into 8 chapters. The first, the introduction, provides a comprehensive review of pertinent work done in the field of photothermal spectroscopy and is intented to make the reader familiar with the subject of the thesis. It also includes a review of photodegradation studies in polyvinyl chloride (PVC) and examines the premise that photothermal techniques are well suited to the study of degradation in polymers. Chapters 2 to 7 are written in the style of papers for publication. Each chapter has a brief introduction relevant to the particular work and is followed by the associated figures and references. Chapter 2 is devoted to frequency domain imaging of of optical polymers, chapter 3 covers the design and construction of a wideband homodyne photothermal spectrometer and chapter 4 shows application of the homodyne technique

to the study of nanometer scale thin films. In chapter 5 we present a new inverse modeling technique to obtain the optical profile of a sample from the photothermal signal. Chapter 6 applies the inversion technique to well characterised optical polymers and characterizes the instrumentataion considerations required. In Chapter 7 amplitude and phase modulated (AM-PM) photothermal spectroscopy is used to image degradation profiles in polyvinyl chloride (PVC). The inversion techniques developed in chapter 5 are used to recover the depth dependence of conjugated double bonds that form in the degradation process. Chapter 8 concludes the thesis with an overview of the work presented and looks forward to possible future studies. The appendices at the back of the thesis contain computer programs, instrument designs and schematics required to continue this work.

#### History

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It was A.G. Bell who first reported in 1881 that samples periodically heated by light absorption emitted an acoustic signal [1,2]. Bell attibuted the signal to heat conduction processes and correctly noted that the magnitude of the acoustic signal was related to the amount of light absorbed and the physical structure of the sample. Photothermal methods were not developed for a specific use until Luft (1943) [3] and Pfund and Fastie (1947) [4] developed photothermal techniques for detecting trace concentrations of anaesthetical gases. The foundation for photothermal methods in solids was advanced by Parker (1973) [5] and Rosencwaig [6-8] who developed analytical methods and showed that the signal generation in photoacoustics could be attributed to the conduction of heat from the sample into the air. Since that time the development of photothermal spectroscopy and thermal wave imaging in condensed media has grown both experimentally and theoretically. To review the advancements made to date it is first necessary to introduce some basic principles and define some of the associated terminology of thermal wave imaging.

## Basic Terminology

It has long been realized that thermal waves are a critically damped phenomenon, meaning that the magnitude of the signal decays exponentially with distance and the rate of decay depending on the thermal diffusivity ( $\alpha$ ) of the medium. The thermal wavelength ( $\mu$ ) is defined as the distance the wave travels before decaying to a value of 1/e.

(1) 
$$\mu = \left(\frac{2\alpha}{\omega}\right)^{1/2}$$

It is noted that the wavelength is inversely proportional to the square root of the modulation frequency ( $\omega$ ). Therefore, at low modulation frequencies the thermal wavelength is the longest permitting thermal probing of buried structures. As the modulation frequency is increased the wavelength is shortened imaging only shallow features. By launching thermal waves of known length into opaque samples one can obtain depth dependent information about the thermal nature of the sample. The thermal properties of a number of substances are given in table 1-1 along with the distance a thermal wave would travel at 10 Hz. Insulators such as wood have shorter thermal

wavelengths than conductors such as aluminum [9].

Thermal coupling coefficients, bij, can be calculated to determine how efficiently heat is transfered from one layer to another.

(2) 
$$b_{ij} = \frac{\kappa_i \alpha_j^{1/2}}{\kappa_j \alpha_i^{1/2}}$$

Here ki is the thermal conductivity of the ith layer. If the two adjacent layers are thermally well matched bij=1. If layer j is an insulator, all the heat preferentially stays in layer i and bij<1. For a highly conductive layer j the coupling coefficient becomes large, bij>1.

The thermal effusivity mismatch  $(\gamma)$  is a more widely used form that relates how well the thermal energy is transferred from one sample to another and can be thought of as "thermal reflectivity" term.

(3) 
$$\gamma = \frac{b_{ij}-1}{b_{ij}+1}$$

The thermal effusivity mismatch is somewhat easier to understand. Values of  $\gamma$  range from -1 for an insulating layer j which totally reflect thermal waves to +1 for a thermally conducting layer j which totally absorbs thermal waves. A value of 0 signifies that layers i and j are thermally well matched.

# Table 1-1

Typical thermal properties of various materials at 300K.

Material	Thermal conductivity	Thermal diffusivity	Thermal wavelength
	κ (W/m·k)	α (m²/s)	@ 10Hz (µm)
Pure Aluminum	237	97.1 x 10 <sup>-6</sup>	4,407
Stainless Steel	15.1	3.91 x 10 <sup>-6</sup>	884
Plywood	0.12	1.81 x 10 <sup>-6</sup>	486
Plate Glass	1.4	7.47 x 10 <sup>-6</sup>	386
Air	0.026	22.5 x 10 <sup>-6</sup>	2,121
Polyvinyl chloride	0.16	1.2 x 10 <sup>-7</sup>	1,550

All valves taken from reference [9] except polyvinyl chloride which was taken from reference [211].

Non-radiative decay of absorbed electromagnetic radiative serves as the source of thermal excitation within the sample. Broadband light sources and lasers can be used to make single wavelength or multi wavelength photothermal studies from the ultraviolet (UV) to the infra-red (IR) range of the electromagnetic spectrum. Electron sources have been used to provide high resolution of grain boundaries in metals and silicon wafers [10,11] and X-rays, microwaves and ion beams have also been adapted for specific use [12-16]. In most samples there is almost no delay between the photoexcitation of the sample and the onset of heating. For these cases the interpretation of results are modeled using linear properties of heat transfer. However for a wide range of samples other nonthermal mechanisms of signal generation exist. These include luminescent samples and semiconductors where absorbed light may produce metastable states or electron hole pairs which have distinctly slow and unique rates of relaxation compared to the non-radiative decay process [17,18]. Also possible are thermally induced elastic waves and thermal elastic deformations in the heated region: both of which need to be modeled coupling the elastic and thermal properties of the samples. For the purpose of this thesis we leave aside these considerations. By using the correct experimental geometry and analyzing non-fluorescent polymers the responses can be correctly modelled as a thermal response alone.

The signal generation process in a homogeneous polymer film is schematically illustrated in Fig. 1-1. In the frequency domain photothermal experiment modulated radiation incident on the sample generates modulated heat within the sample. The modulated heating can be modeled as a damped thermal wave diffusing through the sample which travels a maximum distance ( $\mu$ ) before decaying to 1/e. Sources deeper than  $\mu$  will not launch thermal waves long enough to reach the surface of the sample to be detected. Changing the modulation frequency changes  $\mu$  thereby permitting photothermal depth profiling in the sample. To ensure that the recorded thermal signals can be interpreted quantitatively only linear heat conduction processes are permitted to exist in the sample. In practice this restriction limits the excitation signal to low powers to prevent the non-radiative decay mechanisms and the heat conduction process from being driven into saturation. The linearity criterion is given by the following relationship where L is a generalized operator.

(4) 
$$L(k_1 T_1 + k_2 T_2) = k_1 L(T_1) + k_2 L(T_2)$$
 and  $k_1, k_2$  are arbitrary constants.

In terms of the sample response this means that the observed photothermal signal from the sample is the sum of all the individual responses in the sample. Theoretically one can then divide the sample into N layers, calculate the phtothermal response of each layer then sum the responses to obtain the recorded signal. A linear response is obtained if the signal is proportional to the temperature response of the sample, its derivative, its integral or its average.

To further simplify the signal interpretation the analysis of the heat transfer is limited to one dimension (1-D). 1-D heat conduction implies that the photothermal waves travel



with flat wave fronts and lateral heat transfer in the sample is negligible. This is ensured by using an excitation beam that is at least 3 times as wide as the sample thickness. For the work in this thesis the beam was much wider than the sample thickness ensuring 1-D heat transfer.

## Detection methods for measuring photothermal signals.

When Bell first studied photothermal phenomena he suggested the use of microphones to detect the acousitic emission in the gas next to a heated sample. However, since then a wide range of new detection methods have been proposed. Some of these include optical detection of refractive index changes due to thermal gradients [21-23], secondary infrared emission due to heating [24-27], detection of sample temperature using pyroelectric polymers [28-29], measurement of reflectivity changes due to heating [30,31], thermal lens based detection systems[32-35] and a range of photoelastic detection systems[34-37].

# (i) Photoacoustic Spectroscopy

In Photoacoustic spectroscopy (PAS) the sample is placed in an enclosed cell equipped with a window at the top to transmit the excitation source and a microphone or piezoelectric inside to record the acoustic emission. The signal is generated by the periodic heating of the sample which then adiabatically heats the gas boundary layer and creates a thermal piston through the periodic gas expansion in the chamber. The resulting signal is not strong due to the mismatch of thermal effusivity that exists between the gas and sample. The heated region is typically confined to one thermal wavelength in the air and the pressure change that is detected by the microphone is the spatial average of the temperature change of the gas interphase which is heated [8].

(5) 
$$\Delta P \propto \frac{1}{2 \pi \mu_{gas}} \int_0^{2 \pi \mu_{gas}} \Delta T_{gas} (z, \omega) dz$$

The exact nature of the recorded signal is effected by the design of the cell and the nature of the sample [38]. The frequency response of a PAS instrument is limited by the sensitivity and frequency response of microphones.

Rosencwaig and Gersho first interpreted the PAS signals in terms of a purely thermal model and put forward the interpretation of a thermal piston (R-G theory) [8]. MacDonald and Wetsel expanded on the model to account for the periodic average expansion of the sample as well as the gas [39]. Jackson and Amer introduced the buckling or drum effect which is seen in both piezoelectric and gas microphone detection systems [40]. Korpiun and Tilgner were able to model a phase transition as an oscillating interference [41] then Monchalin *et al.* accounted for the periodic heat and gas flow in a powdered medium [43].

### (ii) Photothermal Deflection Spectroscopy

Photothermal deflection spectroscopy (PDS) or mirage effect spectroscopy uses a laser probe beam skimmed along the sample surface to detect the heat transfer from the sample to air or a coupling liquid. Heat transfer from the sample to the coupling fluid sets up a spatially dependent refractive index gradient that will bend or refract optical waves passing through it. The probe beam can be positioned to deflect transversly, parallel to the sample surface, or normal depending on the experimental geometry. The beam deflection in the normal direction is sensitive to the spatial gradient of the refractive index set up by conduction of heat into the air. The gradient is sensitive to the sample surface temperature and thus the beam deflection is related to the thermal transport in the sample. The change in the temperature (T) in the gas phase can be related to the deflection of the probe beam  $\theta$  according to:

(6) 
$$\theta \propto \frac{1}{\eta} \frac{d\eta}{dT} \frac{dT}{dx}$$

Where  $\eta$  is the reflective index of air on the coupling fluid [22].

The transverse deflection is sensitive to vertical cracks in the sample which inhibits the

flow of heat in the sample and formation of the temperature gradient in the air. The deflection of the probe beam at any point along the probe beam path is defined by  $d\theta = \eta^{-1}xdl$  where dl is the incremental step. The total deflection is calculated as the integral over the entire path length. Deflections of  $1x10^{-19}$  radians have been reported making the technique sensitive to even small temperature gradients [22].

The PDS technique has the advantage of being a nondestructive, noncontact detection scheme making it applicable in harsh environments or possibly as a portable instrument for work in the field. Like PAS PDS requires the heat to be transferred from the sample to the air or an adjacent fluid. As a result, the frequency reponse is limited by the closeness to which the probe can be placed to the sample. The air layer acts as a thermal low pass filter with a roll off frequency that decreases with larger probe beam offsets. PDS was first described by Boccara, Fournier and Badoz [22] and Murphy and Aamodt [21,23].

## (iii) Photothermal Infrared Radiometry

Photothermal infrared radiometry (PTIR) measures the blackbody radiation of a sample after an applied heating pulse. PTIR operates on the premise that with a small change in temperature the spectral emission envelope does not change, but the intensity of the signal will change linearly. The secondary IR emission intensity (W) from a heated source is goverened by

$$(7) \qquad W = \varepsilon \sigma T^4$$

where  $\varepsilon$  is the bulk emissivity of the sample which is assumed to be constant over all space and temperature used in the experiment, and  $\sigma$  is the Stefan Boltzman constant (5.6 x 10<sup>-12</sup> W cm<sup>-2</sup> K<sup>-4</sup>) [24]. For a given change in surface temperature dT there is a change in emittance of

(8) 
$$dW = 4 \varepsilon \sigma T^3 dT$$
.

Monitoling of the IR emission is usually done with Mercury-Cadmium-Telluride detectors or infra red photon counting devices. Samples are assumed to absorb excitation light according to Beer's Law and to reabsorb the emitted IR by Beer's Law. As a result buried features will emit radiation that is absorbed by overlayers according to  $e^{-\beta'x}$ , where  $\beta'$  is the absorptivity of the emitted light. The signal recorded by the camera is the integrated over the thickness of the sample (1) [25].

(9) 
$$S_B = G \varepsilon \sigma \beta' \int_o^l e^{-\beta x} \Delta T(z, r, t) dz$$

Here G is a constant determined by the intensity and bandwidth of radiation. In practice optical filters are used to examine only wavelengths of interest to improve sensitivity. Unlike PAS and PDS PTIR does not rely on heat transfer into the gas phase for signal

generation rather it monitors the surface temperature directly. As such the bandwidth is limited to the speed of the detectors available and the integration times required. Like PDS, PTIR is a noncontact imaging method. However, the large powers required to generate an adequate IR signal can easily damage a delicate sample or at least drive it into a nonlinear thermal response.

PTIR was first proposed by Nordal and Kanstad [24,26] and developed with the help of Busse [25,44] then Leung and Tam [27]. The parallel processing capabilities of this technique make it feasible for imaging large scale objects such as aircraft fuselage sections once the technique becomes well characterized [45].

## (iv) Photothermal Reflectance

Photothermal reflectance (PTR) detection is based on a change in surface temperature causing a change in the optical reflectivity of the sample according to

(10) 
$$\Delta R(x, y, z, t) = R_o + \frac{dR}{dT} \Delta T(x, y, z, t)$$

where dR/dT is the temperature coefficient of reflectivity. The technique is applicable to samples that undergo a relatively large reflectance change with heating. Imaging of silicon devices has been the primary application of this technique. The bandwidth is limited to the response time of photodetectors which are available into the MHz region for visible wavelengths. Rosencwaig *et al.* first proposed the technique to monitor heat and carrier diffusion in semiconductors. [30,31,45]. The thermal reflectance was found to be dependent not only on the change in dielectric properties associated with heat but also the charge carrier distribution which varied with heating [30]. Because the time dependencies of these two reponses are different the two effects can be separated [31,47]. To improve sensitivity temperature sensitive coatings glazes have been developed to coat the samples before imaging [30,48].

### (v) Photothermal Lens

Photothermal lens imaging (PLI) has been adapted from the study of liquid samples to the study of biological and organic structures which transmit specific wavelengths of laser light. PLI involves passing two different laser wavelengths through the same small volume of a sample. One laser is absorbed and sets up a thermal lens in the localized area while the second is deflected by the associated refractive index gradient [32]. Burgi and Dovichi have used this technique to image fine structural features in leaves and measure local diffusivity changes of 1% across the samples [33]. The technique is sensitive to light absorption requiring absorptivities of only 1 x  $10^{-9}$ [49]. Similar ideas have resulted in internal optical beam deflection studies in transparent substrates [50]. Probe beams are no longer restricted to the surface, but rather pass through the sample directly and detect the thermal waves through the spatially dependent refractive index change within the sample itself.

#### (vi) Photopyroelectric Detection

Photopyroelectric effect spectroscopy (PPES), is the photothermal technique used in this thesis. It involves placing the sample in intimate contact with a pyroelectric sensor and measuring the temperature change across the pyroelectric due to thermal waves transmitted through the sample. The technique was first proposed by Luukkala [51] and later Yeack *et al.* used a lead-zirconate-titanate pyroelectric sensor to measure the diffusivity of a metal coated mylar sample [52]. However, the technique was made attractive by Coufal [28] and Mandelis [29] who used polyvinylidene difluoride (PVDF), a pyroelectric polymer as a thin film calorimeter.

Units of the PVDF monomer, vinylidene fluoride ( $CH_2=CF_2$ ), polymerize to give a greater than 90% head-to-tail configuration [34]. For this reason the polymer exhibits a high net dipole moment of its monomer. To obtain significant piezo and pyroelectric activity the polymer is poled in a high electric field above its Curie temperature which aligns the electric dipole moment perpendicular to the surface of the film placing the fluorine atoms on one side of the carbon backbone and the hydrogen atoms on the other. When thermal energy is absorbed the PVDF film expands due to the increasing temperature. This deformation produces a detectable change in the dipole moment which can be recorded. By metalizing the front and rear surfaces of the PVDF, electrodes can be used to obtain the spatially averaged response of the entire PVDF film.

In the experiments by Coufal [28] a 9 µm PVDF film was used to obtain the absorption characteristics of Nd<sub>2</sub>O<sub>2</sub>-doped polymethyl methacrylate films. Later he showed that the 100 nanosecond rise time of the PVDF was fast enough to study nanometer thin polymer films [53-56]. Mandelis demonstrated the potential of the technique by obtaining the optical spectrum of Ho<sub>2</sub>O<sub>3</sub> hydrated powders and monitored the kinetics of the chemical reduction of CuO in to metallic copper by HCl [29]. Ghizoni and Miranda soon after used the method to measure the thermal diffusivity of a silicon crystal using a lateral heating source [57]. Mandelis and Zver developed the one dimension heat conduction reponse of the PVDF signal and categorized the reponse of the detector based on the optical and thermal properties of the sample and the modulation frequency of the excitation source [58]. A number of papers followed from Mandelis et al. covering PPES detection of thermal waves with capacitive electrodes to detect structural flaws [59,60]. They argued that since both the detector and source are localized and can be scanned independently, the apparatus has the potential to perform tomographic imaging. The use of pyroelectric arrays for parallel processing has been discussed by Whatmore [61] and Watton et al. 62]. Sandhu and Gooding constructed a CCD multiplexer for a pyroelectric thermal imaging array with 256 point detection elements [63]. These parallel imaging techniques combined with the potential for tomography using the capacitive techniques suggest that parallel imaging with PPES may soon be feasible.

Spectroscopic studies of polymer films with the TPES technique have recently been published. Power used time domain techniques to accurately recover optical profiles in polymer laminates [64,65] and Fourier Transform infrared photopyroelectric spectroscopy of a variety of polymers and epoxies has been demonstrated on a modified commercial instrument [66].

#### Development of the photopyroelectric effect signal (PPES).

The model used to interpret PPES signals arises from the first photothermal model put forward to describe the photoacoustic signal [8]. From the approach of the R.G. theory many workers have adapted the PAS model for application in all detection strategies and modified the nature of the absorbing medium to span a wide range of sample types. Regardless of the detection method used these theories have application to photothermal spectroscopy in general. A review of the 1-D thermal wave model is presented here and developed to promote a better understanding of the physical processes involved.

As mentioned earlier, the thermal wave is a critically damped wave, the exact length ( $\mu$ ) dependent on the thermal diffusivity of the medium it travels in and the modulation frequency used to generate it according to equation (1). The resulting thermal wave is attenuated to 1/e of its peak amplitude in one thermal wavelength  $\mu$ . In addition, the thermal wave is highly dispersive in nature. The monochromatic phase velocity of the wave is given by  $\upsilon = \omega \mu$ .

A typical photothermal model is set up in Figure 1-2. The sample and the environment are divided into discrete thermal layers each with its own set of optical and thermal
properties. Following the RG theory the sample and its environment are divided into 3 layers: gas, sample, and backing. The heat conduction equation is then written for each layer in the model and a source term S is included in the sample to account for the generation of the thermal wave.

(13) 
$$\nabla^2 T_1 - \frac{1}{\alpha_1} \frac{dT_1}{dt} = 0$$
 *i* gas

(14) 
$$\nabla^2 T_2 - \frac{1}{\alpha_2} \frac{dT_2}{dt} = S$$
 ii sample

(15) 
$$\nabla^2 T_3 - \frac{1}{\alpha_3} \frac{dT_3}{dt} = 0$$
 iii backing

From the point of view of convention and ease the equations are most easily solved in the frequency domain. The nature of the source term S is dependent on the nature of the sample being studied. Polymers absorb light according Beer's law; therefore, for a optically homogeneous layer in a harmonically modulated light field S can be written as

(16) 
$$S(x,t) = A_0 e^{\beta x} (1 + e^{j\omega t})$$

 $A_0$  is a constant that accounts for the light intensity and the non radiative conversion factor. It can be normalized and set to unity. Under the same harmonic assumption the temperature response of the gas, backing and sample due to heating can be written as

(17) 
$$T = T_0 e^{j\omega t}$$

Substituting equation (16) and (17) into equation (13-15) yields the thermal wave equation for each layer (i).

(18) 
$$\frac{d^2T_i}{dx^2} - \frac{j\omega}{\alpha_i} T_i = S_i$$

This can be written and solved as the Helmholtz equation

(19) 
$$\frac{d^2T_i}{dx^2} - \sigma_i^2 T_i = S_i$$

where 
$$\sigma_i = \left(\frac{j\omega}{\alpha}\right)^{1/2}$$
 is the wave number definition.

The Helmholtz equation can be solved in each of the layers in the sample by linearity and the assumption of harmonic excitation. This produces the temperature response for each layer.

(20) 
$$T_1 = \left\{ A_1(\omega) e^{-\sigma_1 x} \right\} e^{j \omega t}$$
 (i) for  $x > 0$ 

(21) 
$$T_2 = \left\{ A_2(\omega) e^{+\sigma_2 x} + A_3(\omega) e^{-\sigma_2 x} - A_0 e^{\beta x} \right\} e^{j \omega l}$$
 (*ii*) for  $-l < x \le 0$ 

(22) 
$$T_3 = \left\{ A_4(\omega)^{+\sigma_3(x+l)} \right\} e^{j\omega l}$$
 (iii) for  $x < -l$ 

The boundary conditions A1-A4 are coupled together through the boundary conditions of constant temperature and constant thermal flux across each interface. For each boundary there are thus two equations, creating a system of 4 equations (2 temperature and 2 flux) and 4 unknowns (the 4 boundry conditions A1-A4).

The temperature response for any point in the sample or outside of the sample can be determined as a function of frequency by solving the appropriate equation. For photoacoustic and photothermal deflection spectroscopy the temperature in the air layer above the sample is solved. Radiometry requires knowledge of the temperature at the sample surface x=0 or x=-1. Photopyroelectric effect techniques require that the temperature in the backing layer be solved. Once the thermal component of the signal

is calculated, it can be substituted into the appropriate electrical equations to obtain the theoretical pyroelectric response. The charge (Q) that accumulates in the pyroelectric due to a change in temperature  $\Delta$  T is given by [67]

$$(23) Q = p \Delta T$$

where p is the pyroelectric coefficient. For a PVDF film of thickness d exposed to a sinusoidally varying field the average change across the film due to the pyroelectric effect is

(24) 
$$Q = p\Delta T = \frac{p}{d} \left\{ \int_{-l}^{-(l+d)} T_3(x) dx \right\} e^{jwt}$$

Therefore, to obtain the average charge across the film one obtains the average temperature response of the backing layer and multiplies it by the pyroelectic coefficient. The voltage response is given as the charge divided by the capacitance of the film.

(25) 
$$V = Q/C$$

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As mentioned, this model has been expanded for a wide range of samples and a wide range of detection techniques. At this point it is of interest to review the theoretical models that have helped forward PPES. Mandelis and Zver developed the PPES signal interpretation in the frequency domain assuming a 4 layer model: gas, sample, pyroelectric, and backing [58]. Power and Mandelis then derived the time domain equivalent of the same 4 layer model [68]. Power expanded on the work by developing the theory for an arbitrary N-layer sample that is optically inhomogeneous but thermally continuous [64]. This work has specific relevance to the study of polymeric systems which have no significant thermal reflections within the sample itself. The frequency domain expressions developed in this work are used in chapter 2 of this thesis. Aamodt *et al.* have developed a N-layer model for thermally inhomogeneous and optically inhomogeneous samples [69]. They model thermal contact resistance as distinct air gaps of varying thicknesses and have applied the model to interpret radiometry results. Their work provided the basis for the thermal model used to inpret the results of ultra thin film studies presented in chapter 4. Iravani and Wickramasinghe developed the scattering matrix approach to forward modeling of the photothermal signal [70].

Many authors have attributed the differences between theoretical and experimental results to a thermal resistance to heat flow between the different sample layers or between the sample and detector. Often thermal mismatches between layers fail to describe the signal and discrete layers of air are required to get a match between theory and experiment. Patel *et al.* tried to model the thermal resistance as an air layer gap of 1.5 µm between two layers in the frequency domain [71] and Cielo [72] has done similar work in the time domain. Spicer *et al.* found that theoretical air gap thicknesses were thinner than those detected by microscopy but attibuted the differences to thermal bridges that promoted some heat to pass between the two layers [73]. Heuret *et al.* [74-75] mentions that the correct description of the thermal response of paint on glass is only possible with a contact resistance; the best fit between theory and experiment required on air gap of 1.3 µm. They concluded that paint is a weakly adhering layer and the photothermal signal was independent of the substrate.

While some authors continue to develop forward models there is an increasing need to develop a robust inverse modelling technique to recover optical and thermal parameters. Forward modelling is an iterative approach where the optical and thermal properties are estimated and put into the model and the theoretical trace is compared to the experiment to check for agreement. The inverse approach uses the photothermal signal directly to obtain the optical and thermal properties of the sample.

A theoretical treatment of an inverse model for a thermally continuous and optically inhomogeneous sample was first proposed by Afromowitz *et al.* [76] who cast the thermal wave problem as the solution of an inverse Laplace transform. Over a decade later Harata and Sawada improved on their inverse Laplace method and presented the first experimental inversion in the frequency domain [77]. To measure hardening in steel Vidberg *et al.* solved the inverse scattering problem for samples that can be depth profiled using a specific radial geometry [78]. The difficulty with these inverse models is that they suffer from ill conditioning which makes them prone to errors created by small amounts of noise. Recently, Mandelis [79] and Glorieux et. al. [80] have proposed more stable models that appear promising. This topic is dealt with in detail in chapter 5 where we propose our own inverse model.

## Signal Recovery techniques in photothermal measurements.

The measurement of the frequency response from linear systems has been adapted to the measurement of photothermal responses. Frequency domain signal recovery with lock-in detection dominated the early work in photothermal studies. The photothermal analytical signal  $(Y_A)$  and a reference signal taken from the chopper are mixed by the lock-in amplifier producing a DC signal and a second harmonic which is filtered. By measuring the in-phase  $(Y_{in})$  and quadrature-phase at 90°  $(Y_{quad})$  of the photothermal signal the magnitude |Y| and phase  $\phi$  of analytical signal can be recovered by:

$$(26) |Y| = \sqrt{Y_{in}^2 + Y_{quad}^2}$$

(27) 
$$\phi = \tan^{-1} \left( \frac{Yquad}{Yin} \right)$$

\_\_\_\_\_

Frequency domain photothermal spectroscopy tends to yield monotonic phase and magnitude responses due to the dissipative nature of thermal signals [81-83]. Although the spectral response is not resonant in nature the phase of the signal has been found to be sensitive to sample thickness [84,85], adhesion quality [86], optical properties [58] and thermal properties [87] of the sample. Adams, Kirkbright et al. first showed how depth profiling can be done by phase rotation of the frequency domain signal [88,89]. Since the response of the photothermal system is linear specific photothermal features can be nulled out or enhanced by adjusting the phase offset on the lock-in amplifier or in software after the signal has been obtained. Mongeau et al. then quantified the process to separate bulk versus surface features in photoacoustic spectroscopy [90]. The phase shift technique has also been adapted by groups studying polymer laminates with FTIR-PAS to recover full spectra of the individual layers [91,92]. The depth profiling capabilities of the phase rotation technique are illustrated in Fig. 1-3 [136]. A polymer bilayer doped with methylene blue on top and  $\beta$ -carotene on the bottom was scanned in a photoacoustic spectrometer over the visible wavelengths at 26 Hz. The amplitude spectrum Fig. 1-3b was similar to the conventional absorption spectrum of the two layer model. Rotating the phase of the signal to null out contributions from the interior of the sample retrieved the phase spectra of methylene blue alone (Fig. 1-3d). Rotation of the phase signal to null out phase contributions from the surface recovers the spectra of the  $\beta$ -carotene alone. All three spectra were obtained from one photothermal scan.

Frequency domain experiments have the advantage of being relatively easy to set up,

simple to operate and any source, coherent or broadband, can be used to excite the sample. The technique has a large dynamic range and excellent noise rejection capabilities due to the narrow band harmonic measurement technique ( only the signal at the same modulation frequency as the reference is used to obtain the photothermal response). The major disadvantage of the technique is that long data acquistion times are required to obtain a relatively small number of data points (20-50) required to characterize the photothermal frequency response of a sample. If enough data points at a wide range of frequencies are recorded the frequency domain signal can be inverse Fourier Transformed to obtain the photothermal impulse response of the sample according to

$$x(t) = \left\{ \int_{-\infty}^{\infty} X(\omega) \ e^{-j\omega t} x(\omega) d\omega \right\} \frac{1}{2\pi}$$

The impulse response would then provide the thermal response of the sample to a pulse of light at time t=0. However, due to the large amount of data points that would be required to obtain an accurate inverse Fourier Transform this is not practical.

The impulse response of the photothermal system can be measured by recovering the sample's thermal response to a pulse of light in the time domain [93-95]. The main advantage of this technique is the short period required to recover the sample response and the resolution of the response is limited by the data aquisition system. Typically, fast data aquisition systems and digitizers with large dynamic ranges are required to recover

the corresponding spectral information of the sample. Besides the expensive data aquisition systems required for impulse measurements there is a fundamental limitation to the dynamic range of the measured signal that can be recovered. The impulse response is equivalent to the zero phase superposition of all the Fourier components into a short pulse duration of  $\Delta t$  [96]. The narrower the pulse the closer all the Fourier components come to having a zero phase and the wider the corresponding spectral bandwidth. The subsequent high power of impulse excitation carries the danger of driving the thermal system into a nonlinear response, and delicate samples may be damaged. The impulse technique with an extremly large fluence is used to intentionally pit samples in photothermal ablation techniques, which are nonlinear in nature.

A third signal recovery strategy utilizes wideband time domain waveforms which have flat spectral responses in the frequency domain [97-104]. Using the Fourier transform properties of the waveform both the photothermal frequency response and impulse response can be recovered using correlation and spectral analysis. There are a number of time domain waveforms which exhibit a relatively flat spectral response: wideband white noise [93], pseudorandom binary sequences [99,100], quadratic phase-modulated signals such as linear FM sweeps or "chirps" [101-103] and amplitude-modulated phase-modulated spectrometry [104]. The time domain sweep techniques have the advantage of not applying all the Fourier components in phase to the sample and thus the power of excitation is much lower. This reduces the chance of non-linearities in the heat transfer process and the risk of damage to delicate samples. The wideband techniques retain the advantage of fast signal acquisitic:: in the time domain, but have a dynamic range improvement of an order of magnitude [97].

Photothermal imaging using time domain techniques has the advantage of generating signals that can be interpreted qualitatively by eye. After heating a sample with a pulse of light the thermal waves reaching the detector first will be generated by sources closest to the dectector. Sources further away will arrive later in the impulse response. The wideband technique was introduced by Sugitani who used correlation photoacoustic spectroscopy (CPAS) to depth profile patterns in PVC laminates [99,105]. Although all time domain methods have the theoretical capabilities to yield the same information, wideband sweep techniques have been found to recover the photothermal signal most Using correlation and spectral analyis techniques optimally flat input accurately. autospectra may be obtained so that the distribution of source energy is applied evenly over all modulation frequencies. Mandelis found that the sweep techniques gave access to wider frequency response and higher time resolution then random excitation techniques [101]. Power later developed the AM-PM spectrometry which has the ability to generate an input autospectrum that is optimally flat over any band(s) of frequencies [104]. The theoretical equations developed permit the user to supply the spectral characteristics needed in an input autospectrum. Then a time domain waveform is customly synthesized to excite the sample. The AM-PM spectrometry technique is used to image PVC degradation in chapter 7 of this thesis.

Signal processing strategies of Fourier Transform Infrared techniques refer to broadband wavelength excitation rather than broadband frequency excitation. These are usually interferometer based instruments with moving mirrors that dictate the wavelength of excitation. The problem with interferometric images is that each wave number (k) is modulated at a different frequency ( $\omega$ ) when a constant scan rate (v) is used. In continuous scan interferometers the modulation of the excitation beam and the wavelength of the excitation beam are changed with the mirror position making interpretation of the results difficult as  $\mu$  is a function of  $\lambda$ . In step scan FT-IR spectroscopy a constant modulation frequency can be applied to the entire spectral range permitting unambiguous depth profiling of thin features. In step scan techniques the spectral depth profile can be obtained by changing the modulation frequency for different scans or using phase rotation techniques of conventional frequency domain measurements.

## Applications of Photothermal Spectroscopy

Photothermal techniques have been applied to a wide range of interests in the natural and applied sciences. To review all the applications is beyond the scope of this introduction. Rather, a few examples from range of applications are provided and a thorough review of applications in paints, polymers and coatings is presented. For details on specific work the reader is referred to the conference proceedings and reviews in references [110-114].

The largest volume of photothermal studies center around applications to electronics and

semiconductors. Modulated reflectance in the technique of choice in this field as the optical, thermal and electronic properties of semiconductors can be studied [30,31]. Characterization of ion implantation, surface topography, structural defect carrier diffusion and recombination effects are all found.

Recently photothermal studies of biological samples have become more prevalent in the literature. Biophysics studies of photo processes for vision and have been studied with PAS [115-117]. The curing of dairy products such as butter and cheese have been studied with PPES techniques [135] and characterization of algae and bacterial strains is now possible with PAS spectroscopy [136]. Early photothermal work has been able to measure the waxy cuticle on leaves [137] and image fine wall structures of various vegetation [33].

Photothermal studies are also wide spread in the field of medicine. Radiometry and PAS is being used to study application of drugs, creams and sunscreens applied topologically through the skin [118-133]. Studies of cancer cells have been able to distinguish between malignant and non-malignant tumors and the effect of therapy on melanoma [134]. Photothermal spectra of normal and diseased aorta in air and in saline solution have been able to detect diseases such as atheroma which is attributed to plaque build up in the aorta wall [138-140]. The study of atrial walls is now primarily implemented using laser ablation techniques in hopes of developing protocols for laser surgery. PAS techniques have been used to study cataracts [141,142] and Boucher *et al.* [117] have done invitro

depth profiling of chromophores in bovine retina and pigment epithelium from 320-600nm. They found that photoreceptors in the retina began 20-25 µm below the surface. Work in the dental sciences and neurobiology has also been reported [143-145].

Ceramic materials are being promoted for everything from engine blocks to sophisticated thin films. Photothermal techniques have proven to be adaptable to studying these new materials as they are produced. Voids in ceramics at different depth [146] and epoxy aluminum interfaces have been imaged with PAS. Weld seams in metallurgy has been evaluated with radiometry [147] showing effects of fatigue and cracks. Thermal conductivity and measurements of 60-450nm thin metal films prepared by sputtering, thermal vaporization were compared to crystals and were found to vary up to a factor of 4 depending on films thickness and film preparation techniques. The conductivity values were always lower than those measured in bulk materials [148]. Highly accurate measurements of the thermal properties of diamond have been made as the ratio of  $C_{12}$  is varied in the lattice structure. The isotopically enriched (0.1% and 0.5%) diamond crystals had higher thermal conductivities than the non-enriched form [149].

Of greatest interest to the present research are the ongoing photothermal studies of paints, polymers, and coatings.

Photothermal studies of paints and polymers

Depth profiling of polymer laminates by step scan Fourier transform infrared photoacoustic spectroscopy of a variety of laminated polymeric materials has been collected. Laminate structures of 12 µm ethylene-vinyl acetate copolymer film cast onto a 60 µm layer of polypropylene were profiled using PAS phase analysis techniques [150]. The depth profiling failed to recover the true infrared spectrum which was corrupted by strongly absorbing features in the other layer. In addition the results failed to measure the film thicknesses; it could only detect the pressure of more than one layer. Photothermal deflection spectroscopy was used to recover absorption spectra of conjugated polymers, poly(1,4-phenylenevinylene) and related derivatives [151]. However, the depth profiling capabilities of photothermal techniques was not exploited and the optical absorption properties were emphasized. The deflection technique was found to be sensitive to small absorption constants as the different C-H stretches could be resolved. Similar sensitivity results on a range of organic polymers have been reported [154]. In the study of bisphenol A polycarbonate overtones and combination resonances for several orders above the fundamental were observed. Assignments to specific C-H bond resonances could be made and molecular potentials could be calculated. This illustrates the sensitivity of the phothermal technique without using the advantages of depth profiling[154,155]. Thermal stabilities of thin polymer films and relaxation of the molecular chain structures have been studied as a function of temperature with PDS [152] and PTIR [153]. Polyamides exhibit larger thermal diffusivities with increased thickness [152] where as PMMA films (50-200 µm) were found to have uniform thermal properties [153]. The temperature dependence of PMMA diffusivity between 150°C and -150°C showed inflections at 140, 30 and -50°C corresponding to chain relaxations and chain rotations [153] (ref. Fig. 1-4). The general problem in radiometric studies of colorless polymers is that they have to be coated with a top or rear absorbing layer to get any optical absorption. This extra layer introduces a source of error in measuring the properties of the polymer alone.

Korpiun *et al.* [156] used PAS to determine diffusivity of polyethylene-therephthalate before and after mechanical drawing (spreading). The thermal waves were able to distinguish the direction of the drawing due to the thermal anisotropy in the polymer film due to the orienting of the polymer chains. Studies done with the mirage effect [157] and radiometry [158] have also found thermal wave anisotropy to exist between the plane in which the polymer was drawn and plane in which no mechanical shear was exerted. This illustrates that orientation of the fibers or mechanical shear effects can be detected in polymer films.

If the diffusivity of the polymer is known the exact thickness may be calculated. Adams and Kirkbright [159] measured polymer film thicknesses between 10 µm to 40 µm on copper using PAS. Using the calibrated slope of phase vs frequency plots the thicknesses were found to be in agreement with weighting measurements. Measurements on black Novolac films (0.65 µm to 2.45 µm) have been performed by Coufal using PPES [160,53-56]. Rosencwaig *et al.* used a combination of thermo-elastic and thermal lens imaging to measure opaque and transparent films on silicon substrates [161]. They were able to



measure films between 100nm to 1 µm using (MHz) modulation frequencies. Radiometry has been used to measure opaque photoresists on steel [162] and epoxy filler in aluminum plates has been imaged and measured PAS [146]. The detection of poor adhesion and surface contamination at polymer aluminum interfaces has also been reported [158,163].

Thermal wave studies of paint have also proliferated in the literature. Paints and polymers have similar thermal properties and subsequently thermal waves pass between them with little reflection. As a result, scuffs and fingerprints under a layer of paint on a polymer surface or a delamination all introduce thermal discontinuities which cause distinct variations in the thermal wave signal [164]. The drying process of paint gives rise to strong phase angle changes with modulated techniques [163] and distortion of the time domain signal with pulsed [164] optical excitation. Imhof *et al.* have shown that paint on metal is also easily studied and have initiated work into studying the weathering processes in paints. [165,166]. Busse *et al.* calibrated film thickness to the phase angle in radiometry studies and used these results to image paint deposited on polymer using spin coating techniques [167]. The reconstructed image of paint deposition is illustrated in Fig. 1-5.

The analysis of cured paint and a study of the weathering of paints has been presented for silicone alkyd, epoxy, acrylic and polyurethane paints [173]. The changes in pigment concentration, the loss of binder, and changes in the absorption spectrum were used as a measure of weathering with FTIR-PAS. The change in spectra showing increased carbonyls and alcohols correlated well to the physical degradation of the paint surface but the authors provided little depth profiling information.

In engineering applications polymers are often strengthened using glass or carbon fibers. The strengthening depends on the amount of fibers, their orientation, and how well they adhere to the polymer matrix. The effects of fiber alignment and polymer fiber mats have been studied extensively using radiometry techniques. Cielo *et al.* detected 1µm steel fibers in polypropylene sheets [168]. After 30 second heating of the mat with 0.2 mW laser, the orientation of the fiber could be imaged using an infrared camera. Deom *et al.* studied carbon fiber composites to examine adhesion of the fibers to the substrate. Results obtained with thermal techniques agreed well with electron micrographs [169]. Busse examined glass and carbon fiber mats [170,171] and Rief continued the work for part of his Ph.D. thesis [172].

PAS imaging of diffusion of ink in thin polymer films [175] and paper [174] has been recorded with time and frequency domain PAS techniques, respectively. The movement of ink through the substrate resulted in phase shifts in the frequency domain and significant changes to the impulse response in the time domain. Results of the diffusion study in the time domain are presented in Fig. 1-6. Ink placed on top of the film absorbed light and caused a fast impulse response. As the ink moved into the film energy was deposited deeper in the polymer and the impulse response was delayed. Using the theory of photoacoustic spectroscopy the authors were able to determine that the ink

diffused into the film according to Ficks law and diffusion co-efficients could be estimated. Recovery of optical profiles in multilayer color photographic film has been done with PAS [176]. Results were interpreted with a modified R.G. model and showed that the film responded uniquely to different wavelengths of visible light.

## Outline of research goals

The objective of this thesis has been to develop techniques for quantitative depth profiling of optical features in polymer films. Work done to date had shown that qualitative profiling of optical and thermal properties is possible in a wide range of polymer samples but little work had been done to determine exactly how much quantitative information can be recovered. Before photothermal techniques will be adopted by chemists for routine analysis it is necessary to develop clear experimental protocols and a strong theoretical understanding of the principles so that we can define the conditions under which meaningful results can be obtained from the signals.

We have chosen to study the photothermal spectroscopy of polymer films because of the broad use of polymers through out the chemical field. Polymer science has extended beyond synthetic chemists to inorganic chemists who dope the films with metal centered complexes [177,178] for application in sensors and to study the chemistry of inorganic species in a thin solid films. Depth profiling of the metal complexes in these films would help determine the uniformity of doping and spatial dependence of the signals generated in sensor applications. Electrochemists now use polymers such as Nafion to coat electrodes and need techniques to study the polymer electrode interface to be certain that the electrochemical signal is a true signal and not an effect of adhesion. Photothermal studies of polymer metal interfaces can be related to the bond strength by studying the thermal reflections at the interface. Chemists in the electronics industry are interested in

characterizing the optical and thermal properties of thin polymer films as a function of film thickness and as a function of the age of the film. This is increasingly important as scientists strive to make devices smaller, faster, less expensive and longer lasting. In some cases only one polymer such as a specific polyamide may have all the characteristics needed for a specific application. Finally the packaging industry uses polymer laminates for carrying and protecting a wide range of consumer products. For example plastic soft drink bottles are multilayer structures with specific layers acting as, respectively, a gas barrier, another as a liquid barrier, one for strength, one for color, and one for the final finish and texture. A nondestructive tool for evaluation of these complex structures would be valuable to the polymer industry as a whole.

A second reason for choosing polymer substrates is that most properties of the common polymers have been reported in the literature; therefore, the results of photothermal analysis can be compared to results using conventional polymer characterization techniques to determine the quality of the data obtained. This is of particular relevance to chapter 7, where photothermal imaging of photodegradation in PVC films is presented. Without a background knowledge of the photodegradation processes in PVC the photothermal images may be more difficult to interpret.

The work in this thesis will be divided into four parts. The first part (chapter 2) will show that the depth dependent optical profiles of multicolored polymer laminates can be quantitatively recovered. We then correlate adhesion of polymer films spin coated output

aluminum substrates to the thermal reflections at the polymer-metal interface (chapters 3 and 4). The third part then develops an inverse model that will recover the thermal flux profile from the photothermal impulse response. This can then be related to the optical profile allowing one to obtain easily interpretable results from the photothermal signal (chapter 5 and 6). This inversion technique can be applied to any photothermal measurement and can be developed for application in other spectroscopic techniques such as fluorescence. Chapter 7 then examines photodegradation in PVC films exposed to high light fluxes.

Before the introduction chapter is concluded we examine what is known about photodegradation in PVC. This will serve as background to the photodegradation study.

# Depth profiling photodegradation in polymer films

The degradation profile of artificially weathered polymer films has been studied in a wide range of polymers including poly (vinyl chloride) (PVC), polypropylene (PP), low density polyethylene (LDPE) and polystyrene (PS). Polymers such as PS that have chromophores absorb UV light and degrade due to the formation of excited triplet state chromophores which provide the energy for the peroxides and radicals to form. This type of polymer has a degradation profile closely related to the light absorption profile in the film. However, as the degradation of the film is initiated the optical absorption profile in the



polymer is changed due to the formation of new chromophores, primarily in the region of the highest light absorption. This dynamic process of light causing degradation and degradation causing a change in light absorption causes a final degradation profile that is centered around the regions of highest light absorption (usually at the surface).

The degradation studies of the first three polymers paralleled each other as none of these polymers absorb UV radiation, rather, impurities and damages in the backbone initiate the degradation process. Secondly, all of these polymers have a very small diffusion co-efficient for oxygen. This results in rapid oxidative degradation near the film surface and non-oxidative degradative processes in the bulk of the material. The different mechanisms of degradation create different byproducts which can be imaged independently at their wavelengths of absorption.

Degradation profiles of polymers with no significant UV light absorption

To model the effect of oxygen diffusion in a relation to the oxygen concentration at a certain depth and time C(x,t), the following equation is usually assumed [179]:

$$dC(x,t) / dt = D \{ d^2C(x,t) / dx^2 \} - f(C(x,t))$$

Here D is the oxygen diffusion coefficient, and f(C(x,t)) is a function describing the

oxidation rate as a function of C(x,t). Simplifying assumptions usually state that D is independent of C [180], D does not change as the polymer oxidizes, and that dC/dt = 0, i.e. the oxygen concentration profile is steady state and that oxygen consumption is matched by the diffusion into the polymer [179,181,182].

A consequence of these assumptions is that the degradation profile remains constant with time and only the level of degradation increases. This, as would be expected, does not fit all of the observed data. Attempts to modify f and vary D in order to match the degradation profiles has lead to the ideas of different regimes of degradation depending on the distance from the surface into the sample [181]. Anomalies in the observed data are attributed to microcracks in the polymer which permit oxygen to penetrate into the polymer film. Results on LDPE suggest that microcracks at the surface do exist and cause a variety of surface degradation profiles, but deep into the sample beyond the cracks there is a region where the degradation profile remains constant with time and only the level of degradation increases [183].

Schoolberg and Vink [184] profiled carbonyl formation and embrittlement of degraded PP samples by microtoming 14 µm slices from the surface. The top most layer was often so brittle that only the dust could be recovered to be packed into KBr for IR studies. Samples were degraded 100-1300 hours and had carbonyl profiles extending 100-600 µm into the sample. The shapes of the profiles changed considerably with time, use of stabilizers, and sample preparation techniques. Typically, a concave carbonyl profile was

seen at short times while a flat region followed by a shoulder was predominant at longer times. Results are illustrated in Fig. 1-7.

Rapport [185] found similar results in thick PP films but found more consistent profiles in the thin PP films. He attributed this to lower internal stress in the thin films and subsequently less microcracking of the films. However studies on LDPE [186] show no change in profiles between thick and thin films. This suggests that polymer type, preparation, and stabilization [183-185] play a major role in crack formation.

Aleksandrov [186] has studied the degradation profile in PVC. It was found that the areas of photoxidation and dehydrochlorination are removed from one another in space: photooxidation (carbonyls) occurred near the surface, while dehydrochlorination products (polyenes) form a layer beneath the oxidized one. The ketone concentration grows to a maximum value at which point Norrish type reactions degrade the chains (see below). Behind the oxidized layer dehydrochlorination occurs resulting in polyene formation. The rate of oxidation along the backbone increases as the polyenes are formed and more light is absorbed. This self feeding reaction is then said to "zipper" along the backbone of PVC promoting the elongation of the polyene sequences. Optical profiles are shown in Fig. 1-8.

Depth profiles obtained by microtoming 15-20 µm layers off the surface showed that polyene concentration rises quickly at 20-30 µm into the film. The polyene layer was

found to grow as large as 200  $\mu$ m thick depending on wavelength of irradiation and duration. In contrast ketone formation appears as a maximum at the surface and drops off very rapidly with depth. After 20  $\mu$ m very little ketone was found. Lemaire [187-190] does not argue these observations but has shown that the degradation profiles change in PVC doped with photoactive pigments such as TiO<sub>2</sub> and the thickness of films used. Specifically he suggests (although has not demonstrated) that films less than 100  $\mu$ m thick will not be deprived of oxygen and subsequently will show less variation in the optical profiles due to photooxidation and bleaching of the polyene sequences. Also, low MW additives such as plasticizers and colorants will diffuse out of the thin films masking whatever minor changes may be due to dehydrochlorination thereby making the results irreproducible and often inconclusive.

The reason for the rapid degradation of pure PVC is somewhat a puzzle as its lower molecular weight analogues are very stable structures. For example 2,4-dichloropentane and 2,4,6-trichloroheptane are stable to over 300°C while PVC will degrade at 80°C [191,192]. Early NMR studies shows that radical polymerization produces a polymer that is about 90% polymerized head to tail while up to 10% of the linkages account for various alien structures such as head to head structures, double bonds, branching and groups containing oxygen which are totally foreign to PVC (i.e. residual initiators, carbonyls and hydroxyls) [193,194,195-197,198-202].

The two most likely sources of backbone defects that initiate degradation are the carbonyl

groups present in PVC as both ketogroups [203,204] and chlorocarbonyl groups [205] and double bonds in the polymer backbone [199,206,207]. The carbonyl groups initiate oxidative degradation through Norrish type I and Norrish type II degradation mechanisms resulting in chain scission along the polymer backbone.

Norrish type 1 - cleavage at the  $\alpha$  carbon.

Norrish type 2 - abstraction of a  $\gamma$  hydrogen and cleavage of the  $\beta$  carbon

$$\begin{array}{c} 0 & 0 \\ I & I \\ CH_2CCH_3CH_3CH_3CH_3 \xrightarrow{h\nu} CH_3CCH_3 + CH_3 = CH_3 \end{array}$$

The double bonds initiate non-oxidative degradation (dehydrochorination) of the polymer backbone due to the labile nature of the tertiary chlorides. Studies of low molecular weight analogues have shown that chlorides next to the double bonds are easily removed from the backbone by both photo and thermal mechanisms. The process is exothermic; therefore, one dehydrochlorination step provides energy to initiate the next and as a result, once the process starts, it proceeds quickly in what has been termed a "zippering" reaction down the backbone of the polymer [208]. The most common method of measuring the dehydrochlorination is conductometric analysis of the HC1 evolved in the degradation process [209-210]. Accompanying the dehydrochlorination is a loss of mass as the HC1 group accounts for over 50% of the atomic mass of a single monomer unit. Loss of mass correlates closely with the conductometric measurements [211]. These trends are summarized in Fig. 1-9.

In the presence of oxygen oxidative processes compete with the non-oxidative process and produce chain scission by the two Norrish reactions. This means that in the presence of oxygen there is increased mechanical and physical degradation of PVC, but the polyene sequences are shorter than equivalent degradation studies under nitrogen.

### Instrumentation used in depth progiling studies

ATR and IR studies [212] have been used to examine surface versus bulk properties of polymer films; however, no attempts to profile functional groups or degradation has been undertaken. Similarly, photoacoustic [91,150,173,213] studies on surface versus bulk polymer properties have not provided any depth profiling information. Most chemists have failed to recognize the advances made in photothermal techniques over the past decade and do not exploit the technique to its full advantage. Initial profiles of polyenes and carbonyls were made by taking microtome slices from the surface of the polymer, mixing the polymer into KBr pellets and studying their spectra using conventional IR and UV techniques. Recently the depth distribution of oxidation products in anhydride cured

epoxy was studied by IR tirration on microtomed slices. The profile was related to oxygen diffusion in the media. However, the technique is destructive and can be only be applied to specific polymers [214]. A Raman microscope has been used to profile polyene sequences in PVC samples along the degradation axis [215]. The Raman microscope scanned with 10 µm resolution by shifting a 100 µm wide beam 10 µm at a time and recording the response of each scan in a box car averager type fashion. No comparison to other techniques was provided to show if this form of data acquisition skewed the observed profile. The high laser powers required for Raman microscopy have been found to burn polymer samples as images are recorded.

Most recently, Gardette *et al.* reported on the effects of experimental conditions such as oxygen pressure and film thickness in PVC [216]. Although a large amount of work has been published on the subject of optical depth profiles in PVC the authors felt the data was still incomplete and attempted to profile both carbonyls and polyenes in photodegraded PVC. Carobnyls were profiled with an FTIR microscope translating a l4 µm beam across the films. The polyene sequences could only be studied by laminating five 125 µm films of PVC together, degrading the laminate, then delaminating the structure to study to optical absorption in each of the five layers. This gave a polyene profile with only 125 µm resolution. The significantly large error bars on the graphs depicting the depth dependent optical profile of polyenes showed that this approach provided no new information about the polyene sequence distribution. Results illustrated in Fig. 1-10 give coarse estimates of the optical profile as a function of depth. The longest polyene bands are located in the central region of the PVC film away from oxygen. The exact polyene profile depends on experimental conditions including temperature. Their techniques were not only coarse but destructive and very time consuming. The preparation of the laminates, the delamination and the spectroscopy on the individual layers could easily take a week.

We feel that the thermal wave techniques would be ideally suited for depth profiling the optical profiles generated during photodegradation of PVC films. Polyene bands absorb in the near UV and visible where laser wavelengths are available for monochromatic studies. Depth profiling at different wavelengths will enable 3-D mapping of specific polyene bands. The short conjugations will absorb at short wavelengths while the longer conjugations absorb in the longer wavelength. We will not profile the oxidative processes as we lack a suitable IR source, but the technique could easily be used at any wavelength. We will show that profiles of polyene bands can be obtained quickly, reliably and non destructively with much higher spatial resolution than is being obtained with conventional optical techniques.

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Fig. 1-1 Modulated light - Modulated heat - Thermal waves

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Fig. 1-3 The depth profiling capabilities of phase rotation of frequency domain signals. The recorded PAS spectrum is Fig 1-3(b). Phase rotation techniques recover the spectrum of the surface layer (d) and the buried layer (f) separately. Details in text. Taken from ref. [136].



Fig. 1-4 Temperature dependence of thermal diffusivity in PMMA films [153].



Fig. 1-5 Paint deposited on polymer substrate by spin coating. Different shades of gray correspond to variations in thickness [167].



(a)



(b)

Fig. 1-6 (a) Sample used in dye diffusion experiments. (b) Impulse responses obtained from the dye diffusion experiment at 3 min. intervals [175].



Fig. 1-7 Carbonyl index versus depth for (a) non-stabilized and (b) stabilized PP at various degradation times. A 100h; ● 200h; ■ 300h; △ 600h; ○ 900h; □ 1300h. [184]



(a)

(b)

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Fig. 1-8 (a) Spatial distribution of absorbing products at

(1) 300 nm, (2) 380 nm, (3) 500nm.
(b) Trace (a) is the total carbonyl content in the PVC film. Trace (b) carbonyl groups due to photooxidation of PVC monitored at 1735 cm -1.[186]



a

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Fig. 1-9 (a) Photodegradation of PVC foils at room temperature under (O) N2, Air, O2, 50%O2/50%N2. (b) Dependence of dehydrochlorination on the weight of PVC foils. Total HCl elimination = 666 ug. [211]

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Fig. 1-10. Depth dependent optical profiles of features absorbing at 500 nm in photodegraded PVC. (a) Sample heated to 60 oC then degraded for 10 hr (a), 20 hr (b), 30 hr (c), 40 hr (d), and 56 hr (e). (b) Sample heated to 35 oC then degraded for 68 hr (a), 120 hr (b), and 146 hr (c). [216] Chapter 2:

Spatial Depth Profiling of Chromophores in Thin Polymer Films Using Frequency Domain Photopyroelectric Spectroscopy

### Introduction

Photothermal spectroscopy comprises a group of newly developed analytical techniques which have applications in various aspects of materials characterisation including the spectroscopic depth profiling of laminates and thin films.

The potential for studying multilayer samples using photoacoustic and photothermal techniques was recognised in the early 1980's (1-9). Early studies using these techniques provided mostly qualitative information about the optical profiles in samples consisting, typically of a small number of discrete layers. Photoacoustic studies have been carried out on multilayer color photographic film (1) and the imaging of optically absorbing impurities in polymer films (3). Other photothermal techniques such as optical beam deflection (6,7), radiometry (8,9), thermoelastic imaging (10,11) and photopyroelectric spectroscopy (PPES) (12,13,14) have shown abilities to depth profile subsurface thermal information in opaque samples. These techniques are also capable in principle, of optical depth profiling. Overall, the photothermal technique of choice becomes dependent on depth profile resolution, sensitivity, sample size, sample geometry and the availability and cost of instrumentation.

Of the above techniques listed PPES is especially well suited for the study of thin films due to its high sensitivity and simplicity. In a typical PPES measurement the sample is secured directly to a pyroelectric detector which is used to monitor thermal waves transmitted through the sample. Recently work has been published showing the application of AM-PM wideband impulse PPES in the study of thin films (14). The work showed that thermally homogeneous and optically inhomogeneous laminates can be spectroscopically depth profiled with micron scale tesolution. The thickness measurement of transparent overlayers on opaque samples was demonstrated and techniques for image enhancement were discussed. One of the drawbacks of AM-PM wideband spectrometry is that it requires a laser (at least in its present form) and a relatively sophisticated instrument setup. In contrast, frequency domain photopyroelectric effect spectrometry (FD-PPES) with lock-in amplifier detection requires less sophisticated signal processing and less expensive instrumentation; it accesses the full optical spectrum when broadband sources are used, and it provides an equally sensitive thermal probe. Pseudo random binary sequence (PRBS) spectroscopic techniques may encode a pseudo random sequence onto a mechanical chopper wheel and therefore, are not limited to laser sources either. However, the PRBS measurement suffers from poor spectral quality (a non-uniform power spectrum) and usually requires an FFT an/alyzer to recover the signal (15).

In this work FD-PPES will be used for the first time as an optical absorption depth profiling tool. The technique will be used to image multilayer samples with a variety of arbitrary depth profiles of the optical absorption coefficient. Experimental and theoretical results presented will demonstrate the high sensitivity of the technique to subsurface absorbing regions and the micron resolution with which they can be profiled. We will describe the required instrumentation and discuss the limitations of the technique.

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References made to impulse studies previously made on similar samples will enable a comparison of the two measurement techniques (14).

#### Instrumentation

The construction of a frequency domain photopyroelectric spectrometer for teh spatial depth profiling of chromophores in polymer films is presented in detail in Appendix A. Important features of the instrument that are relevant to photothermal spectroscopy are discussed here. The experimental apparatus used in this work is diagrammed in Fig. 2-1. The excitation source was an Argon Ion (Coherent Innova-70) pumped dye laser system (Coherent 599-01) operated with Rhodamine 6G. The output of the dye laser was adjusted to 10 mW with a polarizer, modulated with a mechanical chopper (Ealing Scientific) and directed onto the sample surface. A large spot size, between 3mm to 5mm in diameter, was used to ensure one dimensional heat conduction through the sample.

The pyroelectric cell design is shown in Fig. 2-2. The pyroelectric transducer is a 28 µm film of polyvinylidene difluoride (PVDF) with a NiA1 coating as supplied by Atochem corporation. The cell body is made of PMMA Plexiglass with inlaid brass electrodes which contact the upper and lower surfaces of the PVDF film. The PVDF is held flat to the bottom of the cell using a thin layer of silicone vacuum grease and the sample is attached to the top of the PVDF with optical epoxy (EPOTEK #302-3). Thermal



continuity between the sample and cell backing is obtained as the samples, epoxy, PVDF, silicone grease and PMMA all have similar thermal efflux ratios (14). The entire cell is surrounded by an aluminum EMI shield and the signals leaving the pyroelectric detector are shielded by coaxial cables before being coupled into a differential amplifier (Tektronix AM502). The amplifier was adjusted internally to give a 200 M $\Omega$  input impedance and a bandpass of 0.1 Hz to 0.1 MHz was used during all experiments. The output of the amplifier was read by a lock-in amplifier (EG&G PAR 5101) which took the reference from the chopper. The signals were coverted using a 12 bit IBM data acquisition system. The spectrometer was automated and controlled from the keyboard of an IBM PC-XT using a software program written in the ASYST language (Asyst Technologies Inc.). Samples were synthesized from commercial mylar sheets or from Kodak Wratten gel edge filters. The mylar sheets consisted of ca. 2.5 µm of pigment on a sheet of clear mylar (thickness ca. 25 µm). An adhesive backing on the mylar film was removed using methanol to prevent thermal contact resistance between layers of the sample. Adhesion between layers of the composite was achieved using the optical epoxy. Layer thicknesses were measured with a micrometer, optical absorption values for the mylar and Wratten gel films were obtained on a HP-8452 photodiode array spectrometer with a spectral resolution of 2nm.

Theoretical calculations were made based on equation (1) as described in appendix B. The derivation of the equation is based on a N layer laminate that is thermally homogeneous and optically inhomogeneous (14).

### (i) PPES cell design

A critical aspect of FD-PPES is the design of the photopyroelectric cell. The pyroelectric is a transducer for thermal signals as well as background acoustic waves, and electromagnetic interference (EMI). It is also a sensitive receiver for piezo activity, stray light and air currents. In addition, any thermal resistance between the PVDF film and Plexiglass backing potentially causes thermal waves to be partially reflected at the PVDF backing interface, generating an observed thermal response which consists of a sum of the incident plus reflected thermal wave components. Consequently, the observed signal consists of contributions from all these individual sources, making the recovery of the transmitted thermal response alone difficult. To prevent thermal reflections from contributing to the signal a thin layer of silicone grease is deposited between the back of the PVDF and the PMMA holder and the PVDF is laid flat and flush against the cell backing. Stray light due to sample reflections of up to 50% of the incident beam strike the EMI shield and become reflected back onto the surface of the PVDF. If the reflections strike a bare portion of the pyroelectric film, a background signal will be generated which adds to the measured sample response. This contribution will be measured by the lock-in amplifier because it is modulated at the same frequency the thermal waves are generated. In impulse PPES measurements this stray light component is a less serious problem as it is present in the time domain response at very early time delays and it is well separated from the sample response; significantly for polymer samples in the thickness range 10-100 µm. FD-PPES signals, like all frequency domain photothermal responses, tend in general, to be broad and relatively featureless, the observed signal having contributions from all sources that respond at a particular frequency. The magnitude decays monotonically with increasing frequency. Consequently, FD-PPES does not separate the background components with frequency and it is therefore necessary to insure that the light reflected by the sample is directed out of the cell.

An important source of electromagnetic interference is produced in the windings of the variable speed chopper which is in close proximity to the detector. As the chopper increases speed the windings generate increased interference which can be detected by the PVDF film. To reduce the effects of this interference along with air current pulsations generated by the mechanical chopper, a shield is placed around the chopper body to separate it from the cell. Impulse measurements are typically made with pulsed laser or acoustooptically modulated laser sources so that these EMI and air pulsations do not contribute significantly. The presence of these background signals in FD-PPES is most easily detected in the magnitude response of the signal which rises continually as a function of increasing modulation frequency instead of falling off exponentially as the thermal diffusion lengths become shorter.

The design of the electrical coupling network ahead of the differential amplifier is critical in obtaining the true thermal frequency response of the sample. An equivalent circuit of the PPES cell is shown in Fig. 2-3. A description of the circuit response has been given elsewhere (14, 18, 19) but the important frequency domain characteristics are pointed out here. The heated pyroelectric functions as a capacitor with a temperature dependent dielectric constant. Such an element is equivalent to a voltage source in series with the PVDF film capacitance if temperature changes are small. The resistance R<sub>1</sub> and capacitance C<sub>1</sub> are contributed by the input resistance of the preamplifier along with the combined capacitance of the signal leads, bandpass filter and preamplifier. The electrical frequency response of the PPES cell was recorded experimentally by placing a voltage generator in series with the unirradiated PVDF. The high pass filter was fixed at 0.1 Hz and the low pass filter was varied from 3 kHz to 1 MHz. Ideally the voltage frequency response of the pyroelectric transducer should be flat in phase and magnitude so that variations in the signal with frequency are due to the thermal response of the sample/pyroelectric combination. The results presented in Fig. 2-4 reveal that an optimally flat frequency response is obtained using a large input impedance R<sub>1</sub>, and minimizing the bandpass signal filtering, C<sub>1</sub>. The argument for opening the filter bandpass to 100 kHz is the uniformity of the phase frequency response (Fig.2-4a). Below a 100 kHz bandpass the phase falls off linearly with frequency due to the group delay of the filters. Above 100 kHz the phase response of the detector does not change and excess white noise will be let into the signal. The magnitude, Fig. 2-4b, of the signal is also optimally flat with a 100 kHz cutoff frequency. Note that the intensity axis of the magnitude plot has been expanded to accentuate the fluctuations in the detector response with frequency. If the vertical scale is taken down to the origin, all three plots appear flat with frequency due to the decreased resolution of the graph. Fig. 4c shows that as the input impedance of the preamplfier is decreased from 200 M $\Omega$  the transfer function loses its uniformity and at low input impedance values the circuit behaves as a differentiator. The phase plots are linear with frequency. The results presented below have been corrected for the nonuniformities in the transfer function of the phase (c.f. Fig.2-4a) at low frequencies.

# (ii) Optically Homogeneous and Thermally Homogeneous Samples

To study the case of optically and thermally homogeneous samples Kodak wratten gel edge filter #29, measured to be 100  $\mu$ m thick, was attached to the PVDF film and the thermal response investigated between 620 and 580 nm. The results are presented graphically in Fig. 2-5. At 620 nm the absorption coefficient is small. Most of the light is transmitted by the sample, strikes the PVDF, and is partially absorbed by the NiA1 coating. Reflection of the beam at the PVDF surface causes it to be passed through the sample a second time. In this regime of low sample absorption significant high frequency response is observed, much of it due to the contribution of the PVDF. Here the magnitude of the frequency response (Fig. 2-5b) is sensitive to small increases in sample absorption which reduces the contribution from the PVDF and subsequently reduces the high frequency component of the voltage response. The phase of the signal (Fig. 2-5c) is relatively flat with frequency and insensitive to small changes in  $\beta_2$ , the absorption coefficient of the sample.

As the wavelength of excitation is decreased to 610 nm the value of  $\beta_2$  increases and more light is absorbed by the wratten gel. The magnitude response now drops in intensity more quickly and the phase response shifts down the phase axis and falls off increasingly with frequency. In the mid range of  $\beta_2$ , the frequency response is determined by the spatial profile of the optical absorption in the sample. Subsequently, in this region of the spectrum the wratten gel theoretical model shows an acute sensitivity to the reflectivity. R, of the PVDF NiA1 coating. This agrees with earlier findings (20). The higher the R value the more light is reflected back into the absorbing film. Through out all of these experiments a reflection of 90% or R=0.9 was found to give the best match between theory and experiment. This value is consistent with previous work (14).

s  $\beta_2$  is increased to large values (5x10<sup>4</sup> m<sup>-1</sup>) the optical deposition length approaches a spatial delta function located at the top of the sample and photothermal saturation is approached. Subsequently significant thermal response is obtained only at the lowest frequencies. In the frequency range of the experiment (50-400Hz) almost no thermal energy reaches the PVDF from the sample. Consequently a relatively strong background component interferes with the signal causing the observed voltage response and phase signals to level off over and above the result predicted by theory. Therefore to study polymer samples of greater than 100 µm thickness with FD-PPES, the mechanical chopper must have a range which extends below 50Hz, otherwise the sample thickness must be reduced. Since many polymers have a thermal diffusivity in the range 8x10.8 to 4x10.7 m<sup>2</sup>/s it is safe to conclude that the FD-PPES spectrometer is limited to studying polymer films that are less than 100 µm thick.

In contrast, the alternative technique provided by impulse PPES signal is able to resolve the 100 µm edge filters at high  $\beta$  values without the frequency limitations experienced in this study. The main reason for this is that impulse PPES (at least in wideband mode) is capable of resolving frequencies as low as 0.2Hz, where the thicker samples respond strongly. Since there is sufficient signal strength maintained during the frequency sweep, a well resolved background interference, and a much larger data point volume, somewhat thicker samples may be studied (14). The calculated thermal diffusivity of the Wratten gel filter using R=0.9 and a 3 µm epoxy coupling layer is  $1.4 \times 10^{-7}$  m<sup>2</sup>/s.

#### (iii) Optically Inhomogeneous and Thermally Homogeneous Multilayers

The effect of distance on the FD-PPES signal was studied by moving the thermal source away from the pyroelectric and monitoring the frequency domain signals. This was achieved by preparing laminates which consisted of 2.5  $\mu$ m of blue myler ( $\beta$  greater than  $1 \times 10^5$  m<sup>-1</sup> over the entire wavelength region) above 30, 65, and 82  $\mu$ m of clear colorless mylar and optical epoxy. The only function of the thin blue layer was to act as a narrow absorbing region which was much thinner than the thickness of the intervening layer. This gives a good approximation to a spatial Dirac delta function in these studies. The irradiation wavelength was fixed and no spectral dependence of the layer was studied.

Results show that the slope of the phase increases with the distance the source is moved away from the PVDF (Fig. 2-6a). The normalized magnitude frequency response of the signal also decreases more rapidly with frequency as this distance is increased (Fig. 2-6b). At modulation frequencies greater than 200 Hz the linearity of the phase response with frequency is lost and the slope tends to level out. The linear region of the phase response can be used in practical applications to measure the distance between absorbing layers by means of a prepared calibration curve of phase versus thickness for samples of known thickness and thermal diffusivity. A second effect of distance on the phase of the signal is a shift of the entire curve down the phase axis with increasing distance. Theoretical plots made at low frequencies show that the phase curves, while they do approach each other, do not converge to a single value at zero hertz.



Fig. 2-7 gives an illustration of the ability of the phase response to resolve the contributions of two closely spaced absorbers placed a significant distance away from the PVDF. The upper and lower thin absorbing layers consisted of green and red pigment with absorption spectra given in Fig. 2-7a. The sample was made of a 30 um base laver of transparent mylar, two thin absorbing layers (separated by not more than 3 µm of epoxy) and a 25 µm transparent overlayer (Fig. 2-7b). At 620 nm the green layer only, absorbs and the phase of the signal drops off linearly to 200 Hz (Fig. 2-7c). As the wavelength of excitation is scanned towards 600nm the red and green layers both absorb, the absorbing region doubles in thickness moving the thermal source profile away from the PVDF. As a result, the phase of the signal drops along the vertical axis. At 580nm the red region absorbs ca 90% of the light effectively moving the heat source further away from the PVDF. The phase frequency response is shifted further down. Note that for this sample a net change of 5 µm in the position of the thermal source provides an absolute phase shift of one radian. Therefore, for a given polymer system the distance of an absorbing layer can be related to the position of the phase along the phase axis for a set frequency value. Consequently, accurate theoretical modeling of FD-PPES experimental data requires correct correlations with the magnitude of the signal, the slope of the phase signal and the exact offset position of the phase curve along the phase axis. When a match betwen experimental data and these three parameters is achieved one can be confident that the sample response has been modelled correctly.

The presence of a transparent overlayer has been shown to be detectable in the time

domain PPES signal (14). Thermal waves generated at the source extend downwards to the pyroelectric sensor and upwards to the air/polymer interface where they are fully reflected and extend back towards the PVDF. Although this reflected component of the signal is strongly attenuated it does contribute to the impulse PPES signal at low frequencies. Current FD-PPES instrumentation has inadequate low frequency response to resolve these front surface reflections at most thicknesses. Thermal waves which are reflected at the top surface affect the observed signal minimally. Therefore FD-PPES, can be designed to avoid low frequency detection and may be used to depth profile samples without observing contributions due to thermal reflections at the sample-air interface. These reflections yield information about the thermophysical structure of the sample, and are detected in wideband PPES, under inversion, corresponds to the risetime region of the PPES impulse response. Subsequently, the rising portion of the PPES impulse response contains a greater sensitivity to the depth profile of optical absorption, being free of thermal reflections.

Laminate films with well separated absorbing regions show a characteristic response that can be related to the subsurface spatial profile of optical absorption and the distance of individual absorbers from the pyroelectric. This sample type is exemplified in Fig. 2-8(a) which illustrates a multilayer mylar sample composed of a 60 µm spacer between a red and green absorbing region. The sample is contacted to the PVDF with 5 µm of optical epoxy. At wavelengths where the red layer is transparent and the green layer absorbs, the magnitude of the signal remains strong over a range of 50-400 Hz (Fig. 2-8b) and the

phase response is shifted slightly down the phase azis dropping less than 1 radian. Fig. 2-8(c). Both of these traces indicate that the absorbing region is located near the pyroelectric surface. As the excitation wavelength is scanned to 590 nm the incident beam is partially absorbed by the top layer, the transmitted component is then partially absorbed by the bottom layer, the small amount of light that is transmitted through both lavers has 10% ci its energy absorbed by the PVDF. The remainder is reflected, and passes through the sample a second time. The observed phase has contributions from the top layer, the bottom layer and the NiAl coating of the PVDF. At low modulation frequencies the contribution from the top layer dominates the phase response. Fig. 2-8(c), and subsequently the phase is shifted down the phase axis and begins to drop off rapidly. As the modulation frequency is increased the thermal diffusion length is shortened and, as the contribution from the top layer is reduced, the bottom layer contribution begins to dominate the response. The phase response of the bottom layer begins to dominate the observed phase as the contribution from the lower layer is increased. Therefore a minimum and two distinct regions with different downward slopes are observed, indicating two distinct absorbing layers. At 580 nm the red layer absorbs nearly 100% the incident light and subsequently there is a large phase drop due to the large distance of this source from the pyroelectric. A trend is also seen in the magnitude which drops off relatively slowly in the 600-610 nm region. As the red absorbs more of the light there is an inflection point along the wavelength axis below which the magnitude frequency response drops more sharply until 580nm. In the wavelength range where this transition is observed, a concurrent transition in the photothermal phase occurs.

A laminate with the sources separated yet further is illustrated in Fig. 2-9a. It is similar to the previous sample except that it has a green absorbing region on the surface and a red absorbing layer on the bottom. There is an 80 um transparent region in between a 5 µm layer of epoxy coupling the sample to the PVDF. In mylar samples characterized by at least 75 µm separating two thermal sources the magnitude (Fig. 2-9e) exhibits a rise with frequency which coincides with a sharp phase shift (Fig. 2-9c) along the wavelength and frequency axis'. The peak in the magnitude is about 10 nm wide at the base (595-605nm) and can be resolved better in frequency with an increasing distance between the two absorbing regions. The experimental and theoretical results agree within experimental error. One might expect the magnitude of the signal to decrease monotonically with frequency as the thermal wavelength decreases and less thermal energy reaches the pyroelectric. However, this rise in energy can be attributed to a thermal wave interference which occurs in the sample. Polar plots of the theoretical response of each absorbing layer in the sample at 50, 70, 110 and 200 Hz are presented in Fig. 2-10. At 50 Hz (Fig. 2-10a) the magnitude of the PVDF vector (triangle) is 2.5 units and has a phase of 19°. As the frequency of modulation is increased the phase of the vector slowly decreases to 4.5° at 200 Hz (Fig. 2-10d) and the magnitude stays about the same. This shows that the PVDF contribution to the observed signal does not change significantly with frequency. The square symbols represent the thermal response of the bottom absorbing layer of the sample. At 50 Hz the vector has a phase angle of 11.7° (Fig. 2-10a) and a magnitude about 25 units. As the frequency of modulation is increased the phase angle swings into the negative quadrant of the graph and by 200 Hz this vector has



a phase angle of -10° (Fig. 2-10d). Both the phase and magnitude of the bottom layer vector also stay relatively constant indicating that the contribution of the bottom layer to the observed signal does not change significantly with frequency in this region. At 50 Hz the vector representing the top absorbing layer (circles) has a phase angle of 188° and a magnitude about 25 units (Fig. 2-10a). At 70 Hz (Fig. 2-10b) the phase angle is 150° and the magnitude has decreased to 15 units: at 100 Hz (Fig. 2-10c) the phase approaches 90° with a magnitude of 3 units and by 200 Hz (Fig. 2-10d) the phase is -17° with a magnitude less than unity. This illustrates that the top layer contributes less thermal energy and the phase decreases rapidly with increased modulation frequency. Note that at 50 Hz the phase of the top absorbing layer is 180° out of phase with the bottom absorbing layer and the PVDF. Since the thermal waves add vectorially this will reduce the length of the resultant vector of the sample to a minimum in magnitude. However, as the modulation frequency is increased, the phasor from the top layer swings into phase with the other phasors and drops in magnitude simultaneously. Therefore there is an intermediate rise in magnitude at about 110 Hz as the O phasor swings into the 90° quadrant. A decrease in magnitude follows as the thermal wavelength from the top layer becomes shorter and the magnitude of the top phasor is correspondingly reduced.

A sample with three absorbing layers was constructed as shown in Fig. 2-11(a). A 2.5  $\mu$ m from a green absorber which is 30  $\mu$ m above a second red absorbing region. The total sample thickness is 105.5  $\mu$ m placing it at the limit of the spectrometer's maximum thickness resolution capabilities. Fig. 2-11(b) shows the phase frequency response of the

laminate as a function of wavelength. At 610 nm, trace (1), the thermal signal originates from the green layer and dominates the observed response: the phase falls off linearly to about 250 Hz. This response matches that of a single absorbing layer placed 37 µm from the PVDF.

As the wavelength is scanned to 600nm, trace (2), the green layer continues to dominate the phase response at low frequencies. however, as the modulation is increased the thermal waves reaching the pyroelectric are damped, contributions from the bottom red absorbing region begin to dominate the signal and the observed phase approaches the flatter, highter phase response of the closer thermal source. At 590nm, trace (4), the phase response exhibits contributions from all three absorbing regions. The initial phase rise is attributed to the top red layer and green layer dominating the observed signal. As the thermal diffusion length from the top layer becomes too short to reach the pyroelectric the phase rises from a steep drop (occuring below 50 Hz) due to contributions of the green and bottom red absorbing regions. Between 80 and 170 Hz the phase falls with frequency due to the contribution from the green layer, which dominates the phase. Above 200 Hz the phase converges to the response expected for the bottom layer alone. This plot is expanded in Fig. 2-11c to accentuate the rising and falling of the FD-PPES phase signal. Note that there are now three slopes and two minima indicating three absorbing regions. However, the contribution from the top layer is minimal, at even a frequency as low as 50 Hz; a significantly slower chopping frequency would be required to observe the effect clearly. As top red component begins to absorb more of the light the mean position (as averaged spatially over all layers) of the thermal source is shifted further away from the PVDF and the phase responses are shifted down the phase axis. At 585 nm, trace (5), the red source at the top of the sample is absorbing most of the incident light and the green middle layer absorbs most of the transmitted portion. The mean heat source position moves up into the larninate thereby increasing the phase lag with frequency. By 200 Hz the thermal diffusion length is ca. 20 µm, so that the contributions from the middle and top layers are strongly damped before reaching the PVDF. At wavelengths where the top begins to absorb almost all of the light the phase response of the frequency domain signal drops down the phase axis and has an increased slope due to the increased distance the thermal waves must travel before reaching the pyroelectric. At 580 & 570 nm less than 1% of the light passes through the top absorbing region and all the thermal waves must travel the length of the sample to reach the pyroelectric. Subsequently, the thermal signal is very weak and background signals interfere significantly. As a result the thermal response of the sample in these regions are not analytical and are hard to interpret accurately.

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# Conclusion

We have shown that FD-PPES has the capability of depth profiling multilayer polymer laminates in a non-contact. non-destructive manner. The technique provides accurate results with good signal to noise ratios for polymer samples less than 100 µm thick provided the PVDF equivalent circuit is correctly designed and its transfer function is accounted for. Samples with absorbing regions separated by more than 75 µm exhibit thermal wave interference effects which cause the magnitude to rise, rather than fall, with modulation frquency giving a characteristic peak in the magnitude of the frequency domain signal. The phase of the FD-PPES signal is sensitive to the distance that thermal sources are located from the pyroelectric. The ratio of the light absorbed by each of these various sources also contributes significantly to the observed response. The further an absorbing region is positioned from the pyroelectric the steeper the phase drop with frequency, and the lower the modulation frequency range required to interrogate the source. As a consequence, multilayer samples have frequency domain phase signals which exhibit multiple slopes, where a change of slope is observed for each individual absorbing region and where intervening minima appear in the phase response.
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Fig. 2-1. Instrument configuration showing both a dye laser source and a 1000W Xenon arc lamp source which can be used interchangeably.

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Fig. 2-2. The PPES detector cell.



Fig. 2-3. The equivalent circuit of the PPES cell showing the PVDF capacitance (Cp), amplifier input impedance  $(R_L)$  and the input capacitance  $(C_{L)}$ .

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Fig. 2-4. Frequency response of PPES cell as a function of input filter bandwidth with a 200 MΩ input impedance; (a) phase and (b) magnitude. In (a) bandwidths were 0.1Hz-3kHz (\*),0.1Hz-10kHz (#), 0.1Hz-0.1MHz (x), and 0.1Hz-0.3MHz (o). In (b) the filter bandwidths were 0.1Hz-3kHz
(\*), 0.1Hz-10kHz (#), and 0.1Hz-0.1MHz(o).



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Fig. 2-4c. is the transfer function of PPES cell as a function of amplifier and shunt impedance using a bandpass of 0.1Hz to 0.1 MHz; (1)  $\kappa\Omega$  (2) 2.2 $\kappa\Omega$  (4) 4.7  $\kappa\Omega$  (o) 200 M $\Omega$ 



Fig. 2-5. (a) absorption spectrum of Kodak wratten gel #29.

## Experimental magnitude



Fig. 2-5 (b) Experimental magnitude response and (c) experimental phase response of Kodak wratten gel #29.

Theoretical magnitude





Fig. 2-5 (d) Theoretical magnitude response and (e) theoretical phase response of Kodak wratten gel #29.



Fig. 2-6. The effect of source distance on the FD-PPES response. Experimental results from (□) 30 µm, (0) 65 µm, (Δ) 82 µm from the PVDF detector, (6.a) phase response and (6.b) magnitude response. Theoretical calculations are shown in solid.







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- Fig. 2-7
- (b) The sample geometry.
  (c) Trends in the phase response showing the phase curves dropping down the axis as thermal source is moved farther away from the PVDF.



Fig. 2-8 (a) Sample geometry.



Fig. 2-8 (b) Experimental magnitude response of the sample in Fig. 2-8a. (c) Experimental phase response of the same sample.



Fig. 2-8 (d) Theoretical magnitude response of the sample in Fig. 2-8a. (e) Theoretical phase response of the same sample.

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Fig. 2-9 (a) Sample geometry.



Fig. 2-9 (b) Theoretical phase and (c) experimental phase responses of the the sample in Fig. 2-9a.





Fig. 2-10. Polar plots of the contributions from the individual source layers of the sample illustrated in Fig. 9a. In each figure the contributions are from
(o) the top absorbing layer, (□) the bottom absorbing layer, (∇) the pyroelectric. The response at 50 Hz (a), 70 Hz (b), 110 Hz (c), and 200 Hz (d) are illustrated.





Fig. 2-11. (a) Sample geometry for a six layer sample with three absorbing regions.



Fig. 2-11. (b) Phase response as a function of wavelength. (1) 610 nm, (2) 600 nm,
(3) 595 nm, (4) 590 nm, (5) 585 nm, (6) 580 nm, (7) 570 nm,
(c) Expanded phase response at 590 nm.

Chapter 3:

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Rapid Recovery of Wide Bandwidth Photothermal Signals via Homodyne Photothermal Spectrometry: Theory and Methodology

## Introduction

Photoacoustic and photothermal techniques have occupied a unique position in spectroscopy because they are capable of depth profiling the thermal and optical properties of very thin specimens of thicknesses on the order of microns (1.2). These techniques use thermal waves as probes of subsurface structure in materials. A thermal wave (3) can be considered as an oscillating temperature variation in the sample, which, in the case of photoacoustic and photothermal techniques, is established by light absorption from a modulated beam of radiation. The depth profiling capability of these methods derives from the dependence of the wavelength of a thermal wave on the modulation frequency of the heat source generating the wave (3). This relationship is expressed through the frequency dependence of the thermal diffusion length,  $\mu$  on the modulation frequency,  $\omega$ :

$$\mu = \left\{ 2\alpha/\omega \right\}^{1/2} \tag{3-1}$$

where  $\alpha$  is the thermal diffusivity of the sample material.

The depth of penetration of a thermal wave generated at a surface is limited to a subsurface distance of  $2\pi\mu$  because thermal waves are critically damped with distance in a material. Consequently, a variation of the modulation frequency controls the sampling depth from which information may be recovered.

Because of the inverse relationship between the thermal diffusion length and the modulation frequency, very high frequencies are required to analyse shallow subsurface profiles (of the order of hundreds of nanometers). In highly conducting media such as semiconductor materials, for example, modulation frequencies of the order of MHz are

required to image subsurface features of the order of a few microns thickness (4,5). Typically, such measurements require expensive high frequency detection equipment.

The classical signal recovery strategy in cases where high frequency information is recorded, involves the sinusoidal intensity modulation of the excitation beam with detection using a narrowband device such as a lock-in amplifier. In this measurement, the system is allowed to achieve a steady state harmonic response at each frequency. A recovery of the photothermal system's frequency response, as magnitude and phase, is made on a pointwise basis at all frequencies of interest within the system bandwidth. With this method, clearly, long times are required to recover a high resolution depth profile of the sample.

A more rapid depth profiling method is available using pulsed excitation (6). An ideal impulse consists of the zero phase superposition of all excitation Fourier components within a bandwidth which is wide compared to the system response. Consequently, the impulse method applies all excitation frequencies to the sample simultaneously. In the time domain, the effective thermal diffusion length is given by a time dependent quantity:

$$\mu_{\rm p} = \sqrt{4\alpha t} \tag{3-2}$$

The above expression is consistent with the observation that a heat pulse travels to a greater distance with increasing time delay, and that a time lag is required for heat conduction from the surface to some buried subsurface feature.

A third signal recovery technique is provided by wideband photothermal spectrometry, in which the sample is excited by a time dependent waveform whose autospectral density function is uniform over the photothermal response bandwidth (2,7,8). This

approach takes advantage of the Fourier transform relationship existing between the system's frequency and impulse response, and recovers both functions at high resolution using correlation and spectral analysis techniques.

At frequencies above 100 kHz, all of the above methods become expensive to implement instrumentally. The impulse measurement typically requires a fast boxcar integrator or transient recorder. Narrowband detection requires a high frequency lock-in analyser, which is typically available at much greater cost than the usual audio range instrument. Finally, the audio range signal analysers that are typically used by wideband methods, require expensive instrumental modifications to enable measurements to be made above 100 kHz.

The availability of a rapid and inexpensive method of signal recovery at medium to high frequencies would clearly provide ready access to thermal wave depth profilometry and imaging at submicron resolution levels. Homodyne photothermal spectrometry (HPS), which we present here, is a technique which satisifies both criteria. HPS is based on low cost instrumentation, and exhibits bandwidths greater than 10 MHz.

The homodyne spectrometry principle developed here, in addition to solving a high frequency bandwidth problem in photothermal spectroscopy, has general application in all branches of linear spectrometry, a category which includes measurement in FT-NMR, linear FT- mass spectrometry and modulated fluorescence detection. The special value of the homodyne method in photothermal spectroscopy lies in the capability for resolving the depth dependent thermal and spectral properties of very thin layers based on a very low cost apparatus.

This work is divided into two parts. In the first part of this work, the theory and experimental implementation of homodyne photothermal spectrometry is demonstrated. An inexpensive apparatus design is presented. This design may be implemented with readily available laboratory components. The performance of the method for some well characterised photothermal systems is then discussed. In the second part of this work, chapter 4, HPS was applied to photothermal measurements of thermal diffusivity in ultrathin polymer films, at thicknesses less than 200 nm. It is also exhibiting the potential to evaluate interfacial adhesion phenomena in a novel and sensitive measurement. The experimental HPS methodology reported in chapter 4 may also be used, without modification, for depth profiling the optical absorption of thin films on submicron length scales.

## Theory

The principles of homodyne photothermal spectrometry are illustrated in Fig. 3-1. The method uses a linear frequency sweep, x(t), with a duration of milliseconds to seconds to excite the photothermal system. The photothermal system yields an amplitude and phase modulated response waveform, y(t), with a bandwidth extending from a few kilohertz to several megahertz, typically. The photothermal response, y(t) is downshifted to a bandwidth of one kilohertz by multiplication with the drive sweep, x(t) using a mixer stage. The mixer output consists of the sum of a downshifted signal, which is centered near baseband, and additional high frequency signal components swept at twice the drive frequency. The downshifted component, under the conditions derived below, yields an output signal which is proportional to the real or in-phase part of the photothermal system's frequency response, dispersed as a function of time. Its' high frequency bandwidth can be made as low as a few hundred hertz by adjustment of

experimental conditions such as sweep rate. The downshifted component is recovered using a baseband filter, which simultaneously rejects the high frequency sweep components output by the mixer.

From the real part of the system's frequency response, which is given by the downshifted component, it is possible to recover the magnitude and phase, as well as the system's impulse response, via computational procedures, which take advantage of the causality of the response of physical systems (10,11).

The HPS technique resembles lock-in detection in principle, except that there is no requirement for the system under test to achieve a full steady state. As seen in the discussion section below, the capability of HPS for scanning the frequency response in short times is not shared by conventional lock-in techniques.

The conditions for which the homodyne technique yields meaningful results are outlined below.

In a practical system excited by a linear frequency sweep, the excitation waveform is initiated at t=0, and is characterised by an instantaneous frequency,  $(\omega_i)$  which varies as a function of time. The resulting output consists of a 'squeezed wave' as shown in Fig. 3-2. The sweep is initiated at zero frequency and terminates at t=T, which defines the sweep duration. The waveform is written (12,13):

$$x(t) = \frac{1}{2} \{ e^{j\pi St^2} + e^{-j\pi St^2} \} w(t)$$
(3-3)

where S is the sweep rate in Hz/s, and w(t) is a boxcar function, which accounts for the finite duration of the sweep:

$$w(t) = U(t) - U(t-T)$$
 (3-4)

where U(t) is the unit step (Heaviside) function.

In the derivation below, the abbreviations  $\omega_1 = 2\beta t$  and  $\beta = \pi S$  will be frequently used. The former quantity is an instantaneous frequency which varies linearly with time.

The output response waveform of the photothermal system, y(t), is evaluated via the convolution integral:

$$y(t) = \frac{1}{2} \int_{0}^{T} e^{j\beta\tau^{2}} h(t-\tau) d\tau + \frac{1}{2} \int_{0}^{T} e^{-j\beta\tau^{2}} h(t-\tau) d\tau$$
(3-5)

where h(t) is the impulse response of the system under test, and in practice includes the response of the photothermal system, and all filter stages which lie ahead of the mixer stage.

The Fourier transform of the linear frequency sweep of equation (3-3) is given by:

$$X(\omega) = \frac{1}{2} \left[ \frac{\pi}{2\beta} \left[ e^{-j\omega^2/4\beta} \left[ F(\frac{1}{\beta}T - \frac{\omega}{2\beta}) + F(\frac{\omega}{2\beta}) \right] + e^{j\omega^2/4\beta} \left[ F^*(\frac{1}{\beta}T + \frac{\omega}{2\beta}) - F^*(\frac{\omega}{2\beta}) \right] \right]$$
(3-6)

where \* denotes complex conjugation and where F(x) is the Fresnel integral, given by

$$\mathbf{F}(\mathbf{x}) = \begin{cases} \frac{2}{\pi} \int_{0}^{\mathbf{x}} e^{j\mathbf{u}^{2}} d\mathbf{u} \end{cases}$$
(3-7)

At large values of the arguments

$$\omega/2\{\overline{\beta} \text{ and } \{\sqrt{\beta}\overline{\Gamma} \pm \frac{\omega}{2\sqrt{\beta}}\}, X(\omega) \text{ approaches the form:} \\ X(\omega) = \{e^{j(\omega^2/4\beta - \pi/4)} + e^{-j(\omega^2/4\beta - \pi/4)}\} | \overline{\pi/4\beta}$$
(3-8)

This expression corresponds to the Fourier transform of an ideal linear frequency sweep, without the effects introduced by the finite time duration of the sweep. The inverse Fourier transform of the above expression approximates to an acausal waveform of the form:

$$\mathbf{x}(t) = \frac{1}{2} \{ \mathbf{x}_{+}(t) + \mathbf{x}_{-}(t) \}$$
(3-9)

where we use the abbreviations  $x_{+}(t) = e^{+j\beta t^{2}}$  and  $x_{-}(t) = e^{-j\beta t^{2}}$ .

The maximum values of the sweep rate and sweep duration permitted to give a good approximation to the above case is determined by setting the argument  $|\langle B T \pm \frac{\omega}{2} \rangle|_{B}$  $\geq \varepsilon$  where  $\varepsilon$  has a value of 10 or greater, for a maximum error of 5% in the approximation.

Under these conditions, for a given value of S, the region of small error in the frequency domain is given by:  $f_{min} < f < f_{max}$  where  $f_{min} = \varepsilon \sqrt{\pi/S}$  and  $f_{max} = ST - \varepsilon \sqrt{\pi/S}$ , where the error is considered as a deviation from the transform expected from an infinite duration sweep. Homodyne photothermal spectrometry uses bandpass filtering to limit the detection bandwidth of the response signal, y(t), at both high and low frequencies. If  $f_{min}$  lies below the low frequency cutoff and  $f_{max}$  lies above the high frequency cutoff, then the effects of time windowing of x(t) may be neglected in the analysis below.

The expression for y(t) may then be approximated by the integrals:

$$y(t) = \left[\frac{1}{2}e^{j\beta t^{2}}\int_{-\infty}^{\infty}e^{-j\omega_{1}\tau} \{e^{j\beta\tau^{2}}h(\tau)\} d\tau + \frac{1}{2}e^{-j\beta\tau^{2}}\int_{-\infty}^{\infty}e^{-j(-\omega_{1})\tau} \{e^{-j\beta\tau^{2}}h(\tau)\} d\tau\right]w(t)$$
(3-10)

which relate to a pair of Fourier Transforms in the timelike variable  $\tau$  as seen by the following expression:

$$H(\omega_i) = \int_{-\infty}^{\infty} e^{-j\omega_i \tau} \{e^{j\beta \tau^2} h(\tau)\} d\tau$$
(3-11)

This expression may also be written in rectangular form for convenience:

$$\overline{H}(\omega_{i}) = \overline{H}_{R}(\omega_{i}) + j \overline{H}_{I}(\omega_{i})$$
(3-12)

The output of the physical system under test may then be expressed as:

$$y(t) = \frac{1}{2} \{ e^{-j\beta t^2} H^*(\omega_i) + e^{j\beta t^2} H(\omega_i) \}$$
(3-13)

We now examine conditions under which  $\overline{H}_{R}(\omega)$  gives a good approximation to  $H_{R}(\omega)$ , the real part of the photothermal system's frequency response.

Expansion of the exponentials  $e^{\pm j\beta t^2}$  in equation (3-10) in a Taylor's series and application of the elementary theorems of Fourier analysis gives y(t) in terms of the following series:

$$y(t) = \frac{1}{2} \sum_{m=0}^{\infty} \frac{\beta^{m}}{m!(j)} m \left[ e^{j\beta t^{2}} \frac{\partial^{2m} H(\omega_{j})}{\partial \omega_{i}^{2m}} + (-1)^{m} e^{-j\beta t^{2}} \frac{\partial^{2m} H^{*}(\omega_{j})}{\partial \omega_{i}^{2m}} \right]$$
(3-14)

where  $H(\omega_i)$  is the frequency response function of the physical system under test expressed in terms of the instantaneous frequency  $\omega_i$ . The above expressions relate the Fourier transforms of the phase modulated signals  $\overline{H}(\omega)$  to the photothermal frequency response,  $H(\omega)$ . When the rate of variation of  $H(\omega_i)$  with  $\omega_i$  is sufficiently slow, the zeroth order term in the expansions are proportional to the real part of  $H(\omega_i)$ :

$$y(t) \simeq \frac{1}{2} \left[ e^{j\beta t^2} H(\omega_i) + e^{-j\beta t^2} H^*(\omega_i) \right]$$
(3-15)

The above conditions are met when  $H(\omega_i)$  varies sufficiently slowly with the instantaneous frequency, that the values of all derivatives of order higher than m = 0 are very small. This corresponds to the steady state harmonic condition. At higher sweep rates, terms of order m>0 become significant. These terms give the contribution of the non-steady state signal components to y(t). For a known frequency response  $H(\omega)$ , the conditions required for quasi-steady state harmonic detection may be determined theoretically and any departures from this assumption may be quantitatively computed. With a sufficiently slow sweep rate, the quasi steady-state condition can be met, as seen through the direct proportionality between  $\omega_i$  and S. It is also clear that frequency response functions which vary rapidly with frequency require an intrinsically slower sweep rate to meet this condition, than systems whose frequency response is a slowly varying function of the frequency.

The mixer stage yields an output, z(t) proportional to the product of the two inputs. Under the conditions assumed by equation (3-15) above, the mixer output is given by:  $z(t) \simeq \frac{1}{2} H_{R}(\omega_{1}) + \frac{1}{2} \left[ H_{R}(\omega_{1}) \cos(2\beta t^{2}) + H_{I}(\omega_{1}) \sin(2\beta t^{2}) \right]$   $= \frac{1}{2} |H(\omega_{1})| \cos \omega_{1} t + \frac{1}{2} |H(\omega_{1})| \left[ \cos \varphi(\omega_{1}) \cos(2\beta t^{2}) + \sin(\varphi(\omega_{1})) \sin(2\beta t^{2}) \right]$ (3-16) which explicitly relates the mixer signal to the magnitude  $|H(\omega_{1})|$  and the phase  $\varphi(\omega_{1})$ 

which explicitly relates the mixer signal to the magnitude  $|H(\omega_i)|$  and the phase  $\varphi(\omega_i)$  of photothermal frequency response.

The mixer output consists of the superposition of two components: a fundamental, slowly varying component,  $H_R(\omega_i)$ , which is centered at the baseband, and a high frequency term in parentheses, swept at the second harmonic of the drive frequency. We refer to the first of these components as the 'downshifted' or 'down-converted' mixer component, since it is down-converted in the mixer by the homodyning with the drive sweep. The second harmonic terms are also referred to as the 'up-converted' components. A low pass (baseband) filter (referred to below as the mixer post-filter) is used to reject the high frequency up-converted response and cleanly recover  $H_R(\omega)$ . Typically, the passband of the mixer post filter extends from DC to about 1 kHz.

The downshifted component, proportional to  $H_R(\omega_i)$  at low frequency consists of the projection of the magnitude of the complex frequency response in phase with the x(t) drive signal, as seen from equation (3-16). Both phase and magnitude channels of the photothermal system response may be recovered from  $H_R(\omega_i)$  by the procedure outlined below.

In practice, two sets of filters are used by the homodyne method. In addition to the mixer post-filter required to recover  $H_R(2\beta t)$ , a bandpass pre-filter is imposed on the y(t) response signal before it is introduced into the mixer circuit. The function of this pre-filter is to limit the y(t) signal's detection bandwidth, ensuring that the recorded signal trace,  $H_R(2\beta t)$  attenuates to zero smoothly at the start and end of the input record. Thermal waves pose a particular problem in this respect, because the response magnitude typically increases monotonically with decreasing frequency. The bandwidth of the swept photothermal system response cannot be allowed to extend to zero frequency because a well defined low frequency region must be used to detect the time varying mixer component  $H_R(2\beta t)$ . This detection region cannot be allowed to overlap the bandwidth of the swept photothermal response, or the second harmonic component

passed by the mixer will be detected at the low frequency end of the sweep. This second harmonic contributes a systematic interference to the recovered system response.

A schematic diagram outlining these requirements is given in Fig. 3-3. The bandwidth required to detect  $H_R(2\beta t)$  is set by a fixed postfilter with lowpass characteristics extending from 0 Hz to some cutoff frequency  $F_{c1}$ . The larger the value of  $F_{c1}$ , the faster the permitted time variation of  $H_R(2\beta t)$  for detection without distortion. The theoretical analysis of this effect is outlined below. Concurrently, as  $F_{c1}$  is increased, it is neccessary to set the prefilter's low frequency cutoff,  $F_{c2}$ , to a correspondingly large value to avoid overlap of the photothermal information passband with the detection passband for  $H_R(2\beta t)$ .

This low frequency pre-filtering of y(t) carries the penalty of a loss of low frequency information in the measured photothermal frequency response  $H(\omega)$ . As seen in the results section, this loss of low frequency information has no biasing effect on the measured frequency response data (inside the prefilter passband) for the systems studied. In the computation of the photothermal *impulse* response, however, the filtering of the low frequency information has dramatic effects which must be accounted for when comparing the experimental results with theory. While deconvolution comes to mind as a possible solution, a preferred route for signal processing has been *convolution* of the electrical impulse response. This procedure is discussed in detail in chapter 4. The measured electrical transfer function of the instrumental system, in practice, would be obtained from the cascade combination of the photothermal transducer, the AC coupling network normally used at the input of most preamplifiers, and the transfer function of the prefilter placed ahead of the mixer.

The drive sweep delivered to the photothermal system in these experiments has an almost ideal flatband autospectrum, and relative to the information band set by the combination of transducer and prefilter, the sweep's autocorrelation function behaves as an ideal impulse. This condition can easily be arranged in photothermal systems which use acoustooptically 'chirped' CW laser beams. It is easy to ensure that the output of the generator supplying the frequency sweep is flat as a function of frequency. Wide bandwidth acoustooptic modulators (with high frequency cutoffs of up to 50 MHz) are readily available and give flat modulation depth with frequency over their rated bandwidths.

Fig. 3-3 illustrates the relation between the mixer post-filter passband, the pre-filter stopband and the bandwidth of  $H_R(2\beta t)$ . From the theorems of Fourier analysis, the Fourier transform of  $H_R(2\beta t)$  is evaluated as

$$\int_{-\infty}^{\infty} e^{-j\omega t} \{ H_{R}(2\beta t) \} dt = h_{e}(-\omega/2\beta)$$
(3-17)

where  $h_e(t) = h(t)U(t) + h(-t)U(-t)$ . The significance of this quantity is discussed in more detail below.

As seen in the figure, increasing the sweep rate to large values causes the transform of  $H_R(2\beta t)$  to shift to high frequency, where it eventually overlaps with the passband of the mixer post-filter. This condition produces distortion in the recovered response, because the signal variation of  $H_R(2\beta t)$  becomes rapid compared to the impulse response of the mixer post-filter.

In measurements made with conventional lock-in amplifiers, the real and imaginary parts of the photothermal system response are recovered by detection in phase and in quadrature. A direct recovery of the imaginary part of the system response is obviously
possible in HPS by mixing the y(t) response signal with a quadrature frequency sweep. A wide bandwidth quadrature filter would be required in order to make this measurement, adding to the cost and complexity of the apparatus. However, since the photothermal impulse response is causal, a Hilbert transform relationship exists between the real and the imaginary parts of the measured frequency response (10). The real or the imaginary part of the frequency response is, by itself, sufficient to recover the magnitude, phase and impulse response of the system by computational means. Since, in HPS, the real part of the frequency response is recovered over the full bandwidth of the system, it is possible to use computational means to generate the other representations. An outline of the algorithm is given below.

If the system impulse response is causal (Fig. 3-4(a)) it can be written as the superposition of even  $(h_e(t))$  and odd  $(h_o(t))$  components:

$$h(t) = \frac{1}{2} \{h_{e}(t) + h_{o}(t)\}$$
(3-18)

 $h_e(t)$  and  $h_o(t)$  are given by:

$$h_{a}(t) = h(t) U(t) + h(-t) U(-t)$$
 (3-19)

$$h_{o}(t) = h_{e}(t) \operatorname{sgn}(t)$$
(3-20)

where sgn(t) is defined as:

$$\operatorname{sgn}(t) = \begin{bmatrix} 1 & t \ge 0 \\ -1 & t < 0 \end{bmatrix}$$
(3-21)

The even and odd components Fourier transform individually as:

$$\int_{-\infty}^{\infty} e^{-j\omega t} h_{e}(t) dt = H_{R}(\omega)$$
(3-22)

$$\int_{-\infty}^{\infty} e^{-j\omega t} h_{0}(t) dt = H_{I}(\omega)$$
(3-23)

$$H(\omega) = H_{R}(\omega) + j H_{I}(\omega)$$
(3-24)

The system's impulse response, h(t) is readily recoverable via inverse transformation of  $H_R(\omega)$  to give  $h_e(t)$ , followed by imposition of a window on  $h_e(t)$  to suppress all signal energy at t<0 to zero. In systems which use the discrete Fourier transform, this operation is equivalent to zero filling one half of the input time record. Forward transformation of the windowed time function,  $h_e(t)$ sgn(t) then yields the real and imaginary parts of the system response directly (Fig. 3-4(b)).

#### Experimental section

Homodyne photothermal spectrometry was implemented in this work by means of the instrument diagrammed in Fig. 3-5(a). Fig. 3-5(b) shows the time dependence of waveforms observed at various points in the instrument. In these experiments, we tested the HPS principle using laser photopyroelectric effect spectrometry (9,15). The drive signals in the experiment were linear frequency sweeps, supplied by a low cost sweep/function generator (Hitachi model TFG 4613) with source bandwidths of up to 10 MHz. An FM modulation depth of 1000:1 was available from the main generator by means of an internal voltage controlled oscillator (VCO), whose frequency was controlled by an externally applied analog voltage, as is typical of many low cost sweep generators. The VCO control signal consisted of an analog voltage ramp (-2.0 to 0 V) which was supplied by the output of a 10 bit digital-to-analog converter (DAC), driven under computer controland resident on a Labmaster DT 5712 data acquisition board (Scientific Solutions, Solon, Ohio). A frequency counter (Brunelle Instruments) was used to calibrate the generator output as a function of the applied voltage.

The sweep supplied by the main generator, was used to drive an acousto-optic modulator and was simultaneously connected to the reference channel of the mixer circuit described below. The acoustooptic modulator was used to intensity modulate the Argon ion laser beam which irradiated a thin sample deposited on the surface of a thin film pyroelectric detector. The pyroelectric detector yields an output voltage, y(t), proportional to the average temperature change in the thin film. This mode of detection, termed 'photopyroelectric effect spectrometry' has been used to recover spectroscopic and thermal information from thin film samples in a manner analogous to photoacoustic spectroscopy (15).

The modulated signal recovered from the PPES cell was conditioned using a wideband pre-amplifier (TEK AM 502) directed into a bandpass filter (Kronhite model KH 3103A) with a bandwidth adjustable from 10 Hz (highpass) to 3 MHz (lowpass). The conditioning filter was used in order to ensure attenuation of the y(t) wideband signal to zero at both edges of the frequency span as is essential for accurate recovery of frequency and impulse response information.

The filtered y(t) signal was coupled to the input of a downshifter circuit built in house. The output of the downshifter circuit is applied to the input of a 12 bit analog-to-digital converter (ADC) (Labmaster DT 5712, Scientific Solutions, Solon Ohio), where an acquisition time interval of several milliseconds or greater was used for data acquisition. The VCO ramp and data acquisition operations were performed by software routines written in assembly language. The computer used to log all data was an IBM PC-XT compatible operating at a frequency of 8 MHz.

The design of the downshifter circuit was built around the Analog Devices AD 834 four quadrant double balanced mixer. Both x(t) and y(t) inputs are terminated with 50

ohms at the mixer inputs for signal impedance matching. The AD834 outputs consisted of a differential current amplifier pair. These outputs were shunted to ac ground through 50 ohm precision resistors. The differential output voltage appearing across the pair of 50 ohm loads was  $\pm 400$  mV for 1V peak-to-peak input levels in x(t) and y(t).

The differential output signals were filtered using a pair of first order low pass filters whose bandwidths were adjusted to ca. 1500 Hz. These stages consisted of a pair of passive lowpass RC sections buffered by individual voltage followers. The passive RC sections efficiently couple all up-converted sweep components and high frequency feedthrough to ground ahead of the audio range voltage followers, while transmitting the ultra low frequency  $H_R(2\beta t)$  signal. If the high frequency signal components are smoothly attenuated to zero ahead of the voltage follower stage, audio range operational amplifiers may be used without instability. The outputs of the filter stages are coupled to a differential amplifier to eliminate the substantial dc offset which is transmitted by the previous stages. The outputs of the AD 834 are pulled up to 5V so that a large common mode dc offset is present on both signal channels. A balanced differential amplifier is used to eliminate the common mode offset, provide gain, and reference the output signal to analog ground.

The entire circuit was laid out and etched onto a fiberglass/epoxy printed circuit card. Large ground planes, and short lead lengths to ground were used to minimise signal delays. Care was taken in lead placement to avoid radiation of high frequency (>1 MHz) interference components into signal channels, the establishment of ground loops and the generation of high frequency feedthcugh. The latter source of interference my be especially troublesome above 5 MHz. The circuit performance in terms of high frequency bandwidth and electromagnetic interference levels was very sensitive to lead layout procedures. The current design exhibits a bandwidth of > 5 MHz, and

feedthrough levels of less than 2% at 10 MHz.

#### Signal processing algorithms

All high level signal processing was carried out using the ASYST language. The mixer output signal was proportional to  $H_R(2\beta t)$  as shown in equation (3-16). The measured system frequency response is characteristic of the photothermal system in cascade with the preamplifier input filter and the bandpass signal conditioning filter (Fig. 3-3). Due to the causality of the impulse response exhibited by this system, h(t),  $|H(\omega)|$  and  $\phi(\omega)$  were recovered by means of the algorithm outlined in equations (3-21 3-24).

The original recording of  $H_R(2\beta t)$  was recovered in 4096 point format, where the first 2048 points of the record are repeated and time inverted in the second half of the data record (Fig. 3-6(a)). Keeping in mind that the 'time' axis in this plot is actually an instantaneous frequency, the inverse Fourier transform of the input record is computed as in Fig. 3-6(b) to yield  $h_e(t)$ . It should be kept in mind that the discrete inverse Fourier transform (DIFT) assumes that the entire time record is repeated periodically beyond both edges of the data record. In the format used by ASYST, data extending from N/2 to N (where N is the data record length, 4096 points) is a periodic extension of the data extending from -N/2 to 0, and therefore corresponds to the portion of the signal record for t<0 assumed by the DIFT computation (14). Seen in this way, the signal  $h_e(t)$  is clearly both real valued and even, as expected. Also, the operation of forcing the second half of the input record to zero is equivalent to the operation  $h_e(t)$ sgn(t), on the discrete time (Fig. 3-6(c)) data. The latter yields the desired estimate of h(t), which, under forward transformation gives the estimate of  $H(\omega)$  as magnitude and phase (Fig. 3-6(d) and (e)).

#### Operating conditions

In order for the homodyne spectrometry measurement to be properly implemented, the experimental conditions must be maintained in agreement with the assumptions of the theoretical derivations. The main factors to be considered are the sweep rate, S, and the bandpass of the mixer post-filter.

In the present experiments, measurements were carried out close to the harmonic steady state, over most of the frequency span. This gives the advantage of a relatively large signal amplitude, compared to fast sweep systems, where the effective peak response signal amplitude is proportional to  $\{1/\sqrt{S}\}$ .

A key factor limiting the sweep rate in these experiments is the bandwidth of the mixer post-filter used to process the data. As the sweep rate increases, more and more of the signal energy in  $H_R(2\beta t)$  is shifted to high frequencies, and the bandpass of this down-converted signal transient begins to overlap with the roll-off curve of the mixer post-filter as in Fig. 3-3. However, if the passband of the mixer post-filter is increased, its capability for rejecting any contribution from the up-converted signal components present at the lower end of the sweep frequency range is diminished, and the post-filter transmits this leakage, resulting in an oscillatory interference, in  $H_R(\omega_i)$  at low frequency.

The maximum allowable sweep rate is strongly dependent on the form of  $H(\omega)$  recovered for the system. Fig. 3-7 and 3-8 show two different experimentally measured frequency response functions acquired using the downshifter system. In Fig. 3-7, the test system was a four pole Butterworth filter with bandpass set from 1 kHz to 500

kHz, and swept from 1 kHz to 1 MHz. Fig. 3-8 shows the frequency response data recovered for a thin film pyroelectric effect detector. These detectors are characterised by a short risetime (which may be made less than one nanosecond), and a slow decay which is characteristic of thermal conduction.

Because of the highly dissipative character of the photothermal frequency response.  $H(\omega)$  and  $H_R(\omega)$  roll off rapidly with frequency for the pyroelectric sensor. The Butterworth filter response varies much more slowly with frequency. The recorded homodyne signal,  $H_R(2\beta t)$  therefore tends to vary much more rapidly in time for the pyroelectric sensor than for the Butterworth filter. A much slower sweep rate must be used for the photothermal system, therefore, in order to ensure a negligible contribution of the higher order derivatives in equation (3-15) to the mixer output, and to ensure that the variation in time of  $H_R(2\beta t)$  is much slower than the impulse response of the mixer post-filter.

Fig. 3-9 also shows the impulse response recovered for the thin film pyroelectric sensor at various values of the sweep rate. The form of the sensor's impulse response recorded at the slow sweep rate matches the decay profile expected from theory as outlined in chapter 4. The effect of sweep rate is most severe at long times in the impulse response, corresponding to low frequencies. This is not surprising: the response peak in  $H(\omega)$  is centered near 0 Hz and therefore  $H_R(2\beta t)$  reaches a sharp maximum near t=0.  $H_R(2\beta t)$  is made slow in time compared to the impulse response of the mixer output filter only for sufficiently small S. The  $H_R(2\beta t)$  component transmitted by the filter under these conditions is free of broadening effects contributed by the output filter.

The signal fidelity of our homodyne spectrometry apparatus was evaluated by comparing frequency response data, recorded using the homodyne method, with standard lock-in analyser traces. This comparison evaluates whether the magnitude and phase response channels are being correctly recovered at all frequencies within the detection bandwidth. Two different test systems were used to make this confirmation.

At high frequency, a Butterworth bandpass filter with a response from 3 KHz to 3 MHz was used as the test system to ensure that the homodyne recordings accurately recovered the high frequency signal data without distortion. In Fig. 3-10, the homodyne measurement of the frequency response of the filter is compared with independent steady state harmonic measurements. Both magnitude and phase recordings show agreement to within experimental error. This result confirms that the assumptions used to derive equations (3-16 - 3-24) applied in the experiment. It furthermore confirms the absence of feedthrough artifacts as well as phase distortion and other problems related to circuit layout that are common at high frequency.

The second test evaluated the capability of our homodyne apparatus for recording a highly dissipative system response without distortion. To make this test, a thin film pyroelectric sensor was overcoated with a ca. 2  $\mu$ m overlayer of ink, which acted as an opaque blackbody absorber layer. Heat conduction through the ink layer is a relatively slow process and the frequency response associated with the heat conduction process shows a response magnitude which peaks rapidly near zero Hz. This produces a downshifted component, H<sub>R</sub>(2 $\beta$ t), which changes rapidly in time, unless the sweep rate is reduced. If S is set too high, a rapid time variation of H<sub>R</sub>(2 $\beta$ t) results, and the mixer post filter may not be fast enough to respond without distortion. This problem tends to dominate with thermally thick samples for which there is a strong increase in  $|H(\omega)|$  with decreasing frequency. This result, again, directly confirms, the application of the assumptions of equations (3-16 - 3-24) under stringent experimental conditions.

Fig. 3-11 shows the agreement obtained at low frequency between the homodyne

recordings and data recovered with an audio range lock-in amplifier. The agreement obtained between the lock-in data and the HPS frequency response data at low frequency indicate that sweep rate effects are not significant below a value of 800 kHz/s. Homodyne recordings may be made in a fraction of the time required for lock-in detection even under these relatively extreme conditions.

Further evaluations of the response of the homodyne photothermal measurement system were made by recording h(t) and H( $\omega$ ) for the thin film pyroelectric sensor overcoated with ultrathin films of several polymer materials of known thickness and thermal properties. Details of the sample preparation and film characterisation are given in chapter 4. A thickness range of 80-1200 nm was used.

In the study outlined in Fig. 3-12, sample layers were deposited on the surface of a pyroelectric sensor using spin coating techniques. These layers were overcoated with thin films of aluminum which acted as infintesimally thin plane surface heat sources (note that the thermal transit times through these metal layers are negligible compared to thermal transit times through polymer layers of similar thickness). response data recorded in Fig. 3-12 shows the effect of heat conduction through a thin layer of increasing thickness, and into the pyroelectric detector. The peak delay in the impulse response trace increases with sample thickness, consistent with equation (3-2).

The data of Fig. 3-12 compare the experimental impulse response with a theoretical four layer heat conduction model derived for these assemblies in chapter 4. Because the response data are prefiltered in these measurements, and because the electrical response of the pyroelectric sensor is not uniform with frequency, it is neccessary to take into account an instrumental transfer function comprised of the electronic pre-filter and the pyroelectric sensor's electrical network response in modeling the data. This is done in

practice by independently measuring the instrument transfer function (in the absence of the photothermal excitation) and aperiodically convoluting the recovered instrument impulse response with the impulse response profiles predicted from theory (9).

As seen from the results compared in Fig. 3-12, the homodyne photothermal spectrometry measurement is readily accounted for by the heat conduction theory relevant to the problem. The excellent agreement between theory and experiment indicate that the HPS method can be reliably applied to photothermal measurement systems with good signal fidelity.

The combination of the wide bandwidth response of the pyroelectric transducer and the high frequency detection capabilities of HPS provide a sensitive, low cost method for the evaluation of thin polymer films at thicknesses below 100 nm. This technique is being used to measure the thermal properties of such films, and to study the processes of adhesion at metal/polymer and polymer/polymer interfaces on length scales approaching 50 nm or below.

### A comparison of the homodyne method to other signal recovery methods

HPS shows the closest resemblance to signal recovery by a lock-in amplifier, and exhibits many of the advantages of lock-in detection, including dynamic range, linearity and rejection of wideband noise. Both frequency and impulse response data are available at high resolution. The classic lock-in amplifier, on the other hand, is a device which is optimised for extremely narrowband detection, and the attainment of a harmonic steady-state. The reference channel slew rates of conventional lock-in amplifiers are designed to permit tracking of slowly varying signals. Moderate sweep

rates may introduce a phase error which varies with frequency (16). Over the wide frequency ranges and sweep rates successfully used by HPS, this phase error would be large and highly variable over the signal band if conventional lock-in detection were attempted. Furthermore tracking may be lost entirely in lock-in detection if the signal channel frequency varies as rapidly in time as is the case in HPS.

The major operational deficiency of HPS, is that it uses the real part of the input frequency domain response to reconstruct the system magnitude and phase. This procedure is reliable and accurate only if the real or in-phase channel recording is made over the full bandwidth of the system, and  $|H(\omega)|$  properly attenuates to zero at the edges of the drive frequency span  $(\omega_1 - \omega_2)$ . Furthermore, a Hilbert transform relationship must exist between the real and imaginary parts of the system frequency response. This assumption will be true if the impulse response of the system under test is causal (h(t<0) = 0).

HPS compares favourably with wideband photothermal methods such as FM Time-delay spectrometry (7), and AM-PM wideband spectrometry (8). In conventional FM or 'chirp' measurements, a repetitive frequency sweep is applied to the system under test and the response waveform y(t) is averaged in the time domain over many data records. A potential problem in this case is the introduction of wideband noise into the measurements. However, in HPS, because of the self mixing operation used, the signal noise is dispersed as a function of the instantaneous frequency, and does not affect the entire measured frequency spectrum. At frequencies above 100 kHz, linear FM sweep methods become expensive to implement. A primary requirement is for faster data acquisition systems: this requirement is sidestepped entirely by HPS since the detection bandwidth is always fixed at a few kilohertz. Another requirement of linear FM excited systems is that the applied frequency sweep have a reproducible

initial phase if time domain signal averaging is used. Inexpensive waveform generators employing voltage-controller oscillator (VCO) sweep controls do not adequately meet this criterion, and the introduction of a digital based sweep synthesizer entails a significantly increased expense. HPS on the other hand, uses continuous mixing of signal and reference channels, and is therefore much more immune to initial shifts in the phase of the drive waveform.

Similar considerations apply in comparing HPS to direct impulse response measurements. It is essential to use expensive fast transient recording equipment to recover early time pulsed information from a system under test. Like wideband measurements the impulse measurement suffers from the problem of introducing wideband noise into the signal measurements. The chief asset of the impulse measurement which is not shared by HPS (or any of the above methods) is its extremely large peak power, which is an important advantage in recovering information from systems whose signal levels are intrinsically weak.

# Conclusions

Homodyne photothermal spectrometry is a rapid, high resolution, inexpensive wide bandwidth technique for photothermal impulse and frequency response measurement. The method borrows many of the elements of classic lock-in detection with the important difference that the instrumentation is not optimised for steady-state operation, and quadrature filtering of the input signal is bypassed. The HPS apparatus readily provides bandwidths of up to 10 MHz or greater, so that ultrathin films may be photothermally profiled.

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Fig. 3-1: Schematic diagram illustrating the principles of homodyne spectrometry measurements.

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Fig. 3-2: Schematic diagram of a linear frequency sweep, indicating relevant sweep variables.

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Fig. 3-3: Schematic diagram showing correct specifications for pre-filter stopband and mixer post-filter passband, and illustration of the effect of sweep rate on the bandwidth of the detected homodyne signal.





Fig. 3-4: Illustration of the interrelationship between (a) h(t),  $h_e(t)$  and  $h_o(t)$ ; (b)  $H_R(\omega)$ ,  $H_I(\omega)$  and  $h_e(t)$ ,  $h_o(t)$ .

# INSTRUMENTAL MEASUREMENT SYSTEM



Fig. 3-5: (a) Block diagram of homodyne photothermal spectrometry apparatus used in this work (b) time dependence of waveforms observed at various points in the apparatus



Fig. 3-5: (c) electrical schematic of the mixer/filter stage.

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Fig. 3-6: Stepwise results of processing algorithm used for single channel signal recovery on a typical set of experimental data: (a) input time record,  $H_R(2\beta t)$ ; (b)  $h_e(t)$ ; (c) h(t); (d)  $|H(\omega)|$  and (e)  $\varphi(\omega)$ . The test system was a thin film  $\beta$ -poly(vinylidene fluoride) (PVDF) pyroelectric sensor, irradiated with a modulated laser beam.

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Fig. 3-6: (c) h(t); (d)  $|H(\omega)|$  and (e)  $\varphi(\omega)$ .



Fig. 3-7: Homodyne spectrometric measurement of the frequency response of a four pole Butterworth bandpass filter, with passband set 1 kHz- 500 kHz and sweep bandwidth of 1 kHz-1 MHz. Sweep rate was 0.8 MHz/s.



Fig. 3-8: Homodyne spectrometric measurement of the photothermal frequency response of a 9  $\mu$ m  $\beta$ -poly(vinylidene fluoride) (PVDF) pyroelectric receiver. Measurements were made assuming the following conditions: sweep bandwidth: 1 kHz-1 MHz; sweep rate: 400 KHz/s, Number of sweeps averaged: 25, preamplifier passband: 1 kHz - 1 MHz.



Fig. 3-9: Sweep rate dependence of photothermal impulse response recordings recovered for 9  $\mu$ m PVDF pyroelectric receiver. Sweep rates were as noted in the diagram.





Fig. 3-10: High frequency signal fidelity tests on four pole Butterworth bandpass filter. (-----) indicates homodyne measurement; (O) indicates independent steady-state harmonic measurement. Homodyne measurement conditions were as follows: filter passband: 5 kHz - 3 MHz, sweep bandwidth: 1 kHz- 10 MHz, sweep rate: 4 MHz/s, 25 sweeps averaged.



Fig. 3-11: Signal fidelity test on highly dissipative, slow thermal system (see text for details): (a)  $|H(\omega)|$  and (b)  $\varphi(\omega)$ . (------) indicates homodyne spectrometry measurement; (O) indicates independent steady state harmonic measurement. Measurement conditions were as follows: sweep bandwidth: 1 kHz - 1 MHz, prefilter passband: 3 kHz - 500 kHz, sweep rate: 0.4 MHz/s, 25 sweeps averaged.



time (us)

Fig. 3-12: Photothermal impulse response data recorded in thermal transmission mode with polyvinyl chloride films of indicated thickness deposited on the surface of a 9  $\mu$ m B-PVDF pyroelectric sensor. Theory and experiment are plotted together. (Details in chapter 4). Measurement conditions were as follows: sweep bandwidth: 1kHz-1MHz, prefilter passband: 3kHz-500kHz; sweep rate: 0.8 MHz/s; fitted thermal diffusivity; 5.x10<sup>-8</sup>m<sup>2</sup>/s. Thermal effusivities at sample/pyroelectric and pyroelectric/backing had values of 1.1. Chapter 4:

Thermophysical Measurements and Interfacial Adhesion Studies in Ultrathin Polymer Films Using Homodyne Photothermal Spectrometry

# Introduction

In the analysis of synthetic high polymers, thermophysical measurements have traditionally played a key role in physical characterization (1). In addition to identifying melting points and glass transition temperatures, classical thermophysical methods such as differential scanning calorimetry (DSC) are capable of yielding measurements of the heat capacity, C, and the thermal conductivity,  $\kappa$ , of a bulk sample, with proper calibration. These quantities, in combination with the bulk density, enable the recovery of the thermal diffusivity,  $\alpha$ , which is an essential quantity for characterizing transient heat flow in a material (1,2).

The most serious limitation of many classical thermophysical measurement techniques is the requirement for a bulk sample which is thermally homogeneous and available in moderately large quantities (a few hundred  $\mu g$  or greater). In the analysis of ultrathin polymer films, the thermal properties of the sample may vary significantly from the classical bulk values, due to the presence of alignment forces in the film which potentially cause anisotropies in heat conduction (3-5). A thermophysical analysis method which can be applied to the thin film in-situ is essential.

In recent years, photoacoustic and photothermal methods of analysis have evolved a powerful class of techniques for the non-destructive measurement of the thermophysical and optical properties of materials (5-7). These methods use the non-radiative conversion of absorbed light energy to heat the sample. Because of their low values of the thermal diffusivity and conductivity, very thin polymer films are easily studied by these techniques (5). The recently developed technique of laser photopyroelectric effect spectrometry (PPES) shows outstanding characteristics with respect to sensitivity, versatility, and thickness resolution (4,5,8).

In laser PPES (LPPES) a thin film specimen is coated or deposited onto the surface of a thin film pyroelectric sensor (typically beta-poly(vinylidene fluoride)), and heated with a pulsed or modulated laser beam (8). The thin film sensor material exhibits a change in electric polarisation, in response to a change in the average temperature of the film. This is conveniently measured as a voltage change induced by heating the sample. By monitoring the propagation of a heat pulse through a thin film sample attached to the sensor surface, it is possible to directly measure the thermal diffusivity of the sample, at submicron thicknesses, using the thermal transmission geometry (4).

Laser PPES also possesses the potential capability for measuring the interfacial properties of layered systems, due to the presence of thermal contact resistance at poorly bonded interfaces. Previous work using other photothermal techniques has established a relationship between the thermal contact resistance between adjacent layers, and the adhesive bond strength (9,10).

In this work, the technique of homodyne photopyroelectric spectrometry developed in the last chapter is used to make thermophysical measurements on thin films ranging in thickness from 80 to 1200 nm, using two different irradiation geometries. In contrast with previous laser PPES work on thin films, this study emphasizes the use of the so called inverse pyroelectric mode geometry (12), in which the sample is excited through the deposition of energy at the metal-polymer interface existing between the sensor layer and the sample. This geometry, in combination with the high frequency bandwidth of the homodyne laser PPES measurement, enables the convenient study of extremely thin interfacial layers at a metal/polymer interface, approaching the length scale of the macromolecular chains. It may be used to non-destructively evaluate adhesive bonding at the interface between a metal and an ultrathin polymer film. The homodyne laser PPES measurement performs readily in a film thickness regime where

many other techniques, including spectroscopic methods, fail outright, due to a lack of sufficient sample quantity (or pathlength) for analysis.

While the work reported here focuses specifically on thermophysical and interfacial analysis, it should be pointed out that the experimental HPS methodology reported here is equally applicable to the depth profiling of optical absorption in sub-micron thickness films, provided the optical absorption coefficient of the film is large enough.

#### Theoretical section

Laser photopyroelectric spectrometry uses a thin film pyroelectric sensor to monitor heat flow through a sample in thermal contact with the pyroelectric. The pyroelectric sensor material is poled near its Curie temperature, and exhibits a change in the electric polarisation in response to a change in the average temperature of the film. The temperature induced polarisation change is normally measured as a voltage change across the film according to the relationship (8):

$$V(t) = \frac{k_p}{\epsilon d_f} \langle \Delta T(x, y, z, t) \rangle$$
(4-1),

where  $\varepsilon$  and d are the dielectric constant and thickness, respectively, of the pyroelectric thin film sensor,  $k_p$  is a figure of merit for the pyroelectric, and  $\langle \Delta T(x,y,z,t) \rangle$  is the spatially averaged temperature in the film. For one dimensional heat conduction,  $\langle \Delta T(x,y,z,t) \rangle = \langle \Delta T(x,t) \rangle$ , where  $\langle T(x,t) \rangle$  is the temperature profile induced along the axis of the film by heating. Equation (4-1) assumes that the sensor material is homogeneous to a good approximation.

The homodyne laser PPES method enables the recovery of data in both the time or frequency domains. However, this work will emphasize the photopyroelectric impulse response, which is the response of the photothermal system to excitation by a short pulse. Two possible detection geometries are available as outlined in Fig. 4-1. In the transmission mode geometry, the sample under study is deposited onto the pyroelectric sensor and overcoated with a blackbody absorber whose thickness is negligible compared to the sample layer. This surface layer is irradiated with a laser beam , heat generation occurs in a thin sheet at the surface, and the temperature profile propagates from the sample surface to the sensor layer where it is detected.

The inverse mode geometry takes advantage of front surface thermal wave reflections to obtain information about the sample. In the present work, the polymer samples are irradiated at wavelengths where they are optically transparent. In the inverse mode, the sample layer is deposited on the surface as a clear overcoat, light absorption occurs at the surface of the pyroelectric sensor, and heat conduction is divided into two components, as in Fig. 4-1.: a left going component which propagates in the sensor layer directly, and a right going component which propagates in the sample layer. This second component diffuses until it reaches the gas/solid interface at the front surface of the sample, and is effectively, 100% reflected due to the presence of a large mismatch in thermal effusivity existing at that surface. The reflected component is returned to the pyroelectric layer, arriving after a delay time which increases with the sample thickness. The superposition in time of the direct and delayed components causes a broadening of the pyroelectric impulse response as sample layers of increasing thickness are deposited on the pyroelectric sensor.

Both thermal transmission and inverse mode measurements have potential sensitivity to interfacial thermal phenomena, due to the reflection of thermal waves which occurs at interfaces of thermally dissimilar media. The reflection of thermal waves is shown schematically in Fig. 4-1 as a folding of the temperature profile which occurs upon

reflection. This is an accurate depiction of the reflection process occuring at a totally reflecting boundary. These reflections are analogous to the case of acoustic or optical reflections except that the thermal wave is critically damped with distance away from the boundary (13).

The extent of reflection occuring at a thermal interface may be quantified by means of the thermal reflection coefficient,  $\Gamma_{ii}$  where:

$$\Gamma_{ii} = (b_{ii}^{-1})/(b_{ii}^{+1})$$
(4-2)

where the quantity  $b_{ij}$  is the ratio of the thermal effusivities between two adjacent media. The thermal effusivity ratio is given by:

$$b_{ij} = (\kappa_i/\kappa_j) \cdot (\alpha_j/\alpha_i)^{1/2}$$
(4-3)

where  $\kappa_i$  and  $\alpha_i$  give the thermal conductivity and thermal diffusivity of the ith layer, respectively.

In the presence of thermal contact resistance, the thermal reflection coefficient becomes complex (with the imaginary component indicating interfacial loss) (9). An experimental relationship between the thermal contact resistance and the adhesive bond strength between layers has been established by various authors (9,10).

Fig. 4-2 outlines a theoretical model which we have used to evaluate thermophysical properties and interfacial effects in thin polymer films attached to the pyroelectric effect transducer.

The sample-pyroelectric system is described by four thermally distinct layers, consisting of gas[1], sample[2], interfacial contact layer[3], and pyroelectric[4].

The thermal effusivity ratio at the pyroelectric/backing interface is assumed to be approximately unity. This can be assured by design, in the choice of a backing material which is approximately thermally matched to the pyroelectric. Additionally, the thickness of the sample layer is so much less than the pyroelectric, that heat flow is monitored on a timescale which is rapid, relative to the time for significant energy to reach the backing, giving a measurement which is insensitive to backing effects.

The effect of thermal contact resistance at the sample/pyroelectric interface is modeled by inserting a thin layer of low effusivity material between the debonded layers, according to the method of Aamodt et al (14).

Finally, the model neglects the thermal contributions of the metallization layers that are applied to the pyroelectric and ,in transmission mode, to the sample surface. These layers are of the order of 100 nm thickness, and are thermally thin at all times used in this study.

The temperature profile in the pyroelectric, layer (4) was solved by the Laplace transform method of Reference (15). The heat conduction equation is written for each of the layers in the model:

gas: 
$$\frac{\partial^2 \Delta T_1}{\partial x^2} - \frac{1}{\alpha_1} \frac{\partial \Delta T_1}{\partial t} = 0$$
 (4-4)

sample: 
$$\frac{\partial^2 \Delta T_2}{\partial x^2} - \frac{1}{\alpha_2} \frac{\partial \Delta T_2}{\partial t} = \begin{bmatrix} -\delta(x)\delta(t) \text{ (transmission mode)} \\ 0 \text{ (inverse mode)} \end{bmatrix}$$
 (4-5)

contact layer:  $\frac{\partial^2 \Delta T_3}{\partial x^2} - \frac{1}{\alpha_3} \frac{\partial \Delta T_3}{\partial t} = 0$  (4-6)

pyroelectric:  $\frac{\partial^2 \Delta T_4}{\partial x^2} - \frac{1}{\alpha_4} \frac{\partial \Delta T_4}{\partial t} = \begin{bmatrix} 0 & (\text{transmission}) \\ -\delta(x+(\ell+d))\delta(t) & (\text{inverse}) \end{bmatrix}$  (4-7)

A heat flux source is assumed to be present at the sample surface for the transmission mode measurement and at the pyroelectric surface, in the inverse case.

One dimensional heat conduction mechanisms are assumed because the width of the irradiation beam is several orders of magnitude greater than the thickness of the sample and pyroelectric layers. Boundary conditions of heat flux and temperature continuity are imposed at all interfaces in the model and the Laplace transform of the temperature in the pyroelectric layer is evaluated for the transmission mode case as:( details provided in the appendix c)

$$<\Delta T_{4}(x,s) > = \frac{4}{2(d_{f} - d_{ep})(1 + b_{34})(1 + b_{32})} (\alpha_{4}/\alpha_{2})^{1/2}$$

$$\sum_{n=0}^{\infty} \sum_{k=0}^{n} \sum_{j=0}^{k} \frac{n!}{(n-k)!(k-j)!j!} \Gamma_{32}^{n+k-j} (-1)^{j+1} \frac{1}{s} \left[ e^{-\frac{1}{2}\overline{\tau_{15}}} - e^{-\frac{1}{2}\overline{\tau_{25}}} \right]$$

$$(4-8)$$

where  $\tau_1$  and  $\tau_2$  are thermal time constants, defined for the transmission mode measurement as:

$$\tau_1 = \left[\frac{\ell(2(n-k+j)+1)}{\alpha_2} + \frac{d(2(n-j)+1)}{\alpha_3} + \frac{d_{ep}}{\alpha_4}\right]^2$$
(4-9a)

$$\tau_2 = \left[\frac{\ell(2(n-k+j)+1)}{\alpha_2} + \frac{d(2(n-j)+1)}{\alpha_3} + \frac{d}{\alpha_4}f_{-1}\right]^2$$
(4-9b)

The Laplace transform of the temperature for the inverse mode case is given by:

$$\langle \Delta T_4(\mathbf{x},s) \rangle = \frac{1}{2(d_{\tilde{f}}d_{ep})} \sum_{n=0}^{\infty} \sum_{k=0}^{n} \sum_{j=0}^{k} \frac{n!}{(n-k)!(k-j)!j!}$$

$$\Gamma_{32}^{n+k-j} (-1)^{j+1} \frac{1}{s} \left[ \Gamma_{32} \left( e^{-\sqrt{\tau_{1}s}} - e^{-\sqrt{\tau_{2}s}} - e^{-\sqrt{\tau_{5}s}} + e^{-\sqrt{\tau_{6}s}} \right) + \Gamma_{32}^{2} \left( e^{-\sqrt{\tau_{3}s}} - e^{-\sqrt{\tau_{4}s}} \right) - e^{-\sqrt{\tau_{7}s}} + e^{-\sqrt{\tau_{8}s}} \right] + \frac{1}{2(d_{f}^{-} - d_{ep})} \left( e^{-\sqrt{\tau_{9}s}} - e^{-\sqrt{\tau_{10}s}} \right)$$

$$(4-10)$$

where the  $\tau$  factors are thermal time constants given for the inverse mode case by:

$$\tau_1 = \left[\frac{2(n-k+j)\ell}{1\alpha_2} + \frac{2(n-j)d}{1\alpha_3} + \frac{d_{ep}}{1\alpha_4}\right]^2$$
(4-11a)

$$\tau_2 = \left[\frac{2(n-k+j)\ell}{\sqrt{\alpha_2}} + \frac{2(n-j)d}{\sqrt{\alpha_3}} + \frac{d}{\sqrt{\alpha_4}}f^{-1}\right]^2$$
(4-11b)

$$\tau_3 = \left[\frac{2(n-k+j+1)\ell}{\sqrt{\alpha_2}} + \frac{2(n-j)d}{\sqrt{\alpha_3}} + \frac{d_{ep}}{\sqrt{\alpha_4}}\right]^2$$
(4-11c)

$$\tau_4 = \left[\frac{2(n-k+j+1)\ell}{\sqrt{\alpha_2}} + \frac{2(n-j)d}{\sqrt{\alpha_3}} + \frac{d}{\sqrt{\alpha_2}}\right]^2$$
(4-11d)

$$\tau_5 = \left[\frac{2(n-k+j)\ell}{\alpha_2} + \frac{2(n-j+1)d}{\alpha_3} + \frac{d_{ep}}{\alpha_4}\right]^2$$
(4-11e)

$$\tau_6 = \left[\frac{2(n-k+j)\ell}{\alpha_2} + \frac{2(n-j+1)d}{\alpha_3} + \frac{d}{\alpha_4}f_{-1}\right]^2$$
(4-11f)

$$\tau_7 = \left[\frac{2(n-k+j+1)\ell}{4\alpha_2} + \frac{2(n-j+1)d}{4\alpha_3} + \frac{d_{ep}}{4\alpha_4}\right]^2$$
(4-11g)

$$\tau_8 = \left[\frac{2(n-k+j+1)\ell}{\sqrt{\alpha_2}} + \frac{2(n-j+1)d}{\sqrt{\alpha_3}} + \frac{d}{\sqrt{\alpha_4}}f^{-}\right]^2$$
(4-11h)

$$\tau_9 = \left[\frac{d_{ep}}{d_4}\right]^2 \tag{4-11i}$$

.

$$\tau_{10} = \left[\frac{d_f}{d_4}\right]^2 \tag{4-11j}$$

At the gas/sample interface, we assume that the thermal effusivity ratio  $b_{12} = 0$ . This assumes that a negligible component of temperature change reaches the gas layer by conduction. At the pyroelectric/backing interface, the thermal effusivity is set to unity. This assumes that the thermal waves are conducted throught the pyroelectric into the

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rear backing without reflection. The average pyroelectric temperature is obtained from equation 4-1 integrating over the active medium which extends from  $-(\ell+d+dep)$  to  $-(\ell+d+d_p)$  in Fig. 4-2.

In order to simulate the response of a real pyroelectric material on very short timescales, it is necessary to take account of a thin layer of depoled material which exists at the surface of the pyroelectric film (16,17). In commercially supplied sensor materials, this layer may be up to 500 nm thick, and its contribution to the response of the pyroelectric signal cannot be neglected in the time regime accessed by homodyne laser PPES (17). We have assumed here that the depoled region has similar thermophysical properties to the bulk pyroelectric material, and acts primarily as an electrically inactive zone at the surface of the transducer. The validity of this assumption is explored below.

Inversion of the respective Laplace transforms and evaluation of the average temperature in layer (4) yields, for the transmission mode case:

$$<\Delta T_{4} x,t > = \frac{4 b_{12}}{2(d_{\tilde{f}}d_{ep})(1+b_{34})(1+b_{32})} (\alpha_{4}/\alpha_{2})^{1/2}$$

$$\stackrel{\bullet}{\sum} \sum_{n=0}^{n} \sum_{k=0}^{k} \frac{n!}{j=0} \frac{n!}{(n-k)!(k-j)!j!} \Gamma_{32}^{n+k-j} (-1)^{j+1} \left[ \operatorname{erfc} \left\{ \frac{1}{2} \overline{\frac{1}{4}\tau_{1}/\tau} \right\} - \operatorname{erfc} \left\{ \frac{1}{2} \overline{\frac{1}{4}\tau_{2}/\tau} \right]$$

$$(4-12)$$

for the inverse mode measurement:

$$\langle \Delta T_4(\mathbf{x},t) \rangle = \frac{1}{2(d_f - d_{ep})} \sum_{n=0}^{\infty} \sum_{k=0}^{n} \sum_{j=0}^{k} \frac{n!}{(n-k)!(k-j)!j!}$$

$$\Gamma_{32}^{n+k-j} (-1)^{j+1} \left[ \Gamma_{32} \left( \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_1/t} \right\} - \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_2/t} \right\} - \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_5/t} \right\} + \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_6/t} \right\} \right)$$

$$+ \Gamma_{32}^2 \left( \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_3/t} \right\} - \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_4/t} \right\} \right) - \operatorname{erfc} \left\{ \frac{1}{2!} \overline{\tau_7/t} \right\}$$

+ erfc{
$$\frac{1}{2}(\tau_{8}/\tau)$$
] -  $\frac{1}{2(d_{f} - d_{ep})}$  (erfc { $\frac{1}{2}(\tau_{9}/\tau)$  - erfc { $\frac{1}{2}(\tau_{10}/\tau)$  (4-13)

In order to compare theory and experiment in measurements made with the homodyne PPES method, as with the pulsed method(4), it is necessary to take into account the electrical impulse response of the pyroelectric transducer and all filter stages used to process the photothermal signal ahead of the mixer stage. This electrical impulse response is experimentally measured by using a signal generator connected in series with the pyroelectric film as shown in Fig. 4-3(a), to drive the transducer and filter stages. The generator replaces the photothermally induced voltage change which acts in series with the transducer in the equivalent circuit. The measured electrical impulse response for a typical pyroelectric system is shown in Fig. 4-3(b). The theoretically computed impulse response obtained from equation (4-10) or (4-11) (Fig. 4-3(c)) is aperiodically convoluted with the impulse response of Fig. 4-3(b) to yield the theoretical instrumental signal (Fig. 4-3(d)). This latter quantity is compared with the corresponding experimental signal recorded by the instrument.

In this work, all calculations were made on a personal computer using ASYST (TM, Adaptable Laboratory Software Inc.).

#### Experimental section

### Instrumentation

Homodyne laser PPES was implemented using the instrumental apparatus shown in Fig. 4-4. The homodyne signal recovery method used in this work was described in detail in chapter 3 and is used to recover the photopyroelectric impulse response with good early time resolution. Excitation was obtained from an Argon ion laser (Coherent Innova 70-2) which was intensity modulated with an acoustooptic modulator (Isomet 1201E). The modulator was equipped with a model (232C) driver and was driven using excitation sweeps supplied from a low cost sweep/function generator (Hitachi TFG 4613, Rosgol Industries). The modulated beam was directed into a pyroelectric cell of our own design, which is described in detail in chapter 2.

The output of the pyroelectric cell is directed into a wideband preamplifier (Tektronix AM-502) followed by a four pole Butterworth filter (Kronhite model 3103A) with a bandwidth of 3 kHz to 500 kHz. The output of the bandpass filter was then fed into the downshifter circuit.

#### Sample and sensor preparation

Poly(vinylidene fluoride) (PVDF) sensor material as supplied by Atochem was used for pyroelectric detection. The material had a 9  $\mu$ m thickness, and was overcoated on both sides with a 100 nm Nickel/Aluminum metallization. Preliminary photopyroelectric measurements on the as received material indicated that a depoled layer of ca. 400 nm thickness was present at both sensor surfaces (see Results section).

Sample deposition onto the PVDF sensor material was achieved by means of spin coating from solutions of poly(vinylchloride), poly(methyl methacrylate) and polystyrene, ranging in concentration from 0.5-4.0 % weight of dissolved polymer in the appropriate organic solvent (see below). The thickness range provided by our spin coating apparatus ranged from 80 to 1200 nm. Prior to spin deposition, it was necessary to clean the sensor surfaces with methanol (Spectrograde solvent) to ensure that the

films were well bonded to the top aluminum metallization.

Surface metallization of the polymer samples was required for transmission mode photopyroelectric measurements. Aluminum films of ca. 150 nm thickness were deposited onto polymer/PVDF detector assemblies using sputtering methods.

### Thickness characterisation

Individual sample thicknesses were directly measured using transmission electron microscopy after inverse and transmission mode photopyroelectric measurements were made. The sample/PVDF assemblies were cured in an EPON 812 resin matrix (J.B. EM, Montreal Canada) at 60°C and microtomed to a thickness of ca. 80 nm, using a diamond blade (Reichert Ultracut, Austria).

Transmission electron micrographs were run on the thin sections using a Phillips EM410 electron microscope and photographed at a magnification of 52,000 X. A typical micrograph of a sample/PVDF assembly is shown in Fig. 4-5. A 350 nm ( $\pm 10\%$ ) film of polystyrene is sandwiched between a top layer of ca. 200 nm of sputtered Al and 80-100 nm Al overcoated Ni metallization as supplied by Atochem. The PVDF expands while heated in the curing oven and shrinks back when cooled to room temperature putting strain on the metal polymer interfaces. In this case the PVDF-Ni/Al metal bond separated.

### Materials

Poly(vinylchloride) (PVC) of minimum molecular weight 280,000 was obtained from

Aldrich. The as-received material had a glass transition temperature of 85°C and a melting point of 237.5°C, as measured by the supplier. Stabilisers and plasticisers were removed by means of a cleanup procedure which precipitated the PVC from a solution of tetrahydrofuran with methanol. This washing procedure was repeated three times. Removal of impurities was confirmed using infrared spectroscopy. Samples of PVC were spin coated from solutions of tetrahydrofuran.

Polystyrene (PS) was used as received from Aldrich. The molecular weight was greater than 280,000, the glass transition temperature was 100°C, and the melting temperature was 237.5°C, as specified by the supplier. Solutions of polystyrene for spin coating were prepared in toluene.

Poly(methyl/methacrylate) (PMIMA) was used as received from Aldrich. This material had a molecular weight of 120,000, a glass transition temperature of 114°C, and a melting point of 180°C, as specified by the supplier. Solutions of PMMA for spin coating were prepared in toluene.

### Results

### Inverse and transmission mode PPES measurements

Inverse and transmission mode photopyroelectric measurements were made on a series of thin film samples of PVC, polystyrene, and PMMA in order to evaluate thermal diffusivities and any differences in adhesion of the films to the aluminumized surface of the PVDF sensor. A range of sample thicknesses was prepared for each polymer.

Fig. 4-6 shows the results of homodyne PPES measurements made using the inverse

detection mode on a series of samples of PVC contacted to the pyroelectric. Experimental results are shown in Fig. 4-6(a) and theoretical predictions in Fig. 4-6(b). Signals have been dc corrected and normalized to the peak and minimum values of each trace.

The impulse response of the pyrolectric sensor in the absence of sample exhibits a well defined peak delay. This delay is explained by the presence of a layer of depoled material at the surface of the PVDF sensor. The depoling phenomenon is commonly encountered in pyroelectrics (16), where depoled layers of up to 1  $\mu$ m are not uncommon in electret materials. The depoling arises from processing steps which subject the material to transient heating above the Curie point in shallow surface layers. An example is encountered in the processing used to metallize the pyroelectric film. Impact heating by carriers impinging on the film surface in a sputtering chamber is sufficient to cause depoling of a few hundred nm thickness. A thermal pulse method is the classical method for measuring the extent of depoling in a pyroelectric (16,19). However, laser PPES is effectively equivalent, in that it replaces contact heating with laser irradiation. Coufal and Grygier have shown that impulse PPES is capable of detecting depoled layers of thickness as low as 7 nm in electret material (18).

The effect on the impulse response of depoling gives a peak delay which is much greater than any of the delays which could be accounted for by the electrical reponse of the pyroelectric measurement system. In this work, theoretical fits to the impulse response of the PVDF material indicate the thickness of the depoled layer to be approximately 400 nm, which is consistent with measurements reported earlier for similarly processed PVDF sensor material. This figure may vary by about 10% between different lots of the commercially supplied sensor material, and, in some cases, within a single sheet of the sensor material.

The inverse mode measurements shown in Fig. 4-6(a) show a broadening effect as the sample thickness increases. The risetime of the signals is nearly independent of the over layer thickness because the signal is dominated by the direct component of heat conduction at early times. At later times, the delayed or indirect component arrives after making a double transit of the sample layer. This causes the broadening of the impulse response which is observed at later times. If the sample layer becomes thick enough, the returning temperature profile will be strongly damped before it returns to the pyroelectric, and the impulse response will approach the time dependence expected for a bare pyroelectric. Hence, above a certain thickness limit, the broadening of the impulse response profile begins to diminish with sample thickness. The observed value of this thickness limit depends on the low frequency cutoff of the electronic filter used by the detection system, in addition to the sample's thermal diffusivity.

In using the theory to interpret the experimental results, the extent of depoling in the pyroelectric was first estimated from the impulse response for bare PVDF. Sample thickness data were obtained independently by means of a destructive analysis using transmission electron microscopy, after the inverse and transmission PPES measurements were made on each sample. A diffusivity of  $5.\times 10^{-8}$  m<sup>2</sup>/s was found to give a satisfactory fit to the data (comparisons of the theoretical and experimental responses are shown in the figure captions), for thin film samples of PVC. The data could be fitted given an interfacial thermal effusivity of unity at the interface between the sample and the sensor (effectively, a thermal contact resistance of zero). This latter condition, indicates a state of approximate thermophysical continuity between the layers. A more detailed assessment of this result is given in the next section.

In thermal transmission mode measurements, much thicker samples may be studied,

because all of the heat which is detected by the pyroelectric makes a transit through the sample layer. Therefore, a good separation of the impulse response peaks is observed in a transmission measurement. For samples of thickness greater than  $1 \, \mu m$ , however, the low frequency bandwidth limitations of the homodyne technique may preclude the observation of broadening effects associated with multiple thermal reflections at the front surfaces. A lower sweep bandwidth must be adapted, accompanied by a much slower sweep rate.

If the sample layer is not highly opaque, it is necessary to apply an optically opaque overcoat to the sample, so that heat conduction is confined to a thin planar region near the surface. Metal overcoats of 100 nm thickness in addition to ensuring optical opacity, are thermally thin relative to the polymer layers. The thermal transit time through a 100 nm metal overcoat is ca. 200 psec compared with an average value of 200 nsec for a glassy polymer.

Metallization layers may be applied by several means including cold vapor deposition (CVD), thermal vapor deposition (TVD) and sputtering techniques. We have found the CVD method to be less applicable in practice, because very long deposition times are required to transfer enough material to the sample layer in order to ensure opacity, and because the metal films tend to adhere poorly to the polymer. The use of TVD promotes improved adhesion of the metal films. In the case of sputtering, high impact bombardment of the polymer surface is sufficient to still cause some local heating and depoling of the underlying sensor material. Generally, the yield of the sputtering method is about 40-60%, even under moderately low deposition rates. A large proportion of the samples suffer irreversible thermal damage presumably due to heating by carrier impact. The sputtering method was applied to assemblies which consisted of

the metallized PVDF sensor material, overcoated with the thin film polymer sample. Among the assemblies that were successfully metallized, the processing was found to cause an enhanced depoling of the PVDF sensor layer in assemblies which were coated with polymer films thinner than ca. 200 nm. The thickness of the depoled layer increased by 150 nm on average as verified in a blank measurement on uncoated PVDF. For thicker overcoats ( $\ell > 250$  nm), this enhanced depoling was not observed, probably because of the improved insulating properties of the thicker polymer layers.

Experimental and theoretical plots of the transmission mode PPES impulse response compare favorably for a range of thicker samples as shown in Fig. 4-7. Impulse response data for the thinner sample overcoats may also be interpreted provided that the enhanced depoling of the sensor layer referred to above is included in the theoretical calculation. The theoretical model cannot otherwise differentiate between a change in the diffusivity of the thin film caused by heating in the sputtering chamber, and the depoling effect. The former effect is unlikely for the thermoplastic materials studied. If it had been operative, we would have expected to observe it in measurements made on the assemblies which were overcoated with the thicker polymer layers. However, the assemblies which were deposited with overcoats of thickness greater than 250 nm could be interpreted using the same sample/pyroelectric properties as for the inverse mode measurements previously run on each assembly. Based on the independently measured sample thicknesses, and a depoled layer thickness of 400 nm, for the thicker overcoated assemblies the thermal transmission method yielded values of the thermal diffusivity which were in precise agreement with the inverse measurement  $(5.0 \times 10^{-8} \text{ m}^2/\text{s})$ .

Inverse and thermal transmission mode measurements were performed also on samples of PMMA and PS. Detailed comparisons of the impulse response data to theory gave an

agreement similar to that of Figs. 4-6 and 4-7. In the transmission mode PPES measurement, a plot of the peak delay in the transmission mode impulse response versus the square of the sample thickness gives a more compact representation of the experimental data. Such a plot is given in Fig. 4-8 for samples of PMIMA, PVC and PS, and indicates that for the three materials, the thermal diffusivity is  $5.\times 10^{-8}$  m<sup>2</sup>/s. Theoretical values fall along the solid curve which is non-linear due to the low frequency electronic filtering in the instrument.

Table 4-1 summarises the literature values of the bulk thermophysical properties of the three polymers that were analysed by the homodyne PPES method. The various materials are thermophysically similar to each other so that it is not surprising that the diffusivity measurements are in agreement. However, the recovered diffusivity value is below the range of bulk values normally expected for this class of glassy polymers.

Table 1

BULK THERMOPHYSICAL PROPERTIES OF POLYMERIC MATERIALS USED IN THIS WORK

Polymer	thermal diffusivity	density	specific heat
	$(x10^{-7}m^{2/s})$	(g/cm <sup>3</sup> )	kJ /kg oK )
PMMA	1.0-1.25	1.188	1.42
PS	0.8-1.25	1.06	1.226
PVC	1.0-1.2	1.393	1.1
PVDF*	0.6-1.0	1.78	1.35

Thermal properties of these polymers were obtained from references 19 and 24. Starred values were obtained from reference 20.

The lowering of the diffusivity value in the thin film phase relative to the bulk, was observed in previous work by Coufal and Hefferle (4). PPES measurements on thin

films of Novolac resin, yielded a diffusivity which was ca. 20-25% of the value observed in the bulk. The difference could be accounted for by alignment effects in the spin-coated thin films, which induced a probable anisotropy in the thermal conductivity. This latter effect is not expected to be operative in thicker films.

The present work, which uses a very similar thin film preparation methodolgy, yielded the same general trend. However, the lowering of the thin film thermal diffusivity relative to the bulk, observed in this work, was much less than for the Novolac resins (4). In the latter case, the samples were allowed to cross-link following spin coating, which promoted the formation of a rigid lateral network, with a directional enhancement in the thermal conductivity parallel to the sensor surface. This cross-linking contribution would be absent in the present study. However, the dynamical forces accompanying the spin-coating deposition may perhaps account for a transverse alignment in the macromolecular chains and a corresponding drop in the observed axial (x-direction) thermal conductivity. Alternatively, the density may be affected.

### Interfacial thermal discontinuities

Impulse laser PPES is capable of evaluating interfacial phenomena that arise at thermal interfaces. The inverse mode measurement is sensitive to disbonding effects that may occur at the sample/pyroelectric interface. Fig. 4-9 gives an example of a study which was used to diagnose disbonding of a PVC layer at the PVDF sensor surface. In the data of Fig. 4-7(a), the sample layers were well bonded, a condition which was ensured by cleaning the sensor surface with methanol. In Fig. 4-9(a), PVC samples were spin coated onto the as-received sensor material supplied from the

manufacturer. In inverse mode the experimental PPES measurements do not show a strong variation of the impulse response with film thickness for the uncleaned surface. This situation may be explained by the formation of a thermal barrier, which is formed at the metal coated pyroelectric/polymer interface, and is indicative of poor bonding to the surface. In contrast, thermal transmission geometry places the contact resistance in series between the sample and detector causing broadening of the impulse response as illustrated in Fig. 4-9(c). Modeling of the experimental results by theory, fits an interfacial thermal effusivity value,  $b_{32}$ , of 0.1 to both the inverse and transmission mode measurements. This parameter indicates that in the inverse geometry, thermal energy is preferentially conducted into the pyroelectric layer, due to the thermal barrier that accompanies poor surface adhesion. Replicate PPES measurements made over a surface area of 4 mm<sup>2</sup> were repeatable to within 5%, indicating that this was not due to any lack of homogeneity in the film thickness. This was further confirmed by thickness measurements made using TEM.

The effect of very poor bonding to the surface was further observed by surface treating the PVDF metallization with an ultrathin layer of Teflon release agent, and applying spin coats of PVC to the treated surface (Fig. 4-9(c)). A lack of thickness dependence of the impulse response traces was then observed. In thermal transmission mode measurements run on these same specimens, there was evidence of large thickness variations due to the formation of 'islands' of the polymeric material. This latter effect accompanies poor surface adhesion.

The lack of thickness dependence of the inverse mode PPES signal may be interpreted from theory as indicating a condition of poor bonding at the surface. Fig. 4-10 shows a theoretical plot of the inverse mode PPES impulse response expected for a 250 nm polymer thin film with a thermal diffusivity of 5.x  $10^{-8}$  m<sup>2</sup>/s. A very thin theoretical

contact layer (10 nm) is inserted between the sample and the PVDF layer to simulate the effect of the debond. The figure shows the effect of an increased thermal contact resistance between the layers, which is obtained in the model by varying the thermal effusivity ratios  $b_{34}$  and  $b_{32}$  together.

As  $b_{34}$  and  $b_{32}$  decrease together, the interlayer thermal contact resistance increases. The interpretation of this result is straightforward. In the inverse mode measurement, nearly all of the energy which is initially deposited in the pyroelectric metallization layer by the excitation impulse propagates into the pyroelectric directly because for a large contact resistance, the interfacial layer behaves as a thermal barrier, significantly reflecting the temperature profile into the pyroelectric. This effect is shown schematically in Fig. 4-1(b).

Some remarks are in order concerning the assumptions of the theoretical model used here to interpret the results for the debonded cases. The classical modeling of thermal contact resistance in thin layer systems uses the approach of Yeack et. al (23), which introduced a theoretical discontinuity in the temperature and thermal efflux into the boundary conditions at the debonded interface. However, this approach failed to model changing sample thicknesses properly without introducing changes in the boundary conditions. Jaarinen et al (9) further developed this approach in the frequency domain showing that a thermal contact resistance in a system composed of discrete thermophysical layers introduces a quantifiable change in the real and imaginary parts of the thermal reflection coefficient at the interface between adjacent debonded layers. Aamodt et al (14) described the concept of thermal resistance by explicitly introducing into the model a discrete contact layer which can be equated to a thin layer of air. We have used an approach similar to that of Aamodt et al. and have modeled the interfacial layer as a thin contact region having the molecular and thermophysical properties of a polymer with increased thermal diffusivity but reduced efflux relative to the bulk. This is believed to be a more physically realistic picture of the 'contact resistance' change accomanying a debond.

The modeling of the present type of inhomogeneous thermal system requires recourse to methods of inverse problem theory (21) in order to fully evaluate the uniqueness or multiplicity of models which could explain the observed results. In this study, we have used a 'forward' method of inversion (21) (which uses comparison of an assumed model with the observed data), and found that the experimental trends are reproduced by the theory to a good approximation. The assumed model thickness of 10 nm for the interfacial region is based on the approximate dimensions of the polymer chains. We expect that the interfacial region, when debonded, consists of a series of voids interspersed with contact points where the polymer chains are anchored to the metal. If one applies a simple arithmetic averaging to the thermophysical properties of this model interface, the thermal conductivity will be closer to the  $\kappa$  value of a polymer ( $\kappa$ = 0.01 W/m-oK typical of a foam), while the thermal diffusivity will be more like air  $(\alpha = 1.e-6 \text{ m}^2/\text{s})$  (2). These values predict theoretical responses which give a good approximation to the experimental data. A thorough application of the methods of inverse problem theory to this measurement will be required to determine its resolving power and the potential multiplicity of models which could duplicate the data.

While we do not have a conclusive explanation for the role of methanol in promoting adhesion of the films to the aluminum surface, two possible explanations arise. The most likely explanation would involve contamination of the metal surface by an organic impurity adsorbed on the surface. If so, this impurity would be present at the surface at thicknesses approaching one monolayer. The likely source of this contaminant would be the coated paper sleeve in which the sensor material was shipped

by the supplier and the role of methanol as a cleaning agent becomes rather obvious. An explanation involving the role of methanol adsorption on surface oxides appears less probable.

The above results indicate experimentally that the inverse mode PPES signal is readily capable of diagnosing a debond between layers. It may be potentially used to evaluate metal/polymer adhesion phenomena in a relative sense by coating the pyroelectric with various metals and spin coating the polymer of choice onto the surface. It should be kept in mind that the thermal properties of the metallization layer do not enter into the measurement model because this layer behaves as though it is infinitesimally thermally thin. The thermal effusivity parameters, b<sub>34</sub> and b<sub>32</sub> evaluate how well a po<sup>1</sup>ymer overlayer bonds to the aluminization in relation to how well the poly(vinylidene fluoride) sensor material bonds to the bottom nickel metallization. A more complete model would explore the thermal continuity existing at the interface between the metal and the PVDF, especially in Light of the different coating/deposition methods which produce adhesion between the metal and polymer at the two interfaces.

The theoretical profiles of Fig. 4-10 indicate that using the present PVDF detection system, a minimum thermal effusivity ratio ( $b_{34} = b_{32}$ ) of 0.4 is required in order to observe an appreciable effect on the time dependence of the impulse response. This gives a rather insensitive measure of thermal effusivity differences between layers, primarily because of the thick depoxed layer (400 nm) that exists at the PVDF surface in our experimental sensor material. The thickness of the depoled layer,  $d_{ep}$ , slows down the impulse response of the pyroelectric system, and promotes, in essence, an electronic filtering behavior, which attenuates the high frequency, interface-related information. If the thickness of the depoled layer were reduced to 10 nm, theory predicts a greatly enhanced sensitivity to the effects of interfacial thermal effusivity

mismatch, and therefore, to debonding. However, such sensor material can only be obtained, at the present time, using specialized preparation techniques (18). An additional advantage of minimizing the thickness of the depoled region, is the possibility of probing very shallow layers at the pyroelectric/sample interface. With a reduction of the  $d_{ep}$  value to 10 nm, it becomes possible to detect layer thicknesses below 10 nm using homodyne laser PPES.

Fig. 4-10(c) shows the theoretical sensitivity of our homodyne laser PPES measurement for determining  $\alpha$  in cases where the thermal effusivity ratio between the sample and the pyroelectric varies, with a very thin contact (resistive) layer. The interfacial measurements discussed above, take advantage of an approximate condition of thermal effusivity matching which exists between the pyroelectric and polymer bulk layers, as is widely observed for many materials (Table 4-1).

It can also be shown from theory, that the experimentally used pyroelectric behaves as a thermally discontinuous material in the depoled region (17). Previous work by Coufal and Grygier indicated that the thermal conductivity of the depoled region in their sensor material varied by a factor of two compared to the bulk (17). This measurement was made however, on high quality PVDF sensor material where the depoled layer was 7 nm thick, and where the sensitivity to such effects is intrinsically higher. It is also possible that the observed effusivity difference was due to purely interfacial factors at the pyrolectric surface associated with the casting of the film, and independent of the depoling phenomenon per se. It is difficult to make such a distinction on these short length scales. Moreover, a theoretical simulation of an efflux change of this magnitude for the 400 nm depoled layer indicated that such a difference would not be detectable above the experimental uncertainty. This insensitivity may be in part due to the filtering used by our electronic detection system.

While inverse mode PPES measurements have been emphasized so far, maximum information from a sample is obtained from a combination of inverse and transmission data. Fig. 4-11 outlines impulse response predictions for several cases that may be encountered in the practical analysis of adhesion. In the case of a debonded sample, the inverse mode impulse response shows convergence to the PVDF transducer signal, while the transmission mode signal shows a broadening effect due to the reflection of thermal waves incident on the debond interface.

Although we have not encountered it in practice, the possibility may perhaps exist for an ultrathin aligned layer to be present at the interface between the metal and the polymer layer. In that case, the inverse mode measurement may continue to show insensitivity to the presence of the overlayer, while the transmission mode signal could show a more rapid time decay due to the preferential conduction of heat into the aligned layer. This second case, will, however, be much more sensitive to the relative thermal properties of the interfacial layer and the sample, the interfacial layer and the pyroelectric, and the sample and pyroelectric. 3

### Conclusions

This work has demonstrated the versatility and accuracy of homodyne laser photopyroelectric effect spectrometry for measurements of the thermal diffusivity in ultrathin polymer films in two different measurement geometries. The inverse PPES geometry is well adapted to the study of very thin polymer films, and is minimally perturbative of the sample matrix, especially in the thickness range from 50-500 nm. The thermal transmission mode measurement is better suited to the study of thicker polymer films (> 500 nm), but has the disadvantage that a metallization must be applied to the sample overcoat. If sputtering methods of depositions are used to apply

the metallization, the pyroelectric layer may become further depoled, when the overcoat thickness drops below about 250 nm, typically. Also, thermoset materials may be unsuitable for analysis by the transmission method, using the present metal deposition procedure.

The thickness resolution of the homodyne PPES method is limited mainly by the depoling of the PVDF material. With the present apparatus, the method is capable of making general assessments of the relative bonding of the sample to the metal surface. More sensitive measurements would be attainable using sensor material with a thinner depoled layer. Finally, maximum interfacial information is available using a combination of inverse and thermal transmission mode measurements to interpret the data.

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Diagramatic representation of sample configuration for inverse and transmission mode homodyne PPES.

(a) Inverse mode measurements use the pyroelectric sensor surface to launch thermal waves into the sample and pyroelectric simultaneously. (b) As the polymer becomes debonded from the surface the right going thermal waves are partially or totally reflected off the interface back into the pyroelectric. (c) Transmission mode measurements use a black body surface absorbing layer to launch thermal waves through the polymer into the pyroelectric. (d) As the polymer becomes debonded the incident thermal waves are partially or totally reflected off the interfacial layer back into the sample.



Diagram of the four layer model used to derive the theoretical equations. The metallization is considered to be a thermal short circuit and the depoled layer is considered to be thermally continuous with the PVDF.



(a) The electrical circuit used to measure the pyroelectric cell transfer function. V(f) is the applied voltage,  $C_p$ , the PVDF capacitance (ca. 3 nF),  $R_L$ , the load resistance across the PVDF foil (10 K $\Omega$  in our experiments ) and  $C_L$  the, load capacitance (ca. 120 pF).



(b) An experimentally measured transfer function of the homodyne PPES system (c) A thermal response calculated for a 800 nm polymer film in thermal transmission mode.(d) The calculated thermal response is convoluted with the measured electrical response to generate the theroretical homodyne pyroelectrical signal.

## INSTRUMENTAL MEASUREMENT SYSTEM





Block diagram of the homodyne photopyroelectric instrument.



Transmission electron micrograph of a 350 nm film of polystyrene sandwiched between ca. 200 nm Al and 80-100 nm of NiAl. Measurements of the polymer film thickness show about 10% variation from point to point in the film.





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(a) Experimentally measured homodyne PPES of PVC films using inverse detection mode. Measured film thickness as shown. (b) Theoretical predictions using  $b_{32} = b_{34} = 1.0$ ,  $\alpha_4 = \alpha_2 = 5.0 \times 10^{-8} \text{ m}^2/\text{s}$ , 10 nm interface,  $d_{ep} = 400 \text{ nm}$  of depoled PVDF.





(a) Experimentally measured impulse response for a range of PVC films using the transmission mode measurement.

(b) Theoretical predictions using  $b_{32} = b_{34} = 1.0$ ,  $\alpha_2 = \alpha_4 = 5.0 \times 10^{-8} \text{ m}^2/\text{s}$ , 10 nm interface.

sample thickness squared vrs peak delay



### Fig. 4-8

Plot of square of sample thickness vs peak delay in transmission mode measurement (for well bonded specimens), theoretical and experimental values. The effective sample thickness is given by the sum  $(\ell + d + dep)$  where d = 10 nm and  $d_{ep} = 400$  nm except for the thinnest samples (triangles) ( $\ell \le 150$  nm), where  $d_{ep} = 550$  nm. Solid squares represent PVC films of 425, 650, 1050, and 1200 nm. Thicker samples give longer peak delays. Open squares are PMMA films of 255 and 800 nm. Solid circles are polystyrene films of 225, 235 and 350 nm. (\*) give theoretical peak delays for films of 100 nm. All data points can be modelled with an interfacial thermal effusivity of unity (see text for details).



(a) Inverse homodyne PPES measurements on PVC films with  $\ell = 150, 250, 425$ , and 600 nm. (b) Theoretical impulse response data for polymer films assuming a polymer-pyroelectric interface layer thickness of 10 nm,  $b_{32} = b_{34} = 0.1$ . The diffusivity of the polymer was calculated to be  $5.0 \times 10^{-8} \text{ m}^2/\text{s}$  and the uncertainty in the sample thicknesses is  $\pm 10\%$ . With the thermal barrier present the 600 nm film is too thick to contibute thermal energy to the signal and the inverse response is dominated by the thermal component that passes directly into the pyroelectric.



(c) Transmission mode

homodyne PPES measurements on the same series of PVC films shown in Fig. 9(a). (d) Theoretical transmission curves assuming the same thermophysical properties as in Fig. 9(b).





(e) Inverse homodyne PPES measurements of PVC films spin coated onto the pyroelectric after a thin layer of Teflon release agent had been applied, showing thermal barrier effect.



Theoretical calculations showing the effect of an increasing thermal barrier on inverse homodyne PPES measurements ( $\ell = 250 \text{ nm}$ , d = 10 nm,  $b_{32}$  and  $b_{34}$  as shown,  $d_{ep} = 400 \text{ nm}$ ).

The model is insensitive to small changes in the  $b_{32}$  values due to the delay effects introduced by the relatively thick depoled layer.



time (pa)



time (ps)

### Fig. 4-11

Theoretical predictions for homodyne PPES measurements of polymer films with a large thermal barrier (d = 10 nm,  $b_{32} = b_{34} = 0.001$ ) between the pyroelectric and the film. (a) Thermal transmission measurements on 50,100 and 200 nm thick films, showing broadening effect in time from thermal reflections in the sample/pyroelectric interfacial layer.

(b) Theoretical predictions of inverse mode measurements for l = 200, 300, and 400 nm in the presence of a large thermal barrier (d = 10 nm,  $b_{32} = b_{34} = 0.001$ ) (see text for details).

Chapter 5:

Inversion of the ill posed Green's Function solution for transient heat conduction problems with application to optical depth profiling in photothermal spectroscopy.

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## NOMENCLATURE

l	sample thickness
G	Greens' Function matrix
G[m,n]	Matrix G has m rows and n columns.
U	row echelon form of G
k	thermal conductivity
x	depth into the sample
x,	dummy space variable; position of source in sample
P	spatial distribution of absorbing features: $q(x)$
g	one possible solution
Ā	the best solution that can be calculated
t	time
T	recorded temperature: T(t)
T C	recorded temperature: T(t) row echelon form of T
T C c	recorded temperature: T(t) row echelon form of T condition number
T C C B	recorded temperature: T(t) row echelon form of T condition number basis set
Τ C c B α	recorded temperature: T(t) row echelon form of T condition number basis set thermal diffusivity
Τ C C B α r	recorded temperature: T(t) row echelon form of T condition number basis set thermal diffusivity rank
Τ C C B α r N	recorded temperature: T(t) row echelon form of T condition number basis set thermal diffusivity rank number of layers in the sample
Τ C C B α r N LS	recorded temperature: T(t) row echelon form of T condition number basis set thermal diffusivity rank number of layers in the sample least squares

#### 1. Introduction

Over the past two decades there has been considerable interest in photothermal spectroscopic techniques for depth profiling optical and thermal properties in solids. Applications in the study of semiconductors[1,2], paints and polymers[3,4], adhesion[5], biological samples[6,7] and ceramics[8,9] can all be found in the literature. The understanding of photothermal spectroscopy has forwarded through the development of a wide range of mathematical models which are used to interpret the signals[10-14]. Up to now most of the data interpretation has been done through forward modelling of the time or frequency domain data. Here estimates of the optical and thermal parameters are fed into the appropriate equations and the results are compared to those obtained experimentally. This tends to be an iterative approach to data analysis which is not only time consuming but requires in-depth understanding of the physical processes involved. Before photothermal techniques will be widely accepted and used routinely, methodologies which will permit rapid and easy interpretation of the data need to be developed.

Recently there has been a strong interest in obtaining the optical and thermal properties through inverse modelling of photothermal signals. In inverse modelling the recorded photothermal signal is used to obtain the optical absorption profile or the conductivity profile as a function of depth.
Development of a general, reliable and accurate inverse model will go a long way towards making photothermal spectroscopy a widely used tool in the natural and applied sciences.

A theoretical treatment of an inverse model for a thermally homogeneous and optically inhomogeneous solid sample was first proposed by Afromowitz et al [15]. Over a decade later Harata and Sawada improved on their inverse Laplace method and presented a few experimental results for frequency domain measurements [16]. Their inversion effectively profiled slowly varying continuous optical features near the sample surface but failed to accurately recover the spatial profile of absorbing features buried beneath the top layer, discrete sources or rapidly varying continuous profiles which result from moderate to large optical absorption values. In practice the noise associated with high frequency measurements (>700Hz) makes it impossible to recover optical features at the short thermal diffusion lengths and requires all data to be smoothed before use.

To measure the hardening profile in steel Vidberg et al. recovered the thermal conductivity profiles by solving the inverse heat conduction model for samples with surface absorption only [17]. The experimental data were obtained by measuring the radial surface temperature variation due to heating from a point source at a single modulation frequency. The forward problem was posed assuming that the steel hardened uniformily in the transverse dimension although thermal efflux varied with depth  $(k,\alpha)^{1/2}$ . This inversion is applicable only to samples that can be studied using this specific experimental geometry. An inverse scattering model was then derived to recover the

thermal properties as a function of depth. Inversion of the data was found to be ill posed limiting the algorithm to probing only features near the surface due to its acute sensitivity to noise.

A more general inverse model for recovery of thermal diffusivity inhomogeneities has been derived by Mandelis et al. to study conductivity changes in steels and magnetic field effects in liquid crystals [18]. The technique is based on Mandelis' derivation of the Hamilton-Jacobi thermal harmonic oscillator (THO) for a sample heated at a specific frequency and is closely paralleled to the classical harmonic oscillator problem. The inverse problem divides the sample into layers and solves the properties of each layer knowing the properties of all the layers above it. The surface properties are measured or estimated and used to calculate values for the second, underlying layer and so on. Reconstruction of a continuous diffusivity profile requires a measurement of the frequency response over a wide range of frequencies and in small frequency increments (0.1 Hz or less). The data are typically smoothed and filtered before they can be processed. Subsequently the technique is limited to frequency domain experiments with large amounts of smooth data.

Recently, Glorieux et al. proposed the first inversion routine to obtain both the optical and thermal data from a frequency domain experiment [19]. The forward model is constructed using the traditional method of Rosencwaig and Gersho. For N layers in the model a 2Nx2N matrix was constructed with the frequency dependent terms forming the matrix



coefficients and the boundary coefficients providing the source column vector. The 2Nx2N matrix is not inverted but reduced to row echelon form and solved by back substitution. The optimal values of the boundary coefficient at the sample surface are obtained using a non-linear least-squares fit between experimental and calculated phase and magnitude data. The calculated sample surface response is then used to calculate the optical and thermal parameters of each layer. As would be expected both the optical and thermal properties cannot be solved simultaneously using this approach as there are too many variables. As with Mandelis' method a large number of data points spanning a wide frequency range and fairly small step sizes are required to obtain accurate inversions of the profiles. In addition, to obtain continuous depth profiles the sample must be divided into N very thin layers which then requires construction of a large 2Nx2N matrix. This results in 2N unknown boundary conditions to be solved for. Although the authors discussed the technique for recovery of optical profiles none were presented and the recovery of thermal parameters degraded as a function of depth from the surface of the sample.

In this chapter we propose the solution to the time domain inverse heat conduction problem based on a forward model using the free space Greens Function. As posed the inverse problem is ill conditioned, but we will demonstrate that a small amount of uncertainty in the Greens Function greatly improves the conditioning making the problem better posed and much more easily solved. Unlike the inversion techniques above this system is valid for the time domain signals; specifically, the impulse response of the system. We present the model for optically inhomogeneous thermally homogeneous samples and illustrate techniques for expanding the method to optically and thermally inhomogeneous samples. The technique works well on discrete and continuous optical profiles, is insensitive to noise on the recorded impulse response and used in conjunction with a simple Monte Carlo technique, can recover thermal flux profiles from any photothermal experiment. 2. Formulation of the photothermal inverse problem for a thermally homogeneous optically inhomogeneous sample.

The objective of this inverse heat conduction problem is to reconstruct the optical profile in a thermally continuous medium from the photothermal impulse response. The forward model presented is the free space Greens Function for one dimensional heat conduction shown in equation (5-1):

(5-1) 
$$\Delta T(x,t) = \int_0^{t^*} \int_{-\infty}^{-\infty} g(x-x_0, t-t_0), q(x_0, t_0) dx_0 dt_0$$

where

$$g(x-x_0,t-t_0) = \frac{1}{\sqrt{4\pi\alpha(t-t_0)}} e^{\frac{-(x-x_0)^2}{4\alpha(t-t_0)}}$$

and  $q(x_o, t_o)$  is the source profile or driving function. The thermal diffusivity ( $\alpha$ ), the observation point (x) and observation time (t) need to be defined. For a photothermal impulse response t=0 as the record is started at the point the pulse is applied. For the case of front surface detection x=0 and for rear surface detection x=-1. At some time t<sub>j</sub> after excitation the temperature at x can be determined from (5-2).

(5-2) 
$$\Delta T(x,t_j) = \int_{-\infty}^{\infty} g(x-x_0,t_j) q(x_0) dx_0$$

This equation assumes that the sample and its environment are thermally continuous and no thermal reflections are generated at the sample interfaces. The validity of this assumption will be addressed in the experimental section. Using the principles of linearity we can breakdown the continuous thermal response  $T(x,t_j)$  into N arbitrary spatial contributions forming a discrete series equivalent to the continuous integral. Recognizing that the source is generated in the N layers of the sample one can the write an equivalent expression for (5-2) as (5-3).

(5-3) 
$$\Delta T(\mathbf{x},t_j) = \sum_{i=1}^{N} \frac{1}{\sqrt{4\pi\alpha t_i}} e^{\left\{\frac{-(\mathbf{x}-i\Delta \mathbf{x})^2}{4\alpha t}\right\}} q(\mathbf{x}_i) \Delta X_i$$

This series is the spatial discrete convolution of the free space Greens Function. A set of temperature responses for different times  $t_j$  can be generated and the results saved in matrix form with the spatial coordinates in the columns and the temporal coordinates in the rows. The final matrix G[mxn] will contain n columns to fit the N sources in the sample and m rows corresponding to the number of time points in the recorded impulse response. There is no requirement that the time or spatial coordinates be uniformly spaced or that the G matrix be square. However, it will be shown that there is an optimal form of G to obtain accurate inversions. The weighting function for the sources is a column vector q[1,n] and the temperature as a function time of will be a column vector, T[1,m]. The forward model can then be expressed as (5-4).

$$\mathbf{G} \bullet \mathbf{q} = \mathbf{T}$$

Simplistically, one would expect that q can be recovered by the following inversion.

$$(5-5) q = G^{-1} \bullet T$$

However, as written this problem is ill posed meaning that the result is acutely sensitive to noise and prone to inaccurate solutions. For an ill posed system of equations small errors in T will produce large errors in q or conversely a wide range of T will produce nearly equivalent q values. An ill posed system of equations will be also sensitive to round off errors in calculation of G and small systematic errors will be magnified in the inversion process. The remainder of this chapter is devoted to the analysis of this problem and different strategies for its solution.

# 3. Analysis of matrix G

The ill posed nature of G is due to the matrix being rank deficient, ill conditioned and the restriction that the solution vector q be positive to obtain physically meaningful results. Rank deficiency of G[mxn] is the condition that rank r, of G is less than the column space or row space:  $r<\min(m,n)$ . Computationally this means that in the row echelon form of G, matrix U, there will be r linearly independent columns and n-r free variables. There are m-r zero rows in U which act as m-r constraints of the solution to equation (5-4) [21,p54]. A unique solution for every T exists if and only if r=m=n; U will have no zero rows and the solution that Glorieux et al. (19) required for their algorithm to work. For rank deficient systems if one solution exists there will be a set of solutions each differing from the first by a vector in the null space in G (21). Physically, this means that there will be multiple solutions to the inversion problem and it becomes necessary to determine the best solution from the many.

The ill condition of G is the most significant obstruction to inversion of equation (5-4) in the presence of noise. For a system of equations a small perturbation (noise) will be amplified in the inversion process by the condition number of the matrix G.

(5-4)	$\mathbf{G} \mathbf{q} = \mathbf{T}$	noise free equations	
(5-6)	G ( q + dq )= T + dT	noise in q is propagated to I	

Removing the noise free equations leaves the expression describing the propagation of noise.

$$(5-7) G dq = dT$$

(5-8) 
$$dq = G^{-1} dT$$

Thus if G is "large", noise in the experimental response will not affect recovery of a true optical profile. If G is "small" small amounts of noise in T create large errors in q. The condition number is a scalar that replaces G in equation in equation 5-8 giving

$$(5-9) dq = c dT$$

The condition number of a matrix, c, is the ratio of absolute values of the largest to smallest eigenvalues( $\lambda$ ) of the matrix or alternateively it can be defined as the largest to smallest singular values ( $\mu$ ) (21,22).

(5-10)  
$$c = \frac{\lambda_{max}}{\lambda_{min}} = \left(\frac{\mu_{max}}{\mu_{min}}\right)^{1/2}$$

By definition G will be well conditioned as the eigenvalue spread decreases and c approaches unity, and ill posed as c increases to infinity. Therefore the ratio of the eigenvalues of G will be the relative amplification of noise from the experimental trace

to the recovered optical profile (21, p268).

A typical condition number of matrix G is on the order of 1.e17 for the photothermal systems studied. This means that noise on the signal will be amplified 1.e17 times in the inversion process. As one can imagine the results of this inversion technique work well in theory where the data is calculated with double precision, but in a typical experiment where the noise on the signal can reach 10% the optical profiles obtained using direct inversion are hardly informative. Traditionally, scaling of matrix G has been used to reduce the effects of the condition number. However, scaling only works when the determinant of G is not close to zero. Since the matrix has already been determined to be rank deficient (i.e. at least one row of zeros exist in the row echelon form) then the determinant to the matrix must be zero and the matrix does not have an inverse by the following properties of the determinant:

(i) If G or U has a zero row, then det(G) = 0.

(ii) If det(G) = 0 then G is singular and does not have a well defined inverse (21,p148).

It is therefore necessary to increase the rank of G, and the determinant of G without distorting the data.

The final difficulty in solving equation (5-5) is that the solution vector q must be positive to be of meaning. Thermal waves in the sample are generated by sources (positive q) and there are no heat sinks in the sample (negative q). (It is assumed that there are no endothermic photochemical reactions taking place in the sample.) This means that in devising a method of solution for equation (5-5) positivity constraints must be included.

G[m,n]	Gaussian	cond(G)	rank(G)	det(G)
	noise	(c)	(r)	
8	ibsolute level			
32,32	0	6.2e18	16	-1.0e-236
32,32	1.e-4	3.3e5	32	-1.6e-93
32,32	1.e-3	1.5e4	32	-3.0e-68
32,32	1.e-2	8.5e2	32	-3.8e-41
128,32	1.e-3	1.3e3	32	N/A
128,32	1.e-2	1.3e2	32	N/A

Table 5-1: The inversion characteristics of a Greens Function matrix (G) constructed with l=30.e-6m, dt=.2e-3s,  $\alpha=1.e-7$ , xo=0. Low levels of uncertainty helped make the array full rank, improve the condition number and increase the determinant. Rectangular matrices with more time points further made the matrix better posed. Condition numbers (c) are calculated as the ratio of largest to small singular values.

# 4. Solutions to making G well posed

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The G matrix as calculated by equation (5-3) with uniform time and space increments will always be ill posed and acutely sensitive to noise. The first row of table 5-1 shows that G has an extremely large condition number, cond(G), is rank deficient, rank(G), and has a determinant that is close to zero, det(G). However, rows 2 to 4 of table 1 display that with uncertainty added to G the matrix becomes full rank, cond(G) decreases and det(G) increased. The final two rows of table 5-1 indicate that G is made better posed by use of a rectangular matrix with more time than space coordinates. The condition number decreases to 135, a 1.e16 fold improvement. The value of cond(G) can be further improved by increasing the uncertainty on G and making G more rectangular. However, with increased uncertainty in G and increased size there is trade off against further improvement of the condition number of G and the accuracy of recovery of the source profile q, and increased computation time.

An illustration of the ill condition of G is seen in Figure 5-1. A G [32,32] was calculated for the conditions in the first row of table 5-1. The columns of G are plotted together in Fig. 5-1a illustrating the temperature vrs time profiles reaching the surface from each of the N layers. The largest and fastest temperature response comes from the layer at the top of the sample and the slowest and weakest response comes from the layer at the back surface. The G matrix has been normalized to its maximum value so that the values of the coefficients range from 0 to 1. The inverse of  $G, G^{-1}$ , has its columns plotted in Fig. 5-1b. The coefficients of  $G^{-1}$  range from 0 to 3.e11 and are periodic in both the column and row space. One can see now how low noise levels on the temperature response, T(t), will be amplified when multiplied by  $G^{-1}$  and solutions to g will be wildly oscillating with positive and negative values. The effect of 1% Gaussian noise added to G is illustrated in Fig. 5-2a. The individual temperature profiles have the same trends as Fig. 5-1a but are no longer precisely smooth. The columns of  $G^{-1}$  in Fig. 5-2b no longer have all their energy confined to local anti-nodes, and the absolute values have dropped along the vertical axis. Table 5-1 shows that for 1% noise the condition number of G is now 850, an improvement of 1.e16, the determinant has increased and the matrix is full rank making it much better posed and far less sensitive to noise on the recorded temperature response. The seeded G matrix is full rank and a unique solution to  $\mathbf{G} \mathbf{q} = \mathbf{T}$  now exists. However, it only one member of an ensemble G = T where G, q, and Tare now random variables. With enough averaging it will be shown that we obtain  $\bar{\mathbf{G}}$   $\bar{\mathbf{q}} = \bar{\mathbf{T}}$  where  $\bar{\mathbf{G}}$  approaches  $\mathbf{G}$ ,  $\bar{\mathbf{q}}$  approaches  $\mathbf{q}$  and  $\bar{\mathbf{T}}$  approaches  $\mathbf{T}$  as the number of seeded inversions goes to infinity.

For some seeded full rank systems it was found that the equations were inconsistent as determined by rank. The temperature response with large amounts of synthesized noise added could not be described as a linear combination of the G columns. Subsequently, either the uncertainty on G was reduced or the system of equations was solved to obtain the best estimate of q using the pseudoinverse technique discussed below.

Regularization techniques are often used in linear algebra to improve the condition or balance of a matrix before inversion. These techniques tend to scale the matrix to reduce extreme values of coefficients, center the coefficients as close to the diagonal as possible and generally improve the inversion properties of the matrix. For the G matrices in this study regularization techniques failed to improve the overall condition number of the matrix and were not used. A number of different data sampling strategies were also tried without success. One sampling strategy that warrants exploration involved resolving buried features separated by unequally spaced thermal features. This can be approximated by  $x = \sqrt{2\alpha n \Delta t_s}$ , where t is the sampling time and n is the number of time channels into the time record. Features closer to the detector will be more clearly resolved than features buried deeply in the sample. This has the effect of generating a Greens Function matrix that is almost lower triangular with the maximum of each time response along the diagonal. This is illustrated in Fig. 5-3. The G matrix corresponding to Fig. 5-3 is theoretically more easily inverted than the G matrix corresponding to Fig 5-1a as it closer to the Hessenberg form. However, the smooth dissipative nature of the thermal response makes this matrix scale invariant and the computed rank drops to between 4 and 6.

## 5. Solution of the inverse problem

In section 4 the problem of rank deficiency and ill conditioning was addressed. However, making the problem (equation 5-4) well posed does not guarantee that the optimal solution to the inversion can be easily obtained. The difficulties include constraining the solution to be non-negative and characterizing the probability density functions of solutions after seeding G with random noise.

In practice we have found that pseudoinverse inversion and constrained minimizations are the best techniques for obtaining a physically meaningful q solution. This section describes the calculations used in these solution procedures. Section 6 then applies the inversion technique to theoretical temperature responses and examines the accuracy of each technique. 5-ia The pseudoinverse principles.

For inversion of an ill posed system the Moore Penrose pseudoinverse can be used to obtain the least squares projection of T onto the column space of G thereby giving the optimal choice of q for a given T (21,p130).

The pseudoinverse is applied by transforming the ill posed system of linear equations into an orthogonal vector space where it is easily solved. The optimal solution is determined by minimizing the least squares of the euclidean length and transforming the resulting solution back into the original column space.

The pseudoinverse can be applied to any matrix G on the premise that G[mxn] can be factored into orthogonal components according to:

$$\mathbf{G} = \mathbf{Q}_1 \cdot \mathbf{S} \cdot \mathbf{Q}_2^{\mathsf{T}},$$

where  $Q_1[mxm]$  is an orthogonal matrix,  $Q_2[nxn]$  is an orthogonal matrix, and S[mxn] is a diagonal matrix with the singular values of G on its diagonal (21 p135). The orthogonal decomposition of G by equation (5-6) is referred to as singular value decomposition (SVD). The rotations  $Q_1$  and  $Q_2$  just swing the column space of G into line with the row space, and G becomes the diagonal matrix S (21,p 136). The advantage of orthogonal decompositions, such as the SVD, is that the matrices  $Q_1$ , S and  $Q_2$  have many useful properties including well defined inverses. The inverse of any orthogonal matrix is its transpose and the inverse of the diagonal matrix S is the inverse of the individual elements.

The pseudoinverse of G, G+, is calculated by inverting the three factors in (6-6) separately, and multiplying in reverse order.

$$\mathbf{G}^{+} = \mathbf{Q}_{2} \bullet \mathbf{S}^{+} \bullet \mathbf{Q}_{1}^{\mathrm{T}}$$

••

 $G^+$  can now be inserted into equation (5-5) in place of  $G^{-1}$  and the system solved for q.

It is noted that S will have the same dimensions and inversion properties as G. The rank of S<sup>\*</sup> equals the rank of S and the rank of G, which is r. The pseudoinverse of S<sup>\*</sup> brings us back to S: i.e.  $(S^*)^* = S$  or  $(G^*)^* = G$ . However, for most systems, G<sup>\*</sup> multiplied by G does not equal the identity matrix and thus the name pseudoinverse rather than a true inverse.

For an inconsistent system with no solutions or an underdetermined system with a set of solutions it becomes necessary to determine the best solution available for q. We define the "best" solution as the one that minimizes the least squares (LS) of the Euclidean length,  $[Gq-T]^2$ . This problem is most easily solved in the orthogonal vector space using the following property of orthogonal matrices:

For any orthogonal matrix Q the Euclidean length is preserved under multiplication (20).

10.10

$$[Q(Gq-T)]^2 = [QGq-QT]^2 = [Gq-T]^2$$

This means that the LS solution will not be changed by orthogonal transformations and the LS solution in one vector space can be transformed directly to the other.

# 5-ib Implementation of the pseudoinverse

To illustrate the steps involved in the transformation we choose to define a generic set of equations so as not to confuse the reader with Gq=T which is defined strictly as per the photothermal system.

Consider the LS problem  $|Ax-b|^2$  where A[m,n] has rank r.

(5-11) 
$$||Ax-b||^2 = ||(Q_1 \otimes Q_2^T)x-b||^2$$
 from (5-6)

(5-12) = 
$$|(Q_1^T Q_1 S Q_2^T)x - Q_1^T b|^2$$
 from (5-10)

(5-13) = 
$$\|(S Q_2^T)x-Q_1^T b\|^2$$
 from (5-9)

Here  $Q^{T}$  is the transpose of matrix Q. Applying the following orthogonal transformations  $y = Q_{2}^{T}x$ ,  $g = Q_{1}^{T}b$  to (5-13) yields the least squares problem in the orthogonal space. (5-14)  $|Sy - g|^{2}$ .

This is written in matrix form as:

$$\begin{bmatrix} \mu_{1} & & & \\ \mu_{2} & & & \\ & \mu_{3} & & \\ & & \dots & \\ & & \mu_{r} & \\ & & & 0 \end{bmatrix} \begin{bmatrix} y_{1} & & \\ y_{2} & & \\ y_{3} & - \begin{bmatrix} g_{1} \\ g_{2} \\ \vdots \\ g_{n} \end{bmatrix} \\ \vdots \\ y_{n} \end{bmatrix} \begin{bmatrix} y_{1} & & \\ g_{2} \\ \vdots \\ g_{n} \end{bmatrix} \begin{bmatrix} g_{1} \\ g_{2} \\ \vdots \\ g_{n} \end{bmatrix} \begin{bmatrix} g_{1} \\ g_{2} \\ \vdots \\ g_{n} \end{bmatrix} \end{bmatrix}$$

There will be r solutions in the row space and m-r zero solutions in the null space. Since S contains only r singular values along the diagonal, the top left corner contains all the information about the system. We now define the following submatrices:

**R11** = the top left [r,r] corner of S.

R22 = the bottom [m-r,n] rows of S.

(5-14)  $y = y_1 + y_2$  where  $y_1$  is the first r values of y and  $y_2$  contains the final n-r values of y.

(5-15)  $g = g_1 + g_2$  where  $g_1$  is the first r values of g and  $g_2$  contains the final m-r values of g.

We can then write 
$$\|Sy - g\|^2 = \|R_{11}y_1 - g_1\| + \|R_{22}y_2 - g_2\|$$
  
=  $\|R_{11}y_1 - g_1\| + \|g_2\|$ 

This illustrates that the LS solution will be independent of the values of  $y_2$  which projects only onto zeros of the row space. The vector  $y_1$  is unique as it projected onto a square matrix of rank r. To minimize y in equation (5-14) one simply sets  $y_2=0$  and inserts it into y. Transforming y back to x then solves the LS problem as originally posed.

$$\mathbf{x} = \mathbf{Q}_2 \bullet \mathbf{y}$$

Note that the solution of the minimum Euclidean length of  $|AX-b|^2$  is unique and independent of the orthogonal decomposition technique. We have used SVD as mentioned above.

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The pseudoinverse technique applied to equation 5-5 works very well at recovering continuous optical profiles. Its strengths and limitations are fully explored in section 6.

## 5-ii The non-negative least squares minimization

Minimization algorithms are an iterative approach to solving the inverse thermal heat conduction problem (equation 5-5). The algorithms are based on estimating the source profile, q, calculating the corresponding theoretical impulse response by equation (5-4) and comparing it to the experimentally measured impulse response. By generating the appropriate values of q the error between the theory and experiment is minimized and the solution moves towards the true source profile in the sample. When the two impulse traces match exactly the true source profile is obtained.

The choice of coefficients (sources) in q is determined by a convergence criterion based on the norm of the noise on the experimental signal (23). The  $l_1$  norm is for exponentially distributed noise and the residual difference between the experiment and calculated temperature response is minimized. The  $l_2$  norm is for gaussian noise and the sum of the squares of the residuals is minimized. Norms of the orders 2,3,... up to infinity exist for different noise distributions. The  $l_{infinity}$  norm is for noise with a square or box distribution in which case the single maximum residual is minimized.

For a true simplex (the  $l_1$ -norm) the error surface is a cone shaped hyperplane which restricts the possible solutions to equation (5-4). Each intersection of the hyperplane is a vertex corresponding to the coefficients of the vector **q** and has a absolute value representing the  $l_1$  error between theory and experiment. By minimizing the  $l_1$ -norm the simplex moves q towards the apex of the cone where the error is minimum and where q is the best representation of the source profile q. The concept is illustrated in Fig. 5-4 showing the intersection of multiple error planes.

The error surface of a  $l_2$  norm is a smooth parabolic cone with no discrete vertices. Rather, it has a continuous profile similar to a smooth valley. The  $l_2$  minimization simply moves along the error surface checking the error level or the error surface gradient as it moves **q** towards the optimal solution at the bottom.

We have developed a minimization algorithm to solve equation 5-5 which uses gradients of the  $l_2$  error norm to determine the direction of descent towards the optimal q. It has been termed the non-negative least squares fit (NNLS).

For every least squares problem of the form  $\|\mathbf{Gq}-\mathbf{T}\|^2 = \emptyset(\mathbf{q})$  we can define  $\mathbf{q}$  as any point on the error surface and  $\mathbf{p}(\mathbf{q})$  as its gradient. The gradient vector is calculated at any point as the dot product of the vertex vector and its directional derivative.

(6-15) 
$$p(q) = -[G^T(G q - T)]$$

By moving down the error surface following the gradient of steepest descent, one moves towards the optimal solution  $\bar{q}$ . At the minimum the gradient will change sign as it starts to climb the wall of the error surface. By stopping the advance along the error

surface at this point one will obtain the optimal solution  $\bar{q}$  as determined by the  $l_2$  norm. To prevent the minimization from converging to negative values of  $\bar{q}$  the solution is constrained to be positive.

The algorithm for solving the NNLS problem is taken from reference (21,p160) and summarized here. The minimization is initialized with no prior knowledge of the optical profile in the sample and the initial guess is assumed to have no sources (i.e. q=0). A solution matrix E with same dimensions as G is initially set empty as is the working vector z. The direction of steepest descent along the  $l_2$  error norm is calculated using equation 5-15 and the column vector (source) which aligns that direction is copied from G and placed into E. The pseudoinverse is then used to obtain the best fit vector z:

# $\mathbf{E} \mathbf{z} = \mathbf{T}$

Only coefficients of z for which are projected onto the columns of E are retained after the inversion. Thus for the first pass z has only one coefficient. If all coefficients of zare positive then q takes on the values of z and the algorithm starts again to determine the new gradient of steepest descent. This process repeats itself until either the gradient changes direction, at which point the minimum is obtained, or all the source vectors are accounted for in the solution. If at some point one of the coefficients of q becomes negative a constant is added to the entire vector to make all coefficients non-negative. The source that generated the negative values is removed from E and the algorithm returns to calculate the new gradient. This is equivalent to backing up the error surface by one position so that another direction of descent can be selected. At this point the routine will keep trying all directions until a new positive solution can be found or it cannot advance in any direction at which point a minimum will be declared.

There are a number of features about the NNLS minimization that bear comment. First, the direction of minimization is the gradient of maximum descent down the error surface and the convergence is obtained when the gradient changes sign. As a result of the convergence criteria being related to the gradient NNLS will always give a "best estimate" of the source profile. The best estimate of q may not be accurate enough for analytical purposes but the results can easily be checked by placing the recovered q into the forward model and checking the fit between theory and experiment. A poor estimate of q will give a skewed temperature response when substituted into the forward model. Secondly, as more and more column or vectors are pulled into solution sets the matrices become ill posed and the accuracy of the minimization becomes limited by the accuracy of the inversion at each point along the error surface. NNLS uses the pseudoinverse and is limited in its accuracy by the introduction of negative sources at the point of inversion. The NNLS technique works very well at recovering discrete profiles because few columns of G are needed to account for the temperature response. Continuous optical profiles require a larger number of columns and as such are slower to converge and more prone to distortions caused by ill conditioning. However, by seeding G as we did with the pseudoinverse routine the technique is capable of recovering an arbitrary profile with a high degree of accuracy.

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#### 6. Results and Discussion of Inversions of Theoretical Profiles

Both inversion techniques introduced in part 5 can recover arbitrary optical profiles from synthetic data generated with machine precision. However, photothermal experiments rarely generate data with less than 0.1% noise and 1% noise is typical. Therefore along with noise free data we present the theoretical evaluation of these inversion techniques with data only known to 0.1%-10% accuracy, i.e. 0.1%-10% noise on T, G or both.

A variety of thermal source profiles are presented in Fig. 5-5 covering a range of possible conditions that may be encountered in photothermal science. The first is a linear profile, the second is an exponential, the third is a triangular profile, the fourth is a step function and the fifth is a discrete source. All inversions were fit using front surface temperature detection. The sample top surface is defined in the figures at x=0 and the back of the sample is at x=50  $\mu$ m. Fits by the l<sub>2</sub> norm are presented in percent. To make the calculation the theory and experiment are normalized (T or q) and the error at the point of maximum difference is reported.

The seeding process used in this work is implemented as follows. The data to be seeded, G or T, are normalized to the maximum value. This restricts the coefficients to values between 0 and 1. A random number generator is used to fill a matrix of equal size with Gaussian noise characterized by a mean of zero and a standard deviation of unity (24). Each individual coefficient of the "noise" array is multiplied by a scaling factor that is



input by the user. The noise and data arrays are then added together absolutely to obtain the seeded matrix.

### **Pseudoinversion results**

(i) inversion of noise free temperature responses.

Direct pseudoinversion of G works well reconstructing optical profiles using noise free data. Data generated with machine precision is inverted in Fig. 5-6. The pseudoinverse accurately recovers the linear, exponential and discrete profiles when data are known to 17 decimal places. The triangular and step functions present a little more difficulty giving only approximate recovery of the optical profile. Inversion of temperature responses known only to 1% accuracy, using a unseeded G matrix, produces a wildly oscillating inaccurate source profile with negative coefficients as shown in Fig [5-7]. This wildly oscillating nature is due to the ill conditioning of G which can be improved with seeding.

A study showing the recovery of noise free data with a seeded G matrix followed by averaging is presented in Figures 5-8 and 5-9. The results of 100 pseudoinversions are plotted as an ensemble in parts (a-d) while the average of each of the 100 pseudoinversions are plotted in parts (e-h). From the ensemble one is able to view the mean and confidence interval obtainable for a given level of noise in the seeding of G. The confidence level is about similar whether G is seeded with 1% noise (Fig. [5-8]) or 0.01% noise (Fig. [5-9]). However, as can be seen from the averaged results that for 100 averages the signals inverted with the lower level of noise converge more closely to the true optical profiles. The results of inverting the optical profiles 3 times with 100 averages and 1% seeding is presented in Fig. (5-10) clearly showing that the confidence interval is decreasing approximately as one over the square root of N. With enough time and enough averages the solution converges towards the pseudoinverse fit recovered using machine precision data. This is the advantage of simple Monte Carlo seeding of G and averaging of the inverted optical profile. As can be seen the technique satisfactorily recovers the continuous profiles but has difficulty recovering the triangular and step functions. The discrete profile could not be differentiated from the triangular profile and is not shown here.

# (ii) inversion of "noisy" temperature responses

Gaussian or uniform noise of 5% on the recorded temperature impulse response have only minor effects on the technique's ability to recover a continuous optical profile. The robustness of the pseudoinverse is illustrated in Figure 5-11. Theoretical temperature responses are shown in Fig. 5-11a with 5% and 0.5% gaussian noise added. The true exponential source profile is plotted as a dashed line in Fig. 5-11b. The two solid lines are the recovered source profiles using the pseudoinverse technique with the T traces in 5-11(a). Both temperature responses returned similar source profiles after 400

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pseudoinversions seeding G with 1% noise. The accuracy of the recovered profile was found to be related to the uncertainty in G more that T. The psueudoinverse fit the true optical profile in regions where it varies slowly but was skewed in sharply varying regions. When the two optical profiles recovered from noisy data are placed into the forward model the calculated temperature responses matched the original noise free temperature response to within 1.0% over the entire impulse response (Fig. 5-11c). This illustrates three important features of the inversion routine. First, a simple Monte Carlo seeding technique can be used to recover optical profiles form noisy temperature responses. Second the results suggest that the limiting step in recovering accurate thermal profiles is still the inversion process rather than the experimental noise on T. Finally, the least squares projection used in the pseudoinverse effectively fits the source in the presence of noise on the temperature response.

Pseudoinverse fits of a discrete source with 1% uncertainty on the temperature response is presented in Fig. 5-12a. The pseudoinverse inversion technique is able to identify the position of the discrete source but unable to follow the sharp edges. Negative sources are introduced to account for the broadening further distorting the true optical profiles. This smooth inversion is generated from seeding G with 1% noise and averaging 1000 inversions. When G is known to more accuracy the pseudoinverse is effective at recovering the sharp edges. Fig. 5-12b shows that when G and T known to 5 decimal places the inversion recovers discrete sources with minor distortion of the optical baseline. As yet, we know of no orthogonal transformation that will help detect sharp edges and constrain the solution of q to be positive. Until this can be developed the psuedoinverse will be suitable for recovering continuous profiles but not discrete profiles.

## (ii) The NNLS minimization results

In contrast to the pseudoinverse the NNLS routine is extremely effective at detecting discrete sources, sharp edges and rapidly varying optical profiles as the experimental temperature response projects onto only a few column vectors. The method has a very small line spread even for features buried deep in the sample.

(i) NNLS inversion noise free data

The NNLS inversions of noise free data was studied using the four optical profiles in Figures 5-5(a-d) and a multiple discrete profile. Single NNLS fits of the profiles, presented in Fig. 5-13, show the effects of the rank deficient nature of the unseeded G. A sample with two discrete sources was recovered accurately because the number of columns required to describe the temperature response was less than the rank of G (Fig. 5-13a). The continuous profiles in Figs. 5-13(b-e) were not recovered because in each case only 7 sources were pulled in as an estimate of the profiles. Seeding of G effectively increases the rank of G so more sources may be pulled in for each inversion. The ensemble of 100 seeded NNLS inversions plotted together shows the mean with wide



confidence intervals for a single inversion (Fig. 5-14 a-e). However, the average of the 100 inversions produces a smooth curve which converges to the same profile obtained using the noise free pseudoinversion (Fig. 5-14 f-j). This is expected as the NNLS algorithm returns the least squares fit with the solutions constrained to be positive.

Similar results for 1% noise in G and 0.01% noise in G are plotted in Fig. 5-14 and Fig. 5-15 respectively. As with the pseudoinverse technique the NNLS technique will require more averaging for a larger uncertainty in G. The results of inverting the optical profiles 3 times with 100 averages and 0.01% seeding is presented in Fig. 5-16. Again the confidence interval can be seen to decrease approximately as a function of the square root of the number of averages. The most difficult inversion appears to be the step function which is a combination of two very flat sources and a sharp edge. After 1000 averages seeding G with 0.01% noise NNLS recovers the profile in Fig. 5-17. The lower part of the step and the edge are recovered reliably but the position of the step is estimated too high and resembles the response of a Chebychev high pass filter. This error may be due to the finite bin spacing and finite time spacing not allowing for such sharp contrasts to be recovered next to each other.

Inversion of optical profiles that require only one or two columns of G seeded to 0.1% give a resulting line spread of 1:1 or 1:2. Figure 5-18 shows the effect uncertainty in G has on the inversion of an optical profile with two discrete sources. The sample is 50  $\mu$ m thick with one source 16 $\mu$ m from the surface and a second one at 39 $\mu$ m. The sources are

weighted 1:0.8 respectively, the temperature response is monitored at the sample surface and inversions are the results of 25 averages. With G seeded with 0.1% uncertainty the optical profile is recovered with minor distortion. When G is seeded 1% noise the line spread is increased to about 1:4. The top feature nearest the detector is less distorted while the bottom feature is broadened. If G is seeded with 5% noise the line spread is increased to 1:9 broadening both distinct optical profiles. Increased averaging introduces no new sources but will tend to round the features of the inversion with 5% noise.

The major advantage of seeding G is to improve its condition number and rank to make the inversion of equation 5-5 well posed. On the whole the more G is seeded, the better conditioned it becomes and the less sensitive the inversion will be to noise on the experimental signal. However, one must trade off improved conditioning against increased uncertainty in the source position as G is seeded. The optimal noise level on G depends on the nature of the profile that is being recovered. Discrete profiles that require only 1 or 2 sources need G seeded to 0.0001%. This gives accurate an recovery with no line spread. Continuous profiles will require more sources to describe the temperature response and ill conditioning errors will effect the inversion routine. Under these conditions G should be seeded between 0.01% and 1% for best results.

(ii) NNLS inversion of "noisy" data

The effects of noise on T(t) in NNLS inversions is studied for the same discrete and

continuous source profiles discussed above.

The recovery of an exponential profile in the presence of 1% noise is presented in Fig. 5-19. The temperature response was seeded with 1% gaussian noise (Fig. 5-19a) and the inverted optical profiles (Fig. 5-19b) are the average of 25 and 100 minimizations seeding G with 0.5% noise. As with the noise free temperature responses the solutions converge to the true optical profile as the number of averages increases.

Recovery of a single discrete source is illustrated in Fig 5-20. An optical profile two bins wide in a 30  $\mu$ m sample is recovered using temperature responses with 0.05%, 1% and 10% noise and G seeded with 0.05% noise which was shown earlier to provide nearly distortion free inversion (Fig. 5-18). The three temperature responses are plotted together in Fig. 5-20a showing the extreme signal to noise ratios of a typical experiment. The smoothest trace being exceptional, the middle trace typical noise levels and the 10% noise level basically unacceptable. However, after 5 averages all three inversions converged to about the same solution illustrated in Fig. 5-20b. T(t) response with the lowest noise recovered the optical profile with high accuracy, the T(t) with 1% noise had only minor distortion and T(t) with 10% noise recovered a source only one bin wide, but in the correct position.

#### Effects of systematic errors on the inversion process

The effects of incorrect thermal parameters estimation is illustrated in Fig. 5-21 using result from NNLS with theoretical data calculated to machine precision. The model is attempting to recover the magnitude and position of the same two sources illustrated in Fig. 5-18.

First we consider the situation where the sample is measured to be thicker than it really is. A 10% error in estimating the sample thickness results in a error of positioning the source by about 5%. The profiles are broadened slightly and absolute values of q have decreased (Fig. 5-21a). If the estimation of the sample thickness is off by 20% the inverted profile is still not totally distorted although the position is *ï*urther shifted and broadened. The relatively small changes in the profile are a reflection of the thermally continuous model being used. Since the inversion is based on monitoring surface temperature the error due to increased thickness is effectively added to the rear of the sample where no source exists. The corresponding broadening of the optical profiles then solely reflects the effects of an increased bin size in the inversion process.

It is noted here that the important parameter is really the thermal thickness of the sample which can be defined as the sample thickness (1) divided by the square root of the thermal diffusivity.
$l_{therm} = V sqrt(\alpha).$ 

Thus an error in sample thickness is indistinguishable from an error in the measured sample diffusivity. When the recovered "best fit" optical profile is fed back into the forward model it does not produce a temperature response that matches the original temperature response. Thus distortions in the inversion procedure due to incorrect sample properties can be detected comparing the theory and experimental temperature response. We believe that this can be an advantage to other inversion routines in that the NNLS will not distort the recovered source profile without also distorting the temperature response.

Another possible source of error which skews the image is data acquisition. The effects of a DC offset is illustrated in Fig. 5-22. The same T(t) response is normalized after different DC offsets have been subtracted. The T(t) traces in Fig. 5-22a are obviously different and the inverted optical profiles produces three different sources. The true profile is the sample from Fig. 5-18 (50µm thick with two sources). A 10% dc offset in the measurement distorts the weighting of the two recovered profiles, broadens them and shifts their location. A 30% DC offset recovers a single source only.

The effects of systematic errors are dealt with in the next chapter where the inversion is applied to real photothermal signals. However, from the theoretical analysis of this inversion technique it is clear that the greatest source of inaccuracy of this inversion is not noise on the experimental signal but systematic errors in measurement of the thermal response. It is important to realize that random uncertainties in the data are preferable to systematic distortions in the data. If the incorrect thermal data are fed into the model with a low error limit, either of the techniques will return a source profile to explain the temperature response for the erroneously chosen G. An erroneously chosen G is equivalent to choosing the wrong basis for the problem and subsequently it is less likely that the correct source profile will be recovered on inversion.

#### 7. Inversion of thermally and optically inhomogeneous samples

The techniques for recovering optical profiles can be extended to recovering optically and thermally inhomogeneous samples.

The photothermal problem can always be written as equation (5-4).

## $(5-4) G \bullet q = T$

It is possible to separate thermal contributions by metalizing the top of the polymer and recording the photothermal response. Following the method of Aamodt et al. [11] the N layer sample can be written described as N matrices which are then added together to obtain the G matrix for the thermally and optically inhomogeneous sample. This work is not developed any further but left for the future.

#### **Conclusions:**

It is possible to uniquely determine the optical profile of a thermally continuous sample using photothermal spectroscopy and inverting the data using the pseudoinverse and minimization techniques. The dithering of G with random noise makes the problem well posed and solvable. Future work remains to determine the exact interpretation of the seeding routine as seeding G does not directly equate an equal uncertainty in the optical profiles due to the nature of matrix multiplication.

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#### Figure 5-1

(a) The columns of matrix G (source intensity) taken from the first row of table 5-1 are plotted against row position (time). The fastest response represents the temperature as a function time arriving at the surface from the top of the sample. The slowest weakest response is the contribution from the back sample. Each source is separated by 0.97 µm. (b) The columns of  $G^{-1}$  are plotted together. The columns are periodic with extreme values and nodes where they all cross zero. The extreme oscillations are indicative of an ill conditioned matrix.



### Figure 5-2

(a) The 32 columns of matrix G seeded with 1% noise are plotted. The overall shape of the columns are identifiable but low noise perturbs the smooth curves. (b) The columns of  $G^{1}$  from (a) are plotted together. The columns are periodic but not regular and the extreme values have been removed.



# Figure 5-3

The Greens Function matrix calculated to have the maximum of each impulse response along the diagonal of the matrix. This approach to data sampling makes the traces scale invariant and rank(G) decreases.





(a) The  $l_1$  error surface showing the intersection of hyperplanes. The surface has distinct nodes where the planes intersect. (b) The  $l_2$  error surface has a smooth surface with no discrete vertexes. This error surface is used in the NNLS minimization algorithm.

Fig 5-5a





The 5 different source profiles that will be recovered from the photothermal temperature responses to evaluate the inversion procedure. (a) linear (b) exponential (c) triangular (d) step (e) discrete source. Each sample is 50  $\mu$ m thick and has a thermal diffusivity of 1.0e-7 m<sup>2</sup>/s.



Fig 5-5b

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Fig 5-5c

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Fig 5-5d



Fig 5-5e







Pseudoinversion of the 5 different optical profiles using data generated with machine precision. The technique recovers (a) linear (b) exponential and (c) discrete sources but has some trouble recovering the (d) triangle and (e) step function.



Fig 5-6b





Fig 5-6c





Fig 5-6d





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source intensity (arb. units)





source intensity (arb. units)



Pseudoinversion of the discrete source profile (dashed) with 1% noise added to the temperature response. The inverted optical profile (solid) is dominated by the noise in the temperature response due to the ill conditioning of G. (see table 5-1 row 1). Both traces have been normalized to the maximum value. (dt=0.5ms,  $dx=1.2 \mu m$ )







Pseudoinversion of difference optical profiles seeding G[128,32] with 1% noise, n=100 averages, dt=0.5 ms, l=50  $\mu$ m, no noise on T(t). The ensemble are plotted together: (a) linear (b) exponential (c) triangular (d) step. The average of the ensembles are plotted with the true profile: (e) linear (f) exponential (g) triangular (h) step.



Fig 5-8b





Fig 5-8c





Fig 5-8d





Fig 5-8e



Fig 5-8f





Fig 5-8g





Fig 5-8h



Fig 5-9a





The exact same study as Figure 5-8 but G is seeded with 0.01% noise. Note that the confidence band has decreased as the amount of noise on G is decreased.

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Fig 5-9b





Fig 5-9c

1, <sup>5</sup>4



Fig 5-9d



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Fig 5-9e





Fig 5-9f





Fig 5-9g



Fig 5-9h


Fig 5-10a





The result of the recovered optical profiles from the average of 100 inversions done 3 . times. Note that with increasing averages there is increased confidence in the recovered optical profiles. The pseudoinverse can recover the continious optical profiles but has trouble detecting the sharp edge or rapidly varying optical features. Conditions as Figure

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Fig 5-10b





Fig 5-10c





Fig 5-10d



Fig 5-11a





(a) The temperature response for the exponential source in Figure 5-5. The dotted line has 0.5% noise added and the solid line has 5% noise added.

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(b) The recovered source profiles seeding G[128,32] with 1% noise and averaging 400 inversions. The true profile is dotted. The recovered profiles fit equally well for either temperature response used for the inversion. [1=50  $\mu$ m, dt=0.5 ms]





(c) The true temperature response (solid) and the calculated temperature response using source recovered from the temperture response with 5% noise added. The small error is attributed to the fact that T(t) was not reseeded for each inversion and thus the pseudoinverse was trying to fit the same erroneous temperature response each time.

Fig 5-12a

source intensity (normalized)





(a) Recovery of a discrete optical profile with 1% noise on T. The pseudoinversion can detect the location of the source but cannot reconstruct the sharp edges. G[128, 32], 1=50 µm, dt=0.5 ms, N=400 and 1000.



Fig 5-12b

(b) Conditions as in (a) but G is seeded with 0.0001% noise and N=400.



Fig 5-13a



Single NNLS fits to 5 different optical profiles. (a) Two discrete sources are recovered accurately, but continuous profiles that are (b) linear, (c) exponential, (d) triangular and (e) step functions are not recognizable after only one inversion. The step function has all the sources in the correct half of the sample.



Fig 5-13b





Fig 5-13c





Fig 5-13d

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Fig 5-13e



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Fig 5-14a





An ensemble of 100 single NNLS inversions plotted together with G[128,32] seeded with 1% noise and no noise on T. (a) two discrete sources (b) linear source (c) exponential source (d) triangular source (e) step source. The average of the 100 inversion is then plotted with the true source profiles: (f) discrete, (g) linear, (h) exponential, (i) triangular, (j) step.

Conditions are the same as in Fig. 5-8 where the same study was done with the pseudoinverse.

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Fig 5-14b

J. J.



source intensity (arb. units)

8 8.8 8.4 1.4 0 1.2 1.6 1.8 8 .2 8 5 6 Ň 18 sample depth (um) 20 30 مداد 10 50

source intensity (arb. units)

Fig 5-14c





Fig 5-14d



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Fig 5-14e



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Fig 5-14f



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Fig 5-14g





Fig 5-14h





Fig 5-14i





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Fig 5-14j





Fig 5-15a



Same as Fig. 5-14 but G[128,32] is seeded with 0.01% noise. The recovery of the optical profiles are approximately equivalent.

source intensity (arb. units) 8 0 8 0 ۵ 1.4 1.8 1.2 1.6 4.2 8 'n . .0 8 10 sample depth (um) 20 38 10 50

Fig 5-15b



-8.2 8 0.8 8 1.2 1.4 1.6 1.0 3 'n • Ň -18 sample depth (um) 28 30 ..... 5 ٠ -----5

source intensity (arb. units)

Fig 5-15c





Fig 5-15d





Fig 5-15e





Fig 5-15f





Fig 5-15g





Fig 5-15h





Fig 5-15i





Fig 5-15j





Fig 5-16a



The result of 100 NNLS averages plotted three times showing the confidence band decreasing. (a) discrete sources, (b) linear profile, (c) exponential profile, (d) triangular profile, and (e) step profile. The true optical profiles are shown as dashed lines while the recovered profiles are shown in solid.



Fig 5-16b




Fig 5-16c





Fig 5-16d



Fig 5-16e









The average result of 1000 NNLS inversions to recover the step function. The function becomes smoother, but it still cannot accurately recover the entire source profile.

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A line broadening study to examine the effects seeding G has on the line spread. The true sources are at 16 µm and 39 µm and can be recovered without broadening using machine precision data (see Fig. 5-13a). A 0.1% seeding broadens the lind 1:2 (dotted), 1% noise on G has a 1:4 line spread and 5% noise has a 1:9 line spread. Accompanying the increased line spread is a distortion of the optical profile.



# source intensity (normalized)

## Figure 5-18b.

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The results of 1000 averages of seeding G with 5% noise. Note that increased averaging does not introduce more new sources and the profiles do begin to converge to the profile with two discrete sources.



Temperature response normalized (arb. units)

Fig 5-19a



Recovery of an exponential profile with 1% noise using NNLS. (a) Dashed is the theoretical temperature response while solid is the seeded temperature response used to recover the optical profile. (b) solid is the theoretical source profile, dashed is the recovered profile after 25 averages and dotted is the recovered profile after 100 averages.



Fig 5-19b



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Effect of experimental noise on the recovery of the source profile with NNLS. (a) Three temperature responses with 0.05% noise, 1% noise and 10% noise added. (b) The recovered optical profiles. Dashed is the recovered profile with 0.05% noise on T. Solid is from 1% noise on T and dotted is recovered from 10% noise on T. All inversions used G[128,32] seeded with 0.05% noise, 1=50 µm and dt=0.5 ms.



Fig 5-20b









(a) Solid is the true source positions. Dotted, recovered source position for estimating the sample 10% too thick, dashed is the recovered optical profile for estimating the sample 20% too thick. The forward model prediction for the recovered source profile in T(t). G[128,32] seeded with 0.05% noise, l=50µm, dt=0.5ms.



T(t) normalized (arb. units)



#### Fig. 5-22

A DC offset study showing the effects of incorrect electronic measurement. (a) The correct impulse response for the sample made of two discrete sources plotted as a solid line. The dashed trace is the normalized result of adding a 10% DC offset to the true impulse response. The dotted trace is the normalized impulse response after adding a 30% DC offset to the true impulse response.

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(b) The recovered optical profiles using the three impulse responses in Fig. 5-22a. The true profile is the two discrete sources in solid. The recovered profile from the 10% DC offset is the dashed source profile and the single dotted source is the result recovered from a temperature response



with a 30% DC error.



Chapter 6:

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Implementation of the inverse heat conduction problem for recovery of the optical absorption profiles in polymer films by inversion of photopyroelectric spectroscopy time domain signals.

## Nomenclature

- G Greens Function
- $\overline{G}$  Greens Function spatially averaged over the pyroelectric thickness
- H Greens Function spatially averaged and electrically convoluted with the electrical impulse response of the pyroelectric system.
- h(t) impulse response in general. Can refer to the temperature response of the pyroelectric detector or the electrical filter impulse response depending on its context.
- v(t) recorded voltage response.
- he the electrical impulse response of the filters and pyroelectric

## Introduction:

Chapter 5 introduced a new theoretical inversion technique to recover an arbitrary thermal flux profile in a polymer sample from the photothermal impulse response. The calculations used front surface temperature detection to recover the photothermal signal. This approach has application to radiometry measurements but does not describe a photopyroelectric signal. In photopyroelectric spectroscopy considerations such as electronic filter effects and the integrating nature of pyroelectric sensors must be incorporated into the model. In this chapter we will develop methods to account for the electrical filtering and the thermal response of the detector so the technique can be applied to work in this thesis.

Secondly, we will examine the sensitivity of the inversion procedure to small systematic errors and explore the physical limitations of the technique in photopyroelectric measurements. Systematic errors such as incorrect thickness measurement, errors in thermal diffusivity values, small electronic distortions of the thermal signal and the assumption of a thermally continuous model will all be addressed.

Finally, an algorithm to convert the thermal flux profile to an optical absorption profile will be presented. As the inversion algorithm is now employed the thermal flux profile in the sample is reconstructed. The thermal flux profile is closely related to the optical absorption profile as non-radiative decay of absorbed light is the mechanism of heat generation. However, in most imaging applications it is desirable to obtain an accurate  $\beta$  distribution rather than a thermal flux profile.

Methodology for inversion of photopyroelectric signals.

Photopyroelectric impulse response measurements are not just a measure of surface temperature of the sample but rather, the spatially averaged temperature of the pyroelectric sensor convoluted with the electrical response of all electronic filters used in the measurement system. Recovery of thermal flux profiles requires that the averaging and convolution operations be accounted for in the Greens Function matrix (G) before inversion of the photothermal signal proceeds.

The spatially averaged temperature response of the pyroelectric sensor can be approximated two ways. The first is to write the averaging operator as the discrete series approximation of the free space Greens Function at N observation positions spaced through the detector where N is the desired resolution of the series approximation to the averaging operator. In practice this means generating the free space Greens Function response for the system for each of the N source positions from the detector, then taking the average of the N responses as the theoretical pyroelectric signal. The second approach is to use the method of Power and write the photopyroelectric response as a difference of error functions [1]. In this thesis we develop the inversion using the free space Greens Function discrete series approximation and then compare it to the error solution for completeness.

(i) the free space Greens Function spatial average

The general expression of the average temperature measured over a thickness d between  $x_1$  and  $x_2$  is :

[6-1] 
$$<\Delta T(t)>=\frac{1}{d}\int_{x_1}^{x_2}\Delta T(x,t)dx \quad d=x_2-x_1$$

For equal spatial increments this is approximated by:

$$[6-2] \langle \Delta T(t) \rangle \equiv \frac{1}{\Delta x} \sum_{k=1}^{K} \Delta T(x_k, t) \Delta x_k$$

where  $\Delta x_k = x_{k+1} - x_k$  $\Delta x = K \Delta x_k$ 

Equivalently equation 6-2 can be written as 6-3.

$$[6-3] \langle \Delta T(t) \rangle \cong \frac{1}{K} \sum_{k=1}^{K} \Delta T(x_k, t)$$

Discretization of  $\Delta T(x,t)$  was seen in the previous chapter as:

$$[6-4] \Delta T(x,t_j) = \int_{-(1+d)}^{-1} g(x-x_0,t_j)q(x_0)dx_0$$

$$\Delta T(\mathbf{x}, t_j) = \sum_{i=1}^{N} \frac{1}{\sqrt{4\pi\alpha t_j}} e^{\frac{-(\mathbf{x} - i\Delta \mathbf{x})^2}{4\alpha t}} q(\mathbf{x}_i) \Delta \mathbf{x}_i$$

Finally to obtain the spatial average of the pyroelectric we substituting equation 6-4 into 6-3 to obtain 6-5.

[6-5] 
$$\Delta T(x,t_j) = \frac{1}{D} \sum_{k=1}^{D} \sum_{i=1}^{N} \frac{1}{\sqrt{4\pi\alpha t_j}} e^{\frac{-(x_k - i\Delta x)^2}{4\alpha t}} q(x_i) \Delta x_i$$

Here D is the integer corresponding to the desired resolution of the series approximation to the continuous integral of equation 6-1. This is equivalent to writing the free space Greens function for D different observation positions in the pyroelectric and taking the average response. The average temperature response of the pyroelectric can then be written as the product of the spatially averaged free space Greens function,  $\overline{G}$  and the source vector.

[6-6]  $\langle \Delta T(t) \rangle = \overline{G}q$ 

(ii) the electrical convolution operation

A technique for measurement of the electronic impulse response is described in chapter 2. For each filter setting the electronic impulse response was measured and saved as a 256 point array, the same form in which the pyroelectric response was saved. A typical electrical impulse response of a 9 $\mu$ m PVDF film and filters for a 2,500 Hz AM-PM spectrometry sweep is illustrated in Fig. 6-1.

To recover the thermal flux profile from the experimental trace, the photothermal impulse response can be deconvoluted from the electrical response to give the spatially averaged thermal response of the detector, or, the theoretical signals can be convoluted with the electrical response for comparison with the experimental response.

The convolution filter for the recorded voltage response is written as  $v(t)=h_e * <\Delta T >$ where \* is the convolution operation and  $h_e$  is the electrical impulse response of the filters. In matrix form the result is calculated as:

$$[6-8] \qquad \begin{vmatrix} \mathbf{v}(\mathbf{t}_1) \\ \mathbf{v}(\mathbf{t}_2) \\ \mathbf{v}(\mathbf{t}_3) \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{v}(\mathbf{t}_n) \end{vmatrix} = \begin{vmatrix} \mathbf{h}_{e1} & 0 \\ \mathbf{h}_{e2} & \mathbf{h}_{e1} & 0 \\ \mathbf{h}_{e3} & \mathbf{h}_{e2} & \mathbf{h}_{e1} & 0 \\ \mathbf{h}_{e3} & \mathbf{h}_{e2} & \mathbf{h}_{e1} & 0 \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{v}(\mathbf{t}_n) \end{vmatrix} \begin{vmatrix} \langle \Delta T(\mathbf{t}_1) \rangle \\ \langle \Delta T(\mathbf{t}_2) \rangle \\ \langle \Delta T(\mathbf{t}_3) \rangle \\ \cdot \\ \cdot \\ \mathbf{h}_{en} & \mathbf{h}_{e(n-1)} & \mathbf{h}_{e(n-2)} & \cdot & \mathbf{h}_{e2} & \mathbf{h}_{e1} \end{vmatrix} \begin{vmatrix} \langle \Delta T(\mathbf{t}_1) \rangle \\ \langle \Delta T(\mathbf{t}_2) \rangle \\ \langle \Delta T(\mathbf{t}_3) \rangle \\ \cdot \\ \cdot \\ \cdot \\ \langle \Delta T(\mathbf{t}_n) \rangle \end{vmatrix}$$

Here  $v(t)=\{v(t_1),v(t_2), ..., v(t_N)\}$  is the measured impulse photothermal voltage response at specific times after excitation and he={h<sub>e1</sub>,h<sub>e2</sub>,h<sub>e3</sub>,...h<sub>en</sub>} is the time array of the electrical impulse response at the same time points as the sample. The spatially averaged, electrically convoluted Greens Function, written as H, can now be inverted to obtain the source profile according to equation 6-9.

## [6-9] $q(x)=H^{-1}*v(t)$

The columns of a Greens Function matrix accounting for the spatial averaging of the pyroelectric sensor are shown in Fig. 6-2. The same columns of the matrix after accounting for the electronic filtering in the instrument, H, are illustrated in Fig. 6-3. Note that the early times of the electronically filtered impulse responses are less similar than the unfiltered early times; however, the long times all converge to the same trends. This suggests the thermal sources located near the detector surface can be resolved at early times while sources at the top of the sample, away from the detector, will be difficult to resolve at long times.

### Analysis of the thermally continuous inverse model for PPES detection

Results of inversions using the Greens function as developed in the previous chapter were not applicable in practice due to the assumption of the sample being thermally homogeneous with its environment. In practice, thermal waves generated in the thermally continuous sample have an incident component that travels from the source to the pyroelectric and a second component which travels through the sample to the air interface where it is almost totally reflected back towards the detector. An illustration of the thermal waves is presented in Fig. 6-4. The incident component (i) is accounted for in the free space Greens Function but the second component of the thermal wave arrives later and is not accounted for in a thermally continuous model.

The solution to this problem requires that either the sample geometry in the theoretical model be redefined or a new Greens Function be derived to account for the thermal reflection off the air/sample interface. Altering the theoretical model space simply requires that the sample space be made twice as thick as the real sample. The inversion will place incident thermal waves in the bottom half of the sample space closest to the detector and the reflected component will show up in the top half of the sample with the geometry of the sources inverted with respect to the bottom half of the sample space (Fig. 6-5a).

For photopyroelectric effect spectroscopy the modified Greens function can be attained from the theory of Power using the equation to study clear coats on strongly absorbing surfaces [1] (Fig.6-5b). Assuming no other thermal reflections in the sample other than at the air sample interface one can write

$$[6-10] <\Delta T >= \frac{1}{d} \left\{ \operatorname{erfc}\left[\frac{(1-x)}{\sqrt{4\alpha x}}\right] - \operatorname{erfc}\left[\frac{(1-x+d)}{\sqrt{4\alpha x}}\right] + \operatorname{erfc}\left[\frac{(1+x)}{\sqrt{4\alpha x}}\right] - \operatorname{erfc}\left[\frac{(1+x+d)}{\sqrt{4\alpha x}}\right] \right\}$$

where 1 is the sample thickness, x is the position in the smple where the source is generated and d is the pyroelectric thickness. The observed photothermal signal is attributed to the difference in the thermal response across the pyroelectric detector. The

first two terms account for the incident thermal waves being launched from point x in the sample and reaching the front and rear surfaces of the detector. The last two terms account for the thermal waves which travel from point x up to the air sample interface then back down to the front and rear surface of the detector.

By dividing the sample into N layers and writing the equation for each layer,  $(x_i)$ , one can reconstruct the spatially averaged 1-D heat conduction solution for  $\overline{G}$  with one thermal reflection at the sample/air interface.

The second approach is inherently the more accurate inversion as the model must correctly position the sources to match both the incident and reflected terms simultaneously. However, we have found this approach to be sensitive to small errors in the measured thermal properties and sample thickness. This is due to the model's attempt to fit both early and late portions of the impulse response with the same source profile. In terms of the model space, the incident thermal waves are well resolved but the reflected terms are delayed and recovery of precise source profile is difficult. However, contributions from both the incident and reflected terms of the thermal waves are weighted equally in recovering the source profile.

The first approach, modeling the sample twice as thick as measured with the conventional 1-D Greens Function, proved to be less sensitive to small errors in measurement. The early times of the impulse response are modeled strictly by the incident thermal waves and the thermal reflections arriving at later times are recovered from sources in the top half of the sample space. This permits the exact analysis of how much the thermal reflections contribute to the photothermal signal. In interpreting the data the reflected components do not have to be weighted equally to the incident source

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profiles. This reduces possible errors due to truncation of the impulse response before the final thermal reflections have passed through the pyroelectric.

A study to determine the resolving power of the NNLS inversion using photopyroelectric signals is presented in Figures 6-6 to 6-8. Samples of various thicknesses were divided up into 32 equally spaces layers and the ability of the technique to resolve two neighoring features was examined. Initially one would expect that the technique could resolve any features using 32 bins based on the fact that the forward modeling of optical polymers done in chapter 2 was achieved using only 10 bins. However, there are distinct differences between forward modeling and inverse modeling of photothermal signals that make inverse modeling significantly more difficult. First, in forward modeling the optical profile of the sample was known in advance so that the bins in the model space can be adjusted to account for the optical profile. An illustration of this is in Fig. 6-6. The hypothetical sample consists four layers on a PVDF film (Fig. 6-6a). The laminate structure has three absorbing layer (including the PVDF) interspersed with clear layers. In the forward model the sample is physically measured and six bins of unequal size are used to describe the sample (Fig. 6-6b). Fits between theory and experiment require slight adjustment of the exact laye: thickness but nothing else. Exact  $\beta$  values obtained from an optical absorption spectrometer are placed into the model to account for the sources in each absorbing layer.

In inverse modeling no optical properties are assumed to be known about the sample. The best we can do is divide the sample up into 32 equal layers and let the inversion algorithm use the photothermal impulse response to place the optical features in the correct bins. However, while the NNLS inversion routine may obtain the "best" estimation of the source profile in the sample, it may never be able to recover the exact profile in the sample. This is best explained by re-examining Fig. 6-6. The total sample

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thickness is measured to be 96  $\mu$ m. The 32 bins in the inverse model give the inversion spatial resolution of 3 $\mu$ m. When the model tries to reconstruct the sample from the top down it can never get the exact spacing of the optical profile correctly. Thus the top optical layer can never be fit to 28  $\mu$ m from the top, only 27  $\mu$ m or 30  $\mu$ m. In addition, the nature of discretization process used in this inversion places all the energy distributed in each bin in a weighted delta function at the top of the bin. Thus a 2.5  $\mu$ m continuous layer will be modeled as an extremely thin source layer up to 3  $\mu$ m away from its correct position. Our forward model did not discretize the model in the same manner and permitted adjustment of bin position and bin thickness to agree with known (measured) properties; but the inverse model is much more rigid. Thus the best basis available to describe a sample may still be a poor basis. Significantly higher spatial resolution along with longer computation times are required to combat this problem.

The effect of electronic filtering on the ability of the technique to resolve thermal reflections is examined in Fig. 6-7. The columns of a spatially averaged electrically convoluted Greens Function is plotted in Fig. 6-7a. The sample and inversion was characterized by the following properties:  $l=100 \ \mu m$ ,  $\alpha=1.0 \times 10^{-7} \ m^2/s$ , dx=3.125  $\mu m$ , and dt=0.2 ms. This thickness values was chosen so that a sample 50  $\mu m$  could be studied and the entire thermal record including reflections could be recovered. To illustrate the effect electronic filtering has on the ability of the technique to resolve thermal sources the electrical impulse response of a 2500 Hz sweep was convoluted with the thermal signal. In practice one might choose a narrower spectral sweep width if inadequate depth resolution was obtained, but the effects of filtering would still have to be considered.

The three columns of the Greens function corresponding to the three sources furthest away from the detector are plotted after being normalized in Fig. 6-7b. The model shows that sources at 100  $\mu$ m, 96.875  $\mu$ m and 93.75  $\mu$ m can all be separated. However their maximum absolute values are less than 0.00875 of the earliest signal and they are separated by less than 0.001 absolute difference. Thus within the experimental limits of 1% noise not only could these sources not be resolved, they cannot be seen. One might expect that low levels of noise on the signal can be misinterpreted as a source by the model making it place or source that is not there in practice. However, results from chapter 5 showed that with enough averaging of the inversion Gaussian noise levels up to 5% on the photothermal signal nonetheless does not corrupt the recovered optical profile.

The same sample modeled as only 50 µm (i.e. no reflections) will have an inverted optical profile with a spatial resolution of ca. 1.5 µm. Fig. 6-8 shows the resolving power of the model. The largest response (solid) is always the source closest to the detector. The shallowest response (dashed) is always the thermal contribution from the source located 50 µm from the detector at the top of the sample. The dotted line represents the thermal contribution from a source elsewhere in the film. The absolute values are plotted on a normalized scale so that the relative magnitudes of the contributions can be easily visualized. The thermal contribution from a source 48.5 µm from the detector is separated by only 0.1% from the 50 µm source (Fig. 6-8a). Thus the two sources will not be resolvable within an experimental error of 1%. The thermal contribution from a source 42 µm from the detector (Fig. 6-8b) is resolved by a 1.7% difference and can just be distinguished with experimental error. A source located 35 µm from the detector or 15 µm from the farthest source is still only separated by a maximum distance of 0.047 units (Fig. 6-8c). Thus all the sources in the top one third of the sample will be separated by less than 5% of the maximum signal recorded from the pyroelectric detector.

This suggests that the inversion should be modeled using the conventional Green's Function with the model sample thickness set to twice the measured thickness. However, data interpretation should be restricted to sources in the bottom half of the model space. Using the error function approach reflections the weak long time signals are weighted with equal value as the strong early time signals in assessing the position and intensity of sources with in the sample.

#### Effect of small systematic errors

As mentioned at the end of chapter 5 systematic errors will contribute the greatest source of errors in the inversion procedure. Aside from factors such as poor experimental technique there are a number of systematic errors that can contribute to difficulties in inverting the photothermal signals. Factors that are key to our experiments include small DC offsets in the photothermal signal or electrical impulse response and errors in measuring the thermal thickness of the sample.

The effects of very small DC offsets are shown in Fig. 6-9. A theoretical impulse response for a 50 µm sample ( $\alpha = 1 \times 10^{-7} \text{ m}^2/\text{s}$ ) on 9 µm PVDF with a triangular source profile was calculated. The theoretical signal was electrically convoluted with the transfer function shown in Fig. 6-1 to give the theoretical impulse response plotted in Fig. 6-9b. Inversion of the impulse response was attempted with small DC offsets added to electrical impulse response to determine the effect on the recovered source profile. A DC offset of only 0.1% of the electrical impulse response maximum value was found to cause a significant distortion of the recovered profile. The recovered profile is shown in Fig. 6-9a as trace (1). A 0.5% DC offset added to the electrical response prior to inversion of the impulse response recovered the source profile marked trace (2). A 1.0% DC offset resulted in the source profile marked trace (3) being recovered. When these source profiles were put into the forward model the impulse responses shown in Fig.6-9b This suggests that accurate inversion requires very accurate were obtained. characterization of the electrical filtering used in the experiment. The shift and integrate nature of the convolution means that a small DC offset error can translate into a large error in the generation of the impulse response. The fact that the electrical response needs to be known to such high precision suggests that experimental protocols have to be designed to acquire the transfer function to better than 0.1%.

It is expected that electronic filter effects will also be a problem in frequency domain photothermal measurements where the observed phase is the sum of the phase of the photothermal signal plus an instrumental phase offset.

 $\emptyset_{obs} = \emptyset_{photothermal} + \emptyset_{instrument}$ 

The instrumental phase offset will need to accurately measured at each frequency to recover the true photothermal phase before inversion can be applied.

The effects of 2% and 4% error in thickness measurement for three theoretical source profiles are presented in Figures 6-10 to 6-12. Unlike the thickness studies in chapter 5 these measurements account for the integrating nature of pyroelectric sensor. For each source profile the true sample thickness is 50  $\mu$ m with  $\alpha$ =1.0x10<sup>-7</sup> m<sup>2</sup>/s. Inversions were made using the NNLS inversion routine for thicknesses of 48, 49, 51 and 52  $\mu$ m.  $\overline{G}$ [128,32] was seeded with 0.1% noise and the results presented are the average of 100 inversions (dt=0.5 ms, dx=1.5  $\mu$ m).

Inversion of the linear source profile recovered accurate qualitative trends for errors in thickness up to 4% (Fig. 6-10). The samples that were measured too thick recovered profiles that had too much thermal energy and samples that were too thin had source profiles that fell below the true source. The impulse responses obtained by forward modeling the recovered source profiles (Fig.6-10b) show deviations in the signal at long times. Impulse responses from the samples measured too thick tail off too quickly while

impulse responses from the samples too thin tail off too slowly. The same study for a triangular source profile is presented in Fig. 6-11. The inversions all recover a source profile that closely approximates the pseudoinverse profile obtained in chapter 5. The effects of errors in thickness show no clear trend in the recovered profiles; however, the impulse responses obtained by forward modeling the recovered source profile show the same trends as the responses from the linear sources. The source profile recovered from measuring the sample too thick generates a response that tails off too quickly and the samples measured too thin generate impulse responses that tail off too slowly. A third study using a step function is presented in Fig. 6-12. Estimating the sample thickness too large resulted in the inversion overshooting the step function and recovering a profile that was similar to a Chebychev low pass filter response. Samples that were measured too thin had a harder time detecting the exact location of the step function and recovered a smoother "s" profile. The time domain signals generated by forward modeling the recovered profiles showed the same trends that were recovered in the other inversions. The samples measured too thick tailed off too quickly while the samples measured too thin tailed off too slowly. All this leads to the conclusion that errors up to 4% in sample thickness measurement, or more specifically errors in  $\frac{1}{\sqrt{\alpha}}$  up to 4%, will recover source profiles qualitatively. If thermal thickness measurement is thought to be a source of the error then it can be detected in the trends of the forward modeled impulse response. Thus small corrections of the sample thickness will be seen to improve the fit between theory and experiment.

Converting thermal flux profiles to optical absorption profiles

To recover the optical absorption profile from the thermal flux profile a sample of thickness l is divided into N layers. For clarity in this example the layers are equally spaced with thickness (a) although in practice this is not necessary. The relationship between light absorption and thermal flux in a single layer has been well established and is proportional to the light entering the layer  $(I_{i-1})$ , and the optical absorption coefficient in the layer ( $\beta_i$ ) according to equation 6-11.

[6-11] 
$$Q(x) = \sum_{i=1}^{N} \beta_i I_{i-1} e^{-\beta_i a} + I_N R \sum_{i=N}^{1} \beta_i I_{i-1} e^{-\beta_i a}$$

The first term accounts for the first pass of light through the sample until it strikes the pyroelectric. The second term accounts for the light that is reflected off the detector surface back through sample out the top of the film. The pyroelectric reflectivity (R) and the light transmitted through the sample  $(I_N)$  need to be accounted for in the equation.

This can be written in matrix form as equation 6-12.

$$\begin{bmatrix} 6-12 \end{bmatrix} \begin{vmatrix} q_{1} \\ . \\ q_{i} \end{vmatrix} = \exp \begin{bmatrix} -a \begin{vmatrix} 0 & 0 & 0 & \beta_{1} \\ . & 0 & 0 & \beta_{1} \\ . & 1 & 0 & \beta_{i} \end{vmatrix} \cdot \exp \begin{bmatrix} -a \begin{vmatrix} 1 & 0 & 0 & \beta_{1} \\ . & 0 & 1 & 0 \\ 0 & 0 & 1 & \beta_{i} \end{vmatrix} \cdot \left[ \begin{pmatrix} \beta_{i} \\ . \\ \beta_{i} \end{bmatrix} \right]$$
$$q(i) = (I_{(i-1)} e^{-\beta i} \beta_{i})$$
$$+ \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \beta_{i} \\ . \\ \beta_{j} \end{bmatrix} \cdot R^{*} \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 1 & 1 & \beta_{i} \\ . & 0 & 0 & \beta_{j} \end{bmatrix} \cdot \exp \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ 0 & 0 & 1 & \beta_{j} \end{bmatrix} \cdot \exp \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ 0 & 0 & 1 & \beta_{j} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ 0 & 0 & 1 & \beta_{j} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ 0 & 0 & 1 & \beta_{j} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 0 & 0 & 1 & 1 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & \beta_{i} \\ . & \beta_{i} \end{bmatrix} \cdot \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \exp \begin{bmatrix} -a$$

+ 
$$(I_N R I_{(i-1)} e^{-\beta i} \beta_i)$$

Here .\* refers to element by element multiplication of the matrix coefficients rather than true matrix multiplication. The source profile, q(x), the optical transmission of the sample (I<sub>N</sub>) and the reflectivity (R) of the pyroelectric are all input to the equation. The equation can then solve for all  $\beta(i)$  using a simplex routine with the source profile as a first estimate of the optical profile. This works well for simple models but as the number of layers grows above 5 the simplex can not recover  $\beta(x)$  accurately as each  $\beta(i)$  has both a linear and an exponential dependence in equation 6-12. If one ignores the optical transmission term the recovered  $\beta(x)$  profile will follow q(x) as the  $\beta_i$  term dominates the expression and an incorrect result will be obtained. To simplify the problem one can assume the reflected light off the pyroelectric is minimal and the equation can be simplified to a form similar to that presented by Afromowitz et al [2].

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[6-13] q(i) = dx 
$$\sum_{i=0}^{N} \beta_i e^{-\sum_{j=0}^{i-1} \beta_j l_j}$$

The light transmission profile in the sample can be reconstructed from equation 6-14 and the optical profile then recovered from 6-15.

[6-14] 
$$T(x) = 1 - \frac{q(x_i)}{q(l)} (1 - T(l))$$

[6-15] 
$$\beta(x) = -\frac{1}{dx} \ln(\frac{T(x_i)}{T(i)})$$

Here q(l) is the integrated value of the source profile across the total sample thickness and q(x) is the source profile integrated from x=0 to x=x<sub>i</sub>. Similarly T(l) is the optical transmission of the sample as measured from the spectrophotometric measurement and T(x<sub>i</sub>) is the light transmission profile obtained from (6-14).

The errors introduced by the simplifying the thermal flux expression are illustrated in the  $\beta$  recovery of some theoretical profiles. The sample presented in Fig. 6-13 has 3 optical layers. The top is a 5  $\mu$ m clear non-absorbing layer, the second is a 50  $\mu$ m optically homogeneous layer with a  $\beta$  value which changes with wavelength of excitation and the

bottom 5  $\mu$ m layer is clear and non-absorbing. The laminate sits on a 9  $\mu$ m thick PVDF sensor. The sample geometry and the  $\beta$  values were input into equation 6-11 and the flux profile was calculated. The flux profile was then normalized are in our experiments to give an intensity profile with arbitrary units. The optical transmission of the sample T(l) was calculated from Beer's Law and equations 6-14 and 6-15 were used to reconstruct the optical profile  $\beta(x)$  of the sample.

For a  $\beta$  of 1.0x10<sup>4</sup> 60.65% of the light is transmitted through the sample in a single pass before striking the pyroelectric and being reflected back upwards. The corresponding source profile (Fig. 6-14a) is almost a box shape as heat is distributed uniformly in the sample. The dotted line represents heat deposited in the film after a single pass and no reflection off the pyroelectric surface. Note that the largest amount of error in simplification of the source profile occurs closest to the detector surface. The optical transmission profile recovered from equation 6-14 is almost linear (Fig. 6-14b) and the recovered  $\beta(x)$  profile has a magnitude that is slightly greater than the true optical profile. The dashed line is the true optical profile and the solid is the recovered profile. To account for the extra heat energy deposited in the sample from the light reflections off the detector the model assumes an increased local  $\beta$  value. As a result the optical profile is seen to slope upwards to the detector surface. The results are still qualitatively correct.

For a  $\beta$  value of 1.0x10<sup>5</sup> (Fig 6-15) the optical transmission through the film is 0.67%. Thus almost all the light is absorbed in the film and almost no light is reflected off the detector surface. The source profile (Fig. 6-15a) shows that almost no energy is deposited in the final 3  $\mu$ m of the absorbing region of the laminate. The optical transmission profile is an exponential curve (Fig. 6-15b) that resembles the source profile. The recovered optical profile is flat up to the final 10  $\mu$ m of the absorbing region where it "blows up" in values exponentially (Fig. 6-15c). The rapid rise in  $\beta$ 

suggests that the algorithm is sensitive to the relative errors in light deposition introduced during the derivation of the model. The absolute light level has been attenuated to less than 1% of the maximum, but by ignoring the small reflection contributions almost 30% of the energy deposited in that region is lost. If one recognizes this type of distortion can exist the algorithm will recover accurate profiles in the top 40  $\mu$ m of the sample.

For a  $\beta$  value of  $1 \times 10^6$  (Fig. 6-16) no light effectively reaches the back of the sample  $(T(i)=1.0\times 10^{-22})$ . The source profile in the film is a sharp absorbing region at the front surface (Fig. 6-16a). The transmission profile also drops off sharply at the front surface (Fig. 6-16b). This shows that almost no light passes through the first 5  $\mu$ m of the absorbing region. The recovered optical profile is able to obtain  $\beta(x)$  up to 43  $\mu$ m from the top surface due to the fact that the calculations are done in double precision real which have 4 bytes of computer resolution.

Results of the theoretical tests show that the recovered photothermal flux profiles can be converted to  $\beta$  profiles with a high degree of accuracy.

#### **Experiment and Results**

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A study to apply the inversion technique to real photothermal impulse responses was set up by measuring the photothermal impulse response of various optical polymer films and laminates and then recovering their optical profiles using the NNLS inversion routine. Optical profiles were constructed using colored Mylar films and Kodak Wratten Gel edge filters epoxied together with optical epoxy as done in chapter 2 of this thesis. Thicknesses of the laminates ranged from 30  $\mu$ m to 175  $\mu$ m. The photopyroelectric impulse response for each optical polymer was measured with about 1% noise and the response electrically deconvoluted to remove the dependency on filtering. Inversions were made seeding G[128,32] with 0.1% Gaussian noise, the thermal diffusivity was taken to be 1.0e-7m<sup>2</sup>/s [1] and the results presented are the results of 100 averages. The PVDF diffusivity is known to be 0.8x10<sup>-7</sup>m<sup>2</sup>/s. This was accounted for in the thermally continuous model by increasing the detector thickness to 10  $\mu$ m in the model so that the thermal transit time through the pyroelectric would be correct.

Single discrete sources located at the top of the sample are easily recovered using NNLS. Samples were constructed with a 2.5  $\mu$ m absorbing layer at the surface of the film and clear spacers of 32, 60 and 80  $\mu$ m lengths were inserted between the sample and pyroelectric. The geometry is illustrated in Fig. 6-17. The data were modeled with the conventional Green's Function and a model thickness of 100  $\mu$ m was always supplied. This allowed us to see if any thermal reflections were present in the sample and if the model attempted to fit the temperature profile with multiple sources. Results of the recovered profiles are presented in Fig. 6-18. NNLS inversions recovered the correct position of the discrete source to within the error of the bin spacing. For the sample with a 32  $\mu$ m clear spacer the model placed a single source 35  $\mu$ m from the detector. For the

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sample with a 60 µm clear spacer the model recovered the source position at 61 µm from the detector, and for the 80 µm clear spacer the model fit the source to be about 78 µm from the detector surface. The inversion of the sample with a source 80 µm from the detector recovered a second source at the top of the model space as illustrated in Fig. 6-18. Since the model is fit with 32 sources the spatial resolution is 3.125 µm per bin. Thus the small error in placing the sources correctly is due to the fact that the basis is not properly defined for the model. The time domain fits for these recovered sources are presented in Fig. 6-19. The source 32 µm away from the detector and the theoretical profiles have rising edges that match well but are off in their tails. This could be attributed to the fact that the inversion cannot accurately model a 2.5 µm source as a delta function so close to the pyroelectric without distorting the time profile. Work in chapter 2 showed that the frequency domain signals could resolve differences in absorption profiles with sub micron resolution. It is expected that the time domain signal can too. This interpretation is supported by the fact that the source 61 µm away from the detector will generate a time domain fit between theory and experiment that agrees within 1%. The 2.5 µm absorbing layer now resembles more of a delta function and a correctly placed source will accurately recover the profile. The small error in the rising portion of the response suggests that there is still a small error in the basis and the bins of the model do not exactly line up with the exact position of the source. The fit of the sample 80  $\mu$ m from the detector is not as good as the 60  $\mu$ m fit. It is noted that the error seems to be equally distributed over the entire impulse response record. Thus we cannot say that the fit is good at early times and not at late or visa versa. It is noted that the inversion of this impulse response recovered two sources, one at the 80 µm position and another at the top of the sample. This suggests that there may be a thermal reflection at one of the interfaces of the laminate that is effecting the impulse response. This illustrates the fact that when the recovered optical profile begins to deviate from the true optical profile there will be a corresponding difference in the fit between theory and

experimental impulse responses. The NNLS inversion will *not* recover source profile that exactly models the true source profile without obtaining a highly precise match between the experimental and theoretical temperature responses.

Continuous profiles were also qualitatively recovered with the NNLS inversion routine. Samples were fit by generating the Greens Function in equation 6-10 to account for the thermal reflections off the top surface. Inversions were seeded with 0.5% Gaussian noise and the results are the average of 100 inversions. Kodak Wratten edge filters give different continuous absorption profiles that are wavelength dependent and as a result provide a good measure of the inversion's ability to resolve differences in optical absorption coefficients. A 100 µm wratten gel was attached to the pyroelectric and the optical absorption profile was recovered. The source profile for a strongly absorbing sample is shown in Fig. 6-20. As the absorptivity of the sample decreases more light can penetrate the sample further (Fig.6-20a). The recovered optical profiles (Fig 6-20b) obtained using equation 6-15 show that the optical absorptivities can indeed be recovered. For the most strongly absorbing sample ( $B=2.0 \times 10^4 \text{ m}^{-1}$ ) the source profile is distributed in the first 32 µm of the sample. As a result the technique can only recover the optical profile 32  $\mu$ m into the sample. The  $\beta(x)$  profile is shown to be relatively uniform to the cut off point where it drops off due to a lack of signal presumably. The recovered source profile obtained at  $\beta = 1.7 \times 10^4$  extends further into the sample and the optical profile for  $\beta = 5.3 \times 10^3 \text{ m}^{-1}$  extends further yet as would be expected. It is noted that the recovered  $\beta$  values appear to be a factor of 2 to 3 times greater than the true values. An explanation eludes us at this point. Results for samples with a small light absorption coefficient are shown in Fig. 6-21. The photothermal signal is dominated by light striking the pyroelectric. Inversion results suggest that optical absorption coefficients of  $\beta=750 \text{ m}^{-1}$  were not detectable in the photothermal signal. Only the pyroelectric source was recovered. The signal from  $\beta$ =950 m<sup>-1</sup> shows up as a small

source at the top of the sample and the  $\beta$ =1.6x10<sup>3</sup> m<sup>-1</sup> is a larger source. It is of interest to note that once the light starts to reach the back of the sample and strike the pyroelectric the position of the recovered source profile corresponding to the pyroelectric seems to change. The fact that the optical profile corresponding to the polymer appears so small is strictly a function of the inability of the graphics to resolve the large thermal source of the pyroelectric and the small sources generated in a weakly absorbing sample. The time domain fits between theory and experiment for a strongly absorbing sample and a weakly absorbing sample are shown in Fig. 6-22. The fit in Fig 6-22a is for a sample with a  $\beta$ =950 m<sup>-1</sup> and fits only qualitatively. The fit for the a sample with a  $\beta$ =1.7x104 m<sup>-1</sup> in Fig. 6-22b also does not fit perfectly. It is noted that in this case improving the resolution of the inversion by a factor of 2 did help improve the fit. This suggests that the discrete binning of 32 sources does not accurately describe a continuous profile. Increasing the bin number increases the spatial resolution and thus improves the fit between theory and experiment. However the trade off in going from a 128x32 matrix to a 128x64 matrix is significantly increased computation time.

Multiple discrete sources proved to be difficult for the inversion routine. A two layer source as illustrated in Fig. 6-23 was constructed with a red absorbing layer on top and a green absorbing layer on the bottom. By tuning through the wavelengths of absorption we were hoping to be able to recover the relative source contributions at each wavelength. Results recovered the fact that there were two discrete sources present, but the inversion placed the sources at different positions at different wavelengths of excitation and the time domain impulse responses did not match at all. This suggests that the basis for this problem is difficult to choose properly using 32 sources. The inversion routine needs to account for the green layer, the red layer and the pyroelectric absorption as well as all thermal reflections off the front surface. Results are summarized in Fig. 6-24.

## References

- 1. J.F. Power, Appl. Spect., 45(8) 1240 (1991).
- 2. M. A. Afromowitz, P.S. Yeh, and S. Yee, J. Appl. Phys., 48(1) 209 (1977).



Fig. 6-1. A recorded electrical impulse response of a 9  $\mu$ m PVDF film and associated instrument filters used in these photothermal experiments. The response was generated using AM-PM spectrometry with a spectral bandwidth of 2,500 Hz (dt=0.2ms).



G(x-xo,t)

Fig. 6-2 The columns of a Greens Function matrix accounting for the spatial integration effects of 9 $\mu$ m PVDF. (dx=1.5 $\mu$ m, dt=0.2ms)



G(x-xo,t)

Fig. 6-3 The columns of the same Greens Function shown in Fig. 6-2 after convolution with the electrical impulse response shown in Fig. 6-1.



Fig. 6-4 Illustration of a plane source in a polymer film generating thermal waves. The incident component (i) travels directly towards the pyroelectric while a second component (ii) travels up to the air/sample interface where it is almost totally reflected back down towards the pyroelectric due to the poor thermal mismatch between the polymer and air.







Fig. 6-5. Two different model spaces to account for thermal reflections off the sample/air interface. (a) The sample is modeled twice as thick as it is measured. This will place incident thermal waves in the bottom half of the model space and the component of the thermal wave reflected off the air/sample interface will appear in the top half of the model space. (b) The sample is modeled using the theory of Power [1].



Fig. 6-6. An arbitrary sample (a) can be forward modeled if the optical profile is known in advance. In this case (b) the model bin sizes are adjusted to have the correct spacing and correct optical properties. In inverse modeling (c) no knowledge of the optical properties of the sample exist. The sample is divided into N layers and the "best" approximation of the correct optical profile is obtained from the photothermal signal.



Fig. 6-7 (a) The columns of H[128,32]. (dt=0.2ms dx=3.125  $\mu m$ )



Fig. 6-7 (b) The three columns of H corresponding to the 3 sources furthest away from the detector. Each of the columns has been normalized to its maximum value. In theory the model can resolve a source at 100  $\mu$ m from a source at 96.9  $\mu$ m.

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Fig. 6-8 A study to determine the resolving power of the photothermal model for a 2,500 Hz sweep and a 50  $\mu$ m thick sample. (dx=1.5  $\mu$ m dt=0.2 ms  $\alpha$ =1.0x10<sup>-7</sup>) In all cases the solid line is the contribution from the source closest to the detector, the dashed line is from the source 50  $\mu$ m away at the sample surface and the dotted line is the source to be resolved. (a) Dashed line is 48.5  $\mu$ m from the surface and is resolved by a maximum difference of 0.001.



Fig. 6-8 (b) Dashed line is 42  $\mu$ m from the surface and is resolved by a maximum difference of 0.017.

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Fig. 6-8 (c) Dashed line is 35  $\mu$ m from the surface and is resolved by a maximum difference of 0.047.



Fig. 6-9 Dc offset study. (a) A triangular source profile in a 50  $\mu$ m polymer sample. Trace 1 is recovered from the inversion if there is a 0.1% DC offset of on the recorded electrical impulse response. Trace 2 is recovered if there is a 0.5% DC offset added to the electrical impulse response and trace 3 is recovered for a 1% DC offset on the electrical impulse response.



Fig. 6-9 (b) Theoretical photopyroelectric h(t) responses for a triangular source in a 50  $\mu$ m thick sample. The fits of the recovered h(t) responses for the sources in (a) get worse as more DC offset is added to the electrical impulse response.



Fig. 6-10 (a) Systematic error in thickness study for a ramp source profile. The solid line is the true source profile measured to be 50  $\mu$ m thick. The recovered source profiles for estimated thicknesses of 48-52  $\mu$ m are shown on the graph.



Fig 6-10 (b) The impulse response for the recovered source profiles in part (a). The impulse response that corresponds to the true source profile is the solid line down the middle. Samples measured to be too thin have an impulse response that tails too high and samples measured to be too thick have an impulse response that tails off too low.



Fig. 6-11 (a) Systematic error in thickness study for a <u>triangular</u> source profile. The solid line is the true source profile measured to be 50  $\mu$ m thick. The recovered source profiles for estimated thicknesses of 48-52  $\mu$ m are shown on the graph.



h(t) arb. units

Fig 6-11 (b) The impulse response for the recovered source profiles in part (a). The impulse response that corresponds to the true source profile is the solid line down the middle. Samples measured to be too thin have an impulse response that tails too high and samples measured to be too thick have an impulse response that tails off too low.



Fig. 6-12 (a) Systematic error in thickness study for a <u>step function</u> source profile. The solid line is the true source profile measured to be 50  $\mu$ m thick. The recovered source profiles for estimated thicknesses of 48-52  $\mu$ m are shown on the graph.



h(t) arb. units

Fig 6-12 (b) The impulse response for the recovered source profiles in part (a). The impulse response that corresponds to the true source profile is the solid line down the middle. Samples measured to be too thin have an impulse response that tails too high and samples measured to be too thick have an impulse response that tails off too low.



Fig. 6-13 A theoretical sample used to test the recovery of the optical absorption profile,  $\beta(x)$ , from the thermal flux profile, q(x). The sample consists of a clear non-absorbing top layer of 5 $\mu$ m, a 50  $\mu$ m optically homogeneous absorbing layer, a second non-absorbing layer of 5 $\mu$ m and a pyroelectric sensor.



Fig. 6-14 (a). The thermal source profile generated in the sample in Fig. 6-13 with a 8 value of  $1.0\times10^4$ . The dashed line represents thermal energy deposited in the sample after one light pass through the sample and the solid line represents the thermal energy deposited in the sample after the light has been reflected off the pyroelectric surface (R=0.9). The two traces have been normalized to their maximum value.



Fig 6-14 (b). The optical transmission profile (I/I(0)) recovered from the thermal source profile in (a) using equation 6-14.



Fig 6-14 (c). The recovered optical absorption profile,  $\beta(x)$ , from the optical transmission profile in (b). The dashed line is the true optical profile and the solid is the recovered profile.



source intensity arb. units

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Fig 6-15 (a). The thermal source profile generated in the sample in Fig. 6-13 with a B value of  $1.0 \times 10^{5}$ .



Fig 6-15 (b). The optical transmission profile (I/I(0)) recovered from the thermal source profile in (a) using equation 6-14.



Fig 6-15 (c). The recovered optical absorption profile, B(x), from the optical transmission profile in (b). The dashed line is the true optical profile and the solid is the recovered profile.



source intensity arb. units

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Fig 6-16 (a). The thermal source profile generated in the sample in Fig. 6-13 with a B value of  $1.0 \times 10^{6}$ .



Fig 6-16 (b). The optical transmission profile (I/I(0)) recovered from the thermal source profile in (a) using equation 6-14.



optical absorptivity (m-1)

Fig 6-16 (c). The recovered optical absorption profile, B(x), from the optical transmission profile in (b). The inversion routine can only recover the optical profile of the first 42  $\mu$ m of the absorbing region before a divide by zero error is obtained due to lack of light penetration.



Fig. 6-17 A schematic of the geometry used to create laminates with a single discrete source. The nonabsorbing spacer layer thickness is adjusted in each sample. Samples were prepared with x=31  $\mu$ m, x= 60  $\mu$ m and x= 80  $\mu$ m ( $\pm$  1  $\mu$ m).



Fig. 6-18 The recovered source positions for the three samples described in Fig. 6-17. The pyroelectric is located at  $x=100 \ \mu\text{m}$  and the top of the model space is at  $x=0 \ \mu\text{m}$ . In each case the model recovered the position of the source relative to the pyroelectric detector.



Fig. 6-19 (a) Time domain filts between theory (dashed) and experiment (solid) for a source 31  $\mu$ m away from the pyroelectric detector.

h(t) arb. units


Fig. 6-19 (b) Time domain filts between theory (dashed) and experiment (solid) for a source 60  $\mu$ m away from the pyroelectric detector.

h(t) arb. units



Fig. 6-19 (C) Time domain filts between theory (dashed) and experiment (solid) for a source 80  $\mu$ m away from the pyroelectric detector.







(b)

Fig. 6-20 (a) Recovered source profiles for a wratten gel edge filter excited at wavelengths where the optical absorption is measured to be (1)  $2.1\times10^4$  m<sup>-1</sup> (solid) (2)  $1.7\times10^4$  m<sup>-1</sup> (dotted) and (3)  $5.3\times10^3$  m<sup>-1</sup> (dashed).

(b) The calculated optical absorption profiles for the corresponding source profiles in (a).



intensity (arb. units)

Fig. 6-21 Recovered source profiles for a wratten gel edge filter excited at wavelengths where the optical absorption is measured to be 750 m<sup>-1</sup> (dotted) 950 m<sup>-1</sup> (dashed) and  $1.6 \times 10^3$  m<sup>-1</sup> (solid).



(a)



(b)

Fig. 6-22 (a) Time domain fit between theory (solid) and experiment (dashed) for the wratten gel impulse response recorded at a wavelength where the optical absorptivity is 950 m<sup>-1</sup>.

(b) Time domain fit between experiment (solid) and theory with 32 point spatial resolution (dashed) and 64 point spatial resolution (dotted). The optical absorptivity is  $1.7 \times 10^4$  m<sup>-1</sup>.



Fig. 6-23 The experimental geometry used to generate impulse responses from a multiple discrete source sample.



Fig. 6-24 (a) A recovered source profile from the multilayer sample. The inversion recovers the fact that there are two sources present but the sources are not in the correct position. The exact location of the recovered sources shifted depending on the wavelength of excitation.

(b) The time domain fit between between experiment (dashed) and theory (solid) do not match well.

Chapter 7:

Photothermal imaging of dehydrochlorination in polyvinyl chloride films.

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## Introduction:

Accelerated weathering of polymer films to determine long term resistance to degradation has been studied in almost every major polymer [1]. Photodegradation of PVC is one of the most widely studied degradation cycles reported in the literature. The inexpensive production of PVC and subsequent widespread use make it necessary to develop stabilizers, plasticizers, and radical scavengers so that products developed will be stable over time. Long term weathering studies require that samples be periodically studied using non-destructive techniques to record trends in degradation. Conventional spectroscopic tools can recover surface or bulk changes but provide little information on how the degradation spreads with time. Accelerated weathering reduces the amount of time required to weather a sample making destructive analysis less costly. However, many agree that polymers do not degrade by the same mechanisms naturally and in weatherometers.

Presently, a wide range of spectroscopic tools are being used to evaluate the degradation profiles. ATR and IR studies [2] have been used to examine surface verse bulk optical properties of polymer films; however, the techniques are not capable of recovering accurate depth profiles of functional groups without destroying the sample. Initial profiles of polyenes and carbonyls have been obtained by microtoming sequential layers from the surface of the polymer and studying their spectra using conventional optical techniques[3-13]. Typically microtomes of the order of 15-30  $\mu$ m thickness have been required to get measurable light absorption. Subsequently, there has been fairly poor depth profiling information in thin polymer films.

A Raman microscope has been used to profile polyene sequences in microtomed PVC samples along the degradation axis [14]. The Raman microscope shifted a 100  $\mu$ m laser beam 10  $\mu$ m at a time to obtain a box car like average of the optical profile. Raman techniques require relatively high laser powers that tend to damage the polymer while the

measurement is being made. As a result one can not be totally certain that the degradation profile that has been recorded was not enhanced by the degradation inflicted by the laser.

Optical light microscopy of microtomed slices provides a technique for examining broadband absorption by polymer films. However, thin  $(4\mu m)$  slices do not absorb sufficiently for single wavelength studies and thicker cross sections suffer from confocal distortions at the image plane. In addition it is extremely difficult to microtome large samples and as such, optical micrographs are limited to examining small regions of the polymer that have been cut out and then microtomed. Fluorescent images of conjugated sequences are not quantitative, require a highly fluorescing medium and are prone to distortion due to scattering.

It appears that there is a strong need for a simple, reliable, non-destructive imaging technique to profile optical features in polymer films. Along with applications to degradation studies the technique would be applicable to studies of molecular diffusion in polymers and doping of polymer films. As discussed in the introduction of the thesis, photothermal analysis of polymers has been expanding rapidly with applications in the study of thermal anisotropy of polymers [15], adhesion [16], fiber orientation in reinforced polymer mats [17], temperature dependent thermal diffusivity studies [18], and characterization of thin films generated by spin coating techniques [19].

Present photoacoustic studies of optical polymers have only been able to differentiate between surface and bulk polymer properties of polymer films and have not provided any depth profiling information [20-22]. However, recent advances in the understanding of the photothermal signals has lead to the ability to recover the depth dependent optical and thermal properties of a polymer film with a high degree of accuracy in a nondestructive manner.

Power was the first to show that optical profiles can be obtained quantitatively in polymer samples [23]. Power [24] then Prystay [chapter 2] quantitatively recovered optical profiles from colored Mylar laminates and Kodak wratten gel edge filters using time domain and frequency domain photopyroelectric techniques. In this work the photodegradation profiles generated by the dehydrochlorination of PVC will be imaged nondestructively by photopyroelectric spectroscopy. Photothermal tomograms of the degraded samples provide 3-D images of light absorbing features in the polymer films. Depth dependent thermal flux profiles and optical absorption profiles (ß) recovered using the inversion techniques reported in chapter 5 and 6 then provide high resolution profiles of the degradation patterns in PVC.

It is the intention of this chapter to introduce photothermal spectroscopy as a nondestructive tool for evaluating the weathering and degradation of polymer films, in specific, we have chosen PVC. High light fluxes were chosen to provide samples for analysis quickly, cleanly and in a fairly reproducible manner. The exact degradation profiles may not be reproducible each time but the trends are. It is not expected that the work will add any new information to the already extensive volume of literature on PVC degradation but the results obtained by photothermal analysis can be compared to the work done previously thereby establishing the technique as a reliable characterization tool for polymer science.

To evaluate the capabilities of photothermal methods we needed samples with a depth dependent 8 and  $\alpha$  a means of identifying where the photothermal signal is dominated by the sample's optical profile and where changes in the thermal properties of the sample exist. The inversion routine developed in chapter 5 can be applied only to samples that are thermally homogeneous. We also needed some means of verifying the results of the

inversion and some precedent for the results we obtain. PVC is a well suited candidate for such a study as dehydrochlorination (non-oxidative degradation) creates conjugated double bond sequences that are known to change profile depending on degradation conditions. Secondly, they absorb light in the near UV and visible wavelengths allowing inspection with light sources available in our lab. The double bond structures grow in a dynamic fashion giving absorption profiles that are wavelength dependent. In addition, the results can be checked by light microscopy and fluorescence microscopy, scanning transmission electron microscopy can be used to map chlorine, and profiles can be compared to literature values.

Unlike previous work on the photodegradation of PVC, this work examines the degradation of solid phase PVC films (10-90  $\mu$ m) under high optical flux. Here photointiated degradation generates significant heating in the film creating a large temperature gradient between the point where degradation is initiated in the center of film and the cool outside edge of the film. As a result thermal degradation mechanisms compete with the photodegradation process at some points while other regions are degraded solely by the photo related processes. This creates a number of different chemical structures at the molecular level which gives the PVC films interesting optical properties including a strong birefringence. The photodegradation geometry is illustrated in Fig. 7-1.

In this study we are not concerned about the absolute light flux levels, the specific spectral distribution of the light source, the uniformity of the degradation or the exact mechanism of degradation in the films. There are too many variables that need to be controlled: temperature, oxygen pressure, nitrogen pressure, HCl content in the films, mechanism of PVC polymerization and effects of molecular weight distributions to name a few. The work is designed to show application of photothermal techniques and to show

where photothermal imaging can be used to non-destructively characterize polymeric materials.

### **Materials and Methods**

High molecular weight PVC (MW>100,000) was obtained from Aldrich chemicals. Stabilizers and impurities were removed by dissolving the PVC in dry THF and precipitating it from methanol three times. Clear colorless PVC films were prepared by casting 1-4% PVC in tetrahydrofuran solutions in two inch diameter casting rings. The films were covered and dried at room temperature and pressure for 3 days, released from the glass and oven dried at 50 °C under house vacuum for 30 days. Films were 10  $\mu$ m to 90  $\mu$ m (±1  $\mu$ m) thick as measured with a micrometer.

To photodegrade the PVC the dried films were suspended in air two feet from a Xenon Arc Lamp (Oriel Corp.) operated at 700 Watts. A water cell with quartz windows was placed between the lamp and sample to filter out infra red (IR) radiation. The source was directed onto the sample and the central region of uniform thickness was illuminated. However, because the source was not collimated there was a bright spot at the center of the beam where the image of the arc was projected. This tended to coincide with the point where degradation was initiated.

The onset of degradation, as measured by appearance of polyene bands in the visible, occurred within 5-8 minutes and the sample would be completely degraded (black) within another 15 seconds. The rapid degradation under high intensity light had the effect of localizing the formation of polyenes to a small area for imaging.

Photothermal imaging is described in detail in the instrumentation section. Metalization of the films was achieved by magnetic sputtering techniques at the Dept. of Physics at McGill University. Light micrographs of the spot degradation were obtained on a Zeiss light microscope. Cross sections were prepared by setting the sample in an Epon 812 resin matrix (J.B. EM Montreal, Canada) at 60  $^{\circ}$ C and cut to 4  $\mu$ m with a Reichert Ultracut (Austria) microtome. The 100  $\mu$ m cross sections were set in the microtome and cut with a sharp razor blade. The distribution of chlorine in the films was determined with a Jeol JSM-840A scanning electron microscope (Peabody MA) using a 5 kV accelerating voltage and a Tracor Northern energy dispersive x-ray detector. The x-rays were determined to penetrate the film about 1  $\mu$ m as determined by a generic software algorithm. The pyroelectric sensor is 9  $\mu$ m PVDF (Atochem, King of Prussia, PA). The samples were attached using Epo Tek 302-3 optical epoxy (Epoxy Technology Inc., Billerica Ma).

Photothermal images of PVC contain information about the optical and thermal properties of the polymer film. To recover the thermal components separately from the optical component the films were first imaged as degraded (the photothermal image), then top surface was metalized with a 100-200 nm coating of aluminum and reimaged (the thermal image). Metal coatings were done using DC magnetron sputtering (Edwards Auto 306 cryo). Conditions of the coatings were as follows: rate 100Å/88s, power 100 W (402 V), Ar pressure 9mT, background pressure  $3.4 \times 10^{-6}$ T, the target was aluminum (99.9999%) from Kurt J. Lesker Co.. Samples were cleaned with methanol and were dust free. The metal overcoat confined optical absorption to a infitesimally small layer at the surface, acting as a plane heat source which generated thermal waves that travelled through the entire sample before reaching the detector. Samples over 40 µm thick had a thin (1µm) layer of black ink applied to the surface of the aluminum to absorb the

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incident radiation. The aluminum surface was too reflective and not enough energy was absorbed by the metal overcoat to obtain a sufficient photothermal response for the thickest samples.

#### Instrumentation and image processing

The photopyroelectric effect spectrometer used to obtain the images is outlined in Fig. 7-2. A Coherent laser (Innova 70) was used in single line mode for excitation at 458 nm and the output from a Coherent CR-599 dye laser was used for excitation at 620nm. The excitation beam was modulated by an Isomet 1201E acousto optic modulator. The first order was collimated and passed through a 150 µm pin hole before striking the sample. The beam intensity striking the sample was kept below 3 mW to prevent optical damage to the sample. Replicate images were made to ensure that the polymer was not being degraded as it was imaged. Lightly degraded polymers were found to not be effected by the laser; however, the darkest films (black) were lightly etched at the surface. The photopyroelectric spectrometer uses AM-PM wideband spectrometry and the impulse response was recovered using correlation and spectral analysis techniques [25]. To speed the imaging process, the drive and response waveforms are passed from the master processor (an XT) to the slave #2 (a 80486) through the parallel ports. The 486 then performs the spectral calculations while the XT initiates data acquisition at the next image point. The images are obtained on a point by point line scan, each point separated by 100 µm. At each position a 256 point impulse response is recovered. The entire record is 50x50x256 points of single precision real data requiring ca. 2 Megabytes of memory. To accommodate a large number of images the data were transferred to magnetic tape and recalled individually to disk when needed. Individual photothermal

images are obtained by taking a single time slice of the 256 point impulse response for the entire 50x50 point image.

Single wavelength spectrophotometric images were obtained by constructing a double beam spectrometer. The laser wavelength of interest is directed onto the sample and a Hamamatsu photodiode (s1227) recorded the light levels transmitted by the sample. The incident light level was taken as the light reaching the photodiode after passing through the clear colorless region of the PVC film. Prior to being collimated at 150  $\mu$ m the incident laser beam was split and 20% of the light was directed onto a second identical reference diode to record fluctuations and drifts in the laser. The same translation apparatus and optical lens system was used to record the photothermal image, thermal image and optical image. Schematics are provided in the appendix of the thesis.

# Theory and background

It is well known that photodegradation of PVC is initiated by the absorption of light by impurities, trapped solvents, and defects in the polymer backbone. In the absence of oxygen, dehydrochlorination creates polyene sequences that absorb light and release HCl, which in turn accelerates the degradation process [26].

non-oxidative degradation (dehydrochlorination)

-(CH2-CHCl)<sub>n</sub>- 
$$\frac{\lambda_{\upsilon}}{\dots}$$
 -(CH=CH)<sub>m</sub>- + mHCl where m=1 to 16

In the presence of oxygen, oxidative processes cleave the double bonds resulting in photobleaching of the darkened PVC. Oxygen is incorporated into the backbone of the polymer as a radical, peroxide or ketone as a chlorine or hydrogen is abstracted. The hydrocarbon backbone is then cleaved according to Norrish type I (cleavage at the alpha carbon) and type II (cleavage at the gamma carbon) reactions.

о І \_с\_с,\_с,\_с,\_н

oxidative degradation (photobleaching)

Norrish type l

$$-C \xrightarrow{h\nu} -C + C$$

Norrish type ll

$$\begin{array}{c} O \\ CH_{3}CCH_{3}CH_{3}CH_{3}CH_{3} \xrightarrow{h\nu} \pi \xrightarrow{} T \end{array} CH_{3}CCH_{3} + CH_{3} \xrightarrow{} CH_{3}CCH_{3} + CH_{3} \xrightarrow{} CH_{3}CCH_{3} + CH_{3} \xrightarrow{} CH_{3}CCH_{3} \xrightarrow{$$



A scheme showing growth of polyene bands and subsequent photobleaching by Norrish reactions.

Under intense light, such as conditions of these experiments, we have found that for samples suspended in air, one degradation is initiated in the sample it accelerates locally before it has a chance to spread radially and axially through the polymer film. The result is a local spot degradation. The evolution of the spot is illustrated in Fig. 7-3. The first two films were measured to be 45  $\mu$ m and the last film, the darkest, was measured to be 72  $\mu$ m before degradation. The transmission light microscope pictures show the degradation of different films with the spot just starting to form to the point where the film is very strongly degraded. The earliest degradation is light yellow to the eye (7-3a). The degradation then becomes dark yellow (7-3b) and finally black (7-3c). The pictures clearly show the position of the degradation but provides no depth profiling information.

Optical micrographs of the strongly degraded film are shown in Figure 7-4. The broadband white light image (Fig. 7-4a) shows a uniformly dark profile with sharp edges between the degraded and non-degraded region of the film. The image recorded under blue light filter (Fig. 7-4b) filters out the optical wave lengths in the UV and low wavelengths of the visible providing a image of only the longest conjugated double bonds. The micrograph clearly shows a darker inner ring containing elevated concentrations of the longest conjugated double bonds and a outer ring where there is less degradation (although the photocopy of the micrograph may not be as clear). The entire spot is about 4 mm in diameter and the circular nature cannot be attributed to the shape of the arc from the lamp. Rather, the degradation starts locally and spreads radially. Under slightly higher magnification and increased aperturing of the light so the camera is not flooded by the transmitted light outside of the degradation region, one can see that the polymer is sintering (Fig. 7-4c). Small holes in the film are about 2-10 µm in diameter and probably are local spherulites and crystallites which scatter light. The holes are not thought to be the result of local cleavage of the chains due to photobleaching or oxidative processes (Norrish reactions) as they do not show up in either the spectrophotometric images or the photothermal images.

Under polarized light (Fig. 7-4d) the strongly degraded PVC films show strong birefringence over the entire degraded region and beyond, into the undegraded region of the polymer. The Maltese cross structure indicates that order or strain in the degraded region exists. The UV visible and IR dichroism and birefringence of stretched PVC samples containing polyene structures have been reported in the past [27-30]. Optical measurements of chemically deydrohalogenated PVC films have attributed the optical polarization to stress in the polymer chains. We propose that as the polymer degrades it heats, eventually the temperature rises above the glass transition temperature (Tg) and is cooled in air when the light is blocked. As the polymer quickly cools down below the Tg, the chains fold together and strain is placed on molecules.

Heating of the polymer above its Tg was observed for the strongly degraded polymer films. The region of heating was visible by eye as the heated region and nonheated region had a sharp boundary edge which refracted light. The region of the film that heated above the Tg spread outside of the colored region of the polymer but remained clear and colorless.

In Fig. 3 sample (a) showed no birefringence, sample (b) showed mild birefringence and sample (c) showed strong birefringence.

Scanning electron microscopy (SEM) was used to measure relative chlorine levels between the degraded and undegraded regions of the samples. Scans across a 4  $\mu$ m cross section in Fig. 7-5 show that the chlorine levels do not change significantly across the cross section of the film. The slight decrease in chlorine levels at the edge of the films can be attributed to edge effects in the sample. The same pattern of chlorine levels was seen in all three samples regardless of the degradation levels. The reason for the insensitivity in the lightly degraded sample is probably due to the fact that only 0.1% of

the chlorine needs to be lost before degradation is visible to the eye. Thus small changes in chlorine levels create large optical variations in the films. It is expected that the strongly degraded film lost HCl uniformly across the depth of the film due to thermal heating of the entire spot region (26,p407).

The photothermal impulse response trends as a function of increasing light absorption are shown in Figure 7-6. The earliest and fastest response occurs in regions where the polymer does not absorb the incident light and all thermal energy is due to absorption by the detector at the back of the polymer. As the region of degradation is translated into the excitation beam the lightly degraded regions of the polymer absorb the light and the photothermal impulse response becomes delayed. The more strongly the light is absorbed the less light reaches the detector and the sample response becomes well separated from the detector response. At early times, near t=0, the photothermal response will always be dominated by the detector response. The thermal signal from the region of the sample closest to the detector then shows up in the response followed by thermal waves generated at the top of the sample. By selecting a specific time in the impulse response and plotting the value of h(t) as a function of position for the entire photothermal image a 50x50 plot of the image at that time is created. By plotting a image for each time delay a photothermal "movie" is created showing a real time transfer of heat from the polymer to the detector. Interesting features in the photothermal movie can then be identified by their x-y position. The corresponding impulse response can be inverted using the techniques of chapters 5 and 6 to recover the thermal flux and optical absorption profiles at the wavelength of excitation.

The difference between the lightly, moderately, and strongly degraded PVC films is not the concentration of polyene sequences only, but the length and position of the polyene sequences. It is accepted that short wavelength irradiation generates short (n=3-4) polyene sequences and long wavelength radiation generates longer polyene sequences (n=4-16). The longest conjugated sequences have an acidic character and can bind Cl-forming a charge transfer complex [31].

This type of ionic complex has the properties of an onium salt and contributes to the intensification of color in the strongly degraded samples. These charge transfer complexes have significant absorption of light and do not necessarily decay in a non-radiative process. Subsequently, quantitative photothermal analysis of these samples would require analysis of possible photochemical side reactions, possible formation of metastable intermediates and possible delays in the conversion of light to heat within the sample. Subsequently, quantitative analysis will not be undertaken in this thesis.

In the absence of oxygen and oxygen containing impurities these conjugated sequences grow in length as long as light or heat is directed onto the sample. However, in region of the sample with trace oxygen the oxidative process will cleave the polyenes reducing their absorptivity at long wavelengths whenever possible. Thus the formation of a specific optical profile is a dynamic process that depends on the light, heat, oxygen and impurities in the film. Through a 3-D mapping of the heat flux profile one can estimate where the degradation started and where it spread. This would have application in engineering studies or manufacturing of plastic parts. Small components could be studied with the appropriate photothermal technique to determine if degradation started at the outside edge, say due to friction or rubbing generating heat in the sample, or if it started in the interior due to stress or optical degradation.

By imaging the degradation at different wavelengths one can map the distribution of specific polyene sequences. Only the longest polyene sequences absorb at the long wavelengths while both short and long sequences will absorb at lower wavelengths. We have imaged the PVC at 620nm and 458 nm to image polyene bands of at least 10 conjugated units and polyene bands of at least 6 conjugated units [26, p415]. UV-visible spectra of bulk PVC foils showing the position of maximum absorption for each length of polyenes is presented in Fig. 7-7.

All the spectrophotometric, photothermal, and thermal images are plotted on a x,y,z scale as illustrated in Figure 7-8. The x-axis and y-axis are always plotted in millimeter units and the z-axis is the intensity of the signal. For the spectrophotometric images the intensity axis is either a linear plot of light transmission  $(I/I_0)$  versus position or the log of transmission intensity, log $(I/I_0)$ , versus position. The appropriate scales are provided in the captions. The photothermal impulse response and the thermal impulse response plots the intensity of the normalized h(t) versus position. The photothermal movies are presented in two views. View #1 is from the side of the sample showing the photothermal feature growing up and down. View #2 is from the top of polymer showing optical and thermal features that appear in the central core of the image. The data is presented in this manner so that up to 8 images can be presented on a single page without overcrowding.

#### **Results and discussion**

photothermal imaging of lightly degraded PVC films

A single wavelength spectrophotometric image of the lightly degraded spot photographed in Fig. 7-3a is illustrated in Fig. 7-9. The center of the 620 nm image is narrower than the 458nm image and the optical absorption is less for the 620 nm image. This suggests that there are fewer double bonds with 10 conjugations than 6 conjugations in the sample and that they are concentrated primarily in the center of the spot.

A photothermal movie of the same lightly degraded PVC sample is synopsed in Figures 7-10 and 7-11. Two views of the photothermal images are provided for clarity. The 620 nm photothermal image (Fig. 7-10) is interpreted as follows. The image recovered after t=0.22 ms past excitation is equivalent to the optical image as the thermal response is only due to light reaching the detector. All that is seen is a bump in the baseline that is related to the amount of light absorbed by the sample. The thermal image then begins to grow in as heat generated in the sample closest to the detector diffuses to the detector. At t=0.8 ms past excitation the image shows a uniform ring of heat flux suggesting that the degradation spreads uniformly in a radial direction. The thermal image then grows to a maximum amplitude which indicates the largest thermal source contributions are reaching the detector (t=2.19 ms). (ie heat generated in the most degraded region) The photothermal image at this point still shows that the degradation is strongest in the center and spreads radially through the film. The photothermal movie then simply decays into the baseline of the signal as the thermal response dies off. As the image decays it does not distort and does not change shape. This is indicative of a sample with a nearly uniform optical profile that is also thermally continuous. In other words, the mild degradation does not significantly change the thermal properties of the PVC. This is in agreement with the observed fact that only 0.1% of the PVC needs to be deydrohalogenated before polyene bands can be seen in the visible wavelengths [26,p407].

The photothermal movie at 458nm, Fig. 7-11, provides approximately the same information as the 620 nm movie. The image recovered at t=0.2 ms past excitation corresponds to the optical absorption image and the thermal feature then grows to a maximum at t=2.2 ms. The signal again decays into the baseline. Unlike the 620 nm images the 458 nm image suggests that the most central region of the degraded PVC has a non-uniform optical absorption profile. This is seen as a slight dip in the center of the image at t=2.2 ms to t=6.6 ms past excitation. In addition the optical image is slightly wider for the lower wavelength images. This gives evidence that the longest polyene sequences are confined to the more central region of the degradation spot and the smaller polyene bands grow out past.

The thermal images of this sample in Fig. 7-12 shows virtually no spatial dependence in the signal confirming a thermally homogeneous sample, to a good approximation. The small thermal features in the back of the images are attributed to local delamination at the PVC/detector interface. The same features can be seen in the photothermal images.

Inversion of the photothermal impulse response for the PVC samples was done using the NNLS inversion routine of chapter 5. The recovered heat flux profiles are the result of 100 averages, seeding G with 0.5% gaussian noise each time. Individual impulse responses were used as recorded with no filtering or smoothing before the inversion. Photopyroelectric spectroscopy was used to record the impulse responses so that the techniques of chapter 6, including integration of the thermal response and convolution of the electrical transfer function are included in inversion of the signal. Each response was

inverted twice. First is was assumed that the sample was twice as thick as physically measured and inverted against the thermally continuous Green's Function. A second inversion accounted for thermal reflections off the front sample/air interface. Both inversions yielded the same approximate optical profile. The inversions which included the front surface reflections are presented here as they give better spatial depth resolution of the heat flux profile.

The inversion of the photothermal impulse for the lightly degraded PVC sample is presented in Figures 7-13 to 7-15. The exact region of inversion is outlined in 7-13a showing a photograph of a 100  $\mu$ m cross section cut from the sample.

The trends in inversion of the images at 620 nm (Fig. 7-13b) suggests that the polyene bands start at the surface of the PVC sample and spread inward to the center of the film where they grow to their maximum. The optical absorption at the surface simultaneously begins to drop as the degradation spreads. This is consistent with the proposed mechanism of photolytic processes initiating dehydrochlorination followed by rapid cleavage of the double bonds (photobleaching) in the presence of oxygen. The results suggest that the polyene sequences grow to some critical concentration before they begin to be cleaved by Norrish processes. This implies that oxygen permeates the sample about 15  $\mu$ m from the front surface inhibiting the formation of long conjugated sequences. Although the PVC films are initially transparent to the radiation the polyene bands seem to grow in from the side of the film facing the source (Fig. 7-13a).

The quality of fit between the theory and experimental traces give a good estimation of the accuracy of the inversion procedure. Three source profiles corresponding to points (a), (b) and (c) in the photograph are shown as point (a) (b) and (c) on the photothermal image (Fig. 7-13c). The inverted profiles corresponding to these exact positions are plotted in Fig. 7-13d. In the regions of weak photodegradation, the response recovered is

primarily due to light striking the PVDF. In regions of higher degradation there are two distinct sources attributed to the polyenes in the PVC and the surface of the pyroelectric. The time domain fits corresponding to these inversions are given in Figs. 7-13(d-f). The traces agree fit quite well. The difference in the fits of the impulse response for the weakly degraded region (Fig. 7-13d) at early times is attributed to the randomization broadening the Green's Function matrix coefficients and would need more averages to accuately resolve. Conditions for the inversion are H[128,32] is seeded with 0.1% full scale noise and N=200 averages.

The optical absorption coefficients were recovered from the photothermal q(x) profiles using equations 6-14 and 6-15. The q(x) record truncated at the position where the pyroelectric signal was observed and the optical transmission reading for each point was obtained from the spectrophotometric image. The results in Fig. 7-14 clearly show the optical profile shifting from the front surface and low  $\beta$  values towards the central channel of the film and much higher  $\beta$  values.

Inversion of a photothermal impulse responses recorded at 458 nm for point (c) in the photograph of the lightly degraded sample is shown in Fig 7-15. The thermal flux profiles at 458 nm showed the same trends as the 620 nm inversions with the degradation starting at the surface and spreading inwards. The width of the thermal flux profile is wider for the 458 nm inversion indicating that the shorter polyene sequences are more widely distributed in the film and the longer sequences are more confined to the central channel. The time domain theory matches the experiment well at early times and diverges at long times. This suggests that the region of largest error in the signal will come from the top of the sample furthest from the detector surface.

Microscopic inspection of cross sections were not conclusive in their results. Single wavelength studies with fluorescent imaging techniques were dominated by scattering at the edge of the films and broadband light images could not help identify specific polyene sequences. The photographs did show the degradation starting at one edge and spreading to the center of the film as depicted in Figure 7-13a. However the black and white photograph does not show the photobleaching effect at the front surface and is unable to distinguish between polyene sequences of different lengths. In addition the sharp dark lines due to refraction of the light at the sample edges or light scattering at the PVC-EPON interfaces may be masking photobleaching close to the surface.

#### photothermal imaging of moderately degraded PVC films

A photothermal study of a slightly more degraded polymer (Fig. 7-3b) is presented in Figs 7-16 to 7-21. The single wavelength spectrometric image (Fig. 7-16) shows the PVC films absorbs significantly more light at 458 nm than 620 nm although the spot diameter is about the same size.

The 620 photothermal movie is synopsed in Fig. 7-17 with 7 images. The early time image (t=0.96 ms after excitation) closely resembles the optical image. The photothermal image then develops in an annular fashion as the thermal waves begin to reach the detector. The growing ring has sharp edges indicative of a large thermal flux gradient probably set up by a large change in the spatial optical absorption within the PVC film. At t= 9.84 ms after excitation the image flattens off due to photothermal saturation. The photothermal image cannot resolve any increased absorption in the sample. The image then drops off into the baseline of the image. The 620 photothermal image at t=14.76 ms and t=24.6 ms shows that as the image decays there is a small

inhomogeneity in the most degraded region of the sample. From the single wavelength optical image of the film it is not conclusive if there are optical variations in the sample. The pure thermal contrast image of the sample shown in Fig. 7-19 shows a very slight dip at long times accounting for a small thermal variation near the top of the film in the film.

The 458 nm image is presented in two views in Fig. 7-18. Again the early time image (t=0.96 ms after excitation) is similar to the optical absorption image the sample. The 620 and 458 nm early image shows that there is significantly more light absorption in the sample at 458 nm than at 620 nm. This is indicative of a larger amount of polyene sequences with approximately 6 conjugations than with 10 conjugations. The physical width of the base of the photothermal features are the same at both wavelengths indicating that the degradation spread radially to a maximum radius and then degradation intensified locally within that region. This is further supported by the fact that the peaks of the photothermal signals are narrower at 620 nm suggesting that the longer sequences are more concentrated in the center of the photodegraded spot. The 458 nm photothermal movie peaks later at t=14.76 ms after excitation with a flat top signifying either uniform optical absorption in the center of the film or probable photothermal saturation which is unable to distinguish any increased optical absorption. The decay of the photothermal image shows very little spatial variation in agreement with the 620 nm images.

Two points of interest were located in the photothermal movie and inverted to recover the thermal flux profile (Fig. 7-20). Point 1 is along the rising edge of the PVC spot degradation and point 2 is on the plateau of the image in a region of photothermal saturation or optical homogeneity.

Inversions were done on impulse responses recorded at 620 nm, H[128,32] was seeded with 0.1% noise and N=200 averages. The recovered source profiles suggest that the longest polyene sequences are still confined to the central channel and are well separated from either the front or rear surface of the film. However, as can be seen in the time domain fits of Fig. 7-21, the sources do not generate accurate impulse responses when placed into the forward model. It is unclear where the error lies precisely as the fits appear to equally poor over the entire impulse time record. This appears to be a feature of the inversion procedure which is very sensitive to the choice of a correct basis set. As noted in chapter 6, when the recovered thermal flux profile is inaccurate the entire time record will not match. An explanation for the poor fit could be that the degradation of the PVC has altered the thermal properties of the PVC film and the diffusivity is no longer constant with depth. As a result the basis set is poorly conditioned and the recovered result is simply the best projection onto the assumed basis. The change in thermal properties certainly varies more in the regions of strongest degradation. This would probably occur at the sufface where oxidative process cause rapid scission of the polymer chains.

### photothermal imaging of strongly degraded PVC films

A photothermal study of a highly PVC film that is black in color (see Fig.7-3c and Fig. 7-4) is presented in Figures 7-22 to 7-27. The monochromatic spectrophotometric image at 620 nm in Fig. 7-22 shows a distinctly higher polyene concentration in the center of the degradation spot and less degradation around the perimeter. This image is very similar to the photograph obtained with white light under a blue filter in Fig. 7-4b. The 458 nm spectrophotometric image is strongly absorbing over the entire region of the

film. This again gives evidence that the shorter polyene sequences are distributed more widely than the longer sequences. This image closely resembles the photograph taken under white light (Fig. 7-4a). From these differences in optical properties we expect to see a significant difference in the photothermal signals. This is borne out in Figs. 7-24 and 7-25.

The 620 nm photothermal movie (Fig. 7-24) shows the optical image at early times (t=0.2ms after excitation) with the halo effect included. The image evolves out of the baseline with a smooth ring around the edge of the film and distinct bump in the center that was not visible in the optical images. The image continues to slowly rise up out of the baseline until it reaches a maximum at t=4.0 ms after excitation. At this point it is clear that the image is not thermally homogeneous as there is significant variation across the image as it decays into the baseline of frame.

At early times, (t=0.24 ms) the 458 nm photothermal movie (Fig. 7-25) agrees with the optical image of the non filtered picture (Fig. 7-4) and at >0.96 ms the subsequent growth of the photothermal feature. The image shows a distinct outer ring and central bump (t=4.0 ms) which then spreads into a second inner ring (t=7.9 ms), the two rings merge at t=12.0 ms and then decay into the background of the photothermal image. This is most easily seen in view #2 of Fig. 7-25.

The thermal movie (Fig. 7-26) shows distinct features at t = 19.69 ms as the thermal waves launched from the front surface begin to reach the detector. The thermal image can detect a central dip clearly and also shows the annular structure. At this point it is unclear to whether the poor resolution of the images is due to gradual change in  $\alpha$ , the thermal efflux or thermal wave diffraction between the front and rear surfaces.

Interpretation of this set of photothermal images is much more difficult as there are distinct changes in both optical and thermal properties of the sample. We first compare the two photothermal movies and examine the purely thermal movie before presenting our assessment of the signals. At 620 nm the movie (view #2) shows the rise of a central bump that spreads and fuses with the outer ring between t=4.0 ms and t=8.0 ms before it decays. The 458 nm image shows the central bump evolving then splitting into a second ring feature at t=7.9 ms before it spreads and merges with the outer ring. The difference in images at two different wavelengths can only be attributed to optical effects as both images then show that the absorbing polyene band are uniquely distributed through the degraded region in a radial fashion. More discussion of this will follow below.

In the 620 nm movie, at early times, the width outer ring is significantly wider than the 458 nm early time images. This is the same annular ring that is seen in the 620 nm spectrophotometric image and the blue filtered white light photograph. This ring is attributed to a decreased concentration of long conjugated sequences along the backbone of the polymer at the periphery of the degradation. The 458 nm image is sharper at the edges because the shorter length polyene sequences are present out to the edge of the darkened spot in elevated concentrations. It is apparent that the interface between the region of optical absorption and optical transmission in the PVC film is a sharp boundary at 458 nm.

Finally it is noted that both photothermal movies are distorted at the front bottom edge corner of the picture frames (point 0,0) at intermediate and long times after excitation (t>8.0 ms after excitation). This distortion of the annular structure is due to the fact that the samples were suspended vertically when degraded. As the local heating increased the temperature of the film rose above the Tg and the polymer was pulled downward by gravity. At the same time energy continued to be absorbed in the central core of

degradation and molten PVC was pushed to the edge where it was cooled there by creating a channel or hole in the film itself. In addition, dehydrochlorination of the PVC released HCl which accounts for over half of the molecular weight of a single monomer unit. Thus when the degradation is permitted to continue to a point where more than a few percent of the PVC is degraded loss of mass will result in a change in thickness of the film along with a change in the thermal properties. The rapid cooling of the film occurs when the light beam is blocked allowing the PVC film to harden in the conformation it was in. This stress then creates the birefringence in the film.

Profilometry scans across the degraded film support this interpretation. A line scan across the film through the center of the black spot is shown in Fig. 7-27. The edge of the film that was left undegraded remained at the 72  $\mu$ m thickness measured before degradation, the edges increased in thickness up to 80  $\mu$ m and there was a central channel that dropped to 55  $\mu$ m at the center. Thus the film had lost 1/3 of its total thickness at the center of the degraded region. It is expected that some of the sample was lost to deydroclorination and some moved to the edge of the film by convection.

Polymer films degraded in air under large optical fluences degrade locally because heat generated by light absorption cannot be conducted significantly into the air due to the poor thermal mismatch between the sample and air. The thermal diffusivity of PVC is reported to be in the range of  $1.2e-7m^2/s$  [26] making it a poor thermal conductor of heat. Thus heat in the film is not conducted away fast enough to prevent local heating which eventually causes the local temperature to rise over the Tg of PVC (84°C).

Results of a large number of photothermal images suggest that the dehydrochlorination is initiated by photo related mechanisms and in the early stages spreads radially from a central spot as seen in the lightly degraded PVC film. As dehydrohalogenation proceeds the degraded film then begins to absorb increased light levels and heat due to nonradiative decay mechanisms. The rate of dehydrochlorination increases in the region of heating causing local degradation to occur more quickly than the degradation can spread along the chains of the polymers. This is seen in the moderately degraded sample as a less pointed and more square optical profile. The 458 nm image is more square than the 620 nm image suggesting that the polyene up to n=6 have formed through out the degraded spot in the film. The heating eventually causes the polymer to rise above its Tg and deform the polymer film as it begins to flow under the pull of gravity (the strongly degraded PVC film). The degradation still spreads in the film as evidenced by the increasing diameter of the spot size between the early degraded and late degraded films. However, under these conditions the kinetics of local dehydrochlorination are significantly faster that lateral dehydrochlorination.

A discussion of the merits of photothermal techniques in the study of polymer degradation

Once a photothermal movie is obtained there is significant information about the optical profile that generated the thermal waves. Inversion of points of interest can recover the light flux profile in the sample and even the optical profile can be obtained. The polyene density as a function of position can then be calculated by the method of Brown et al [32] generating a map of functional densities. The advantage of the photothermal technique is that the sample is returned to the chemist intact and unmodified. Long term studies can be done on the same sample to study processes that may evolve slowly; such as natural weathering. The technique can be used to probe any chromophore for which an excitation source exists allowing 3-D imaging over the entire electromagnetic spectrum. The imaging process requires only low powers and is ideally suited to study films between 1-100 µm thick. No other technique we are aware of has these capabilities.

The photothermal movie provides qualitative information about the location of spot degradation but line scans can provide the equivalent information over broad areas where imaging of a large surface would be too time consuming. The time required to capture a single photothermal movies depends on the thickness of the film and sweep rate required. Thin films (10-30  $\mu$ m) require about 2 hours while the 100  $\mu$ m films will require about 6 hours to image. It is a long time compare to a single UV of IR scan but nonetheless significantly less time than the days required to microtome and image individual cross sections as is being done now.

In addition, step-scan FT-IR photothermal techniques can then be used to monitor the change in the spectra as a function of time and depth. This can be used in conjunction

with depth profiling of specific functional groups to help clearly elucidate the mechanisms of degradation.

## **Conclusion:**

Photoinitiated degradation generates significant heating in the film creating a large temperature gradient between the point degradation is initiated in the center of film and the outside edge of the film. If the film is not cast onto a suitable heat sink PVC will not be able to conduct the heat away from the local region of degradation resulting in rapid growth of long polyene bands. This creates a number of interesting features at the molecular level which gives the PVC films interesting optical properties including a strong birefringence.

Photothermal imaging of degraded PVC provides a tool to nondestructively profile the depth dependent growth of the polyene bands and inversion provides a method to generate 3-D reconstruction of specific optical features in the film.
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light



polymer film

in air

Fig. 7-1 The experimental geometry used to photodegrade the PVC films. PVC films were suspended in the air in front of a high intensity light source resulting in local photodegradation.

## COMPUTER - INSTRUMENT INTERFACING



Fig. 7-2. Computer and instrument interfacing used to construct the photothermal spectrometer for 3-D imaging. A master computer acquires the photothermal signal and controls the timing of slave #1 which drives the spectrometer, slave #2 which does the spectral calculations and recovers the impulse responses, and slave #3 which controls the x-y translator.



Figure 7-3. The evolution of a spot degradation in PVC films hung in air. The photographs are of (a) lightly (b) moderately (c) strongly degraded films.



Figure 7-4. Light micrographs of the strongly degraded PVC sample. The sample is photographed under (a) broadband white light (b) white light with a blue filter (c) white light at higher magnification to show the center degraded region and (d) under polarized light.





relative number of chlorine

Fig. 7-5 Scanning Electron micrograph with a dispersive x-ray detector element set to monitor Cl level across a 4 µm cross section cut from the lightly degraded PVC film. The slight decrease of Cl at the edges are thought to be due to edge effects in the film. The Cl levels provide no depth profiling information about the distribution of degradation products.



Fig. 7-6. Impulse trends towards regions of increasing light absorption. Regions of the polymer that do not absorb light have a fast response. The strongest absorbing region of the polymer will have a peak delay well separated from the non-absorbing region and a broader peak width.



Fig. 7-7 UV spectra of bulk-PVC foils photodegraded under (a) 100% N2: (b) 95% N2/5% O2; (c) air; (d) 70% N2/30% O2; (e) 50% N2/50% O2; (f) 100% O2.



Fig. 7-8 Axis scales and axis labels for all 3-D images presented in this chapter. The images are presented as (i) view #1 from the side to show the profile of the feature being imaged or as (ii) view #2 to show a more topographical effect. The x and y axis' are relative positions of the xy translator and units are always in millimeters. The signal intensity is (I/Io) or  $\log(I/Io)$  for spectrophotometric images and h(t) for the photothermal and thermal images. Each 3-D graph is not labeled so that up to eight images can be presented on a page each time.



Fig. 7-9 Single wavelength spectrophotometric image of a lightly degraded PVC film. (a) Log transmission image at 620 nm and (b) linear and log transmission images at 458 nm.



t= 0.22 ms





t= 0.8 ms



tm 1.4 ms

t= 2.19 ms



t= 4.37 ms



Figure 7-10 Photothermal movie of a PVC film lightly degraded in air. (View El) Times correspond to the time after excitation by pulse of light at 620 nm.









t= 0.8 ms



t= 1.4 mm



t= 2.19 ms



tm 4.37 mm



t= 6.55 ms



Figure 7-10 continued. View #2 of the photothermal movie of a PVC film *lightly* degraded in air. Times correspond to the time after excitation by palse of light at 620 nm.





t= 0.2 ms



t= 0.4 ms



t= 0.8 ms



t= 1.4 ms

t= 2.2 ms

t= 4.4 ms



Signer 7-11 Photothermal movie of a PVC tilm lightly legraded in wir. (View #1) Times correspond to the time after excitation by pulse of lists at 458 nm.









t= 0.8 mm







t= 1.4 ms

t= 2.2 ms

t= 4.4 ma



t= 6.6 ms



t= 8.8 ms

Figure 7-11 continued. View 42 of the photothermal movie of a PVC film *lightly* degraded in air. Times correspond to the time after excitation by pulse of light at 458 nm.



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Fig. 7-12 Thermal images of a lightly degraded PVC film at t=21.1, t=42.0 and t=78.7 ms after excitation.





Fig. 7-13. (a) Broadband photograph of a 100 um cross section through the lightly degraded PVC film. The PVC is between two layers of EPON resin. The degradation is darker on the right hand side of the PVC film (marked (c)) and lighter to the left hand side of the photograph (marked (a)).

(b) Trends in the photothermal inversion of the impulse response in the various region of the film at 620 nm. Degradation in region (a) is located at the front surface of the film. Degradation in region (b) starts at the front surface but is more progressed in the center of the film. Degradation in region (c) is the most strongly degraded region and is confined to the center of the film.

(a)



Fig. 7-13 (c) A photothermal image showing the points of interest to be inverted. The arrows correspond to the same positions on the photograph.

(d) The inverted optical profiles corresponding to the positions indicated by the arrows in Fig. 7-13c.





sample depth (µm)

Fig. 7-14 Estimated optical absorptivity as a function of depth. (a) Point (a) in the photograph, (b) point (b) in the photograph, (c) point (c) in the photograph.

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Fig. 7-15 Inversion of the lightly degraded PVC film at the position indicated by arrow (a) in Fig. 7-14(a) using an impulse response recorded at 458 nm. The recovered thermal flux profile is broader than the corresponding profile at 620 nm suggesting that the polyene sequences absorbing at 458 nm spread closer to the front and rear surfaces.



(c)

Fig. 7-16. Spectrophotometric images of a moderately degraded PVC film. The 620 nm image is plotted on a linear scale of (I/Io) (a), and a log(I/Io) scale (b). The 458 nm spectrometric image of the same sample is plotted in (c) on the log scale.



Figure 7-17 Photothermal movie of a PVC film moderately degraded in air. (View #1) Times correspond to the time after excitation by pulse of light at 620 nm.



Figure 7-17 continued. View g2 of the photothermal movie of a PVC tilm moderately degraded in air. Times correspond to the time after excitation by pulse of light at 620 nm.



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t= 24.6. ms





t= 34.4 mm

- 1



t= 0.96 ms





t= 4.92 ms



t= 9.84 ms

t= 14.76 m#

t= 24.6. ms



Figure 7-18 continued. View #2 of the photothermal movie of a PVC film moderately destaded in air. Timer correspond to the time after empitation by pulse of light at 458 nm.

t= 34.4 ms



Fig. 7-19 Thermal images of a moderately degraded PVC film at t=24.6 ms and t=54.1 ms past excitation.



Fig. 7-20 Source profiles recovered from points (1) and (2) on the moderately degraded PVC sample.



Fig. 7-21 Comparison between the experimental impulse response (solid) and the impulse response obtained by forward modeling the inverted optical profiles (dashed). (1) The fit between theory and experiment at point (1) in Fig 7-20. (2) The fit between theory and experiment at point (2).



Fig. 7-22 Spectrophotometric image of a strongly degraded PVC film at 620nm. Both the (a) linear and (b) log transmission plots are shown.



Fig. 7-23 Spectrophotometric image of a strongly degraded PVC film at 458nm. Both the (a) linear and (b) log transmission plots are shown.



t= 0.2 ms



t= 1.0 ms



t= 2.0 ms



t= 4.0 ms

t= 8.0 ms



t= 12.0 ms



t= 18.0 m#



t= 30.0 ms

2

Figure 7-24 Photothermal movie of a PVC film strongly degraded in air. (View  $\pm$ 1) Times correspond to the time after excitation by pulse of light at 620 nm.

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t# 2.0 ms







t= 4.0 ms

t= 8.0 ms

t= 12.0 ma



t= 18.0 ms



t= 30.0 ms

Figure 7-24 continued. View 12 of the photothermal movie of a PVC film strongly degraded in air. Times correspond to the time after excitation by pulse of light at 620 nm.

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t= 0.24 ms







t= 12.0 ms



Flaure 7-25 PERformal movie of a PVC film strongly Henraded in air. (View #1) Times correspond to the size atter encitation by pulse of light at **458** nm.



t= 0.24 ms





t= 1.9 ms



t= 18.0 ms



t= 30.0 ms

Figure 7-25 continued. View #2 of the phototherma. movie of a PVC film strongly degraded in air. Times correspond to the time after excitation by pulse of light at **458** nm.



Fig. 7-26 Thermal images of a strongly degraded sample at t= 14.8 ms and t= 19.69 ms showing a distinct thermal feature in the center region of the degraded spot.

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Fig. 7-27 A profilometry line scan of sample thickness across the strongly degraded PVC film.



**Chapter 8: Conclusions** 

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The objective of this thesis has been to develop techniques for quantitative depth profiling of optical features in polymer films. Work done to date had shown that qualitative profiling of optical and thermal properties is possible in a wide range of polymer samples but little work had been done to determine exactly how much quantitative information can be recovered. Before photothermal techniques will be used routinely by chemists it is necessary to develop clear protocols and a strong theoretical understanding of the principles so that we can define the conditions under which meaningful results can be obtained.

We believe that the work presented in this thesis has shown that photopyroelectric spectroscopy has the capabilities to quantitatively recover optical and thermal features from a wide range of polymer samples.

In chapter 2 it was shown that photopyroelectric spectroscopy has the capability to nondestructively image optical absorption profiles in thin polymer films. Frequency domain measurements have shown that the phase of the photopyroelectric signal is able to resolve the distribution of the absorbing features on a sub micron resolution scale. The magnitude response, which typically is less sensitive to the photothermal signal, can be enhanced in the presence of photothermal interference where the vector components of each contributing layer line up in phase with each other. The effect is seen as an increase in the frequency domain signal as a function of frequency rather than a decrease in the signal intensity.

Wideband homodyne photothermal spectrometry is capable of studying ultrathin polymer films of thickness 80 nm to 1500 nm. The technique is limited to the study of polymer films thicker than 80 nm by a 400nm depoled layer at the surface of commercially supplied PVDF films which effectively filters the thermal response. The technique is

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limited to a maximum thickness of 1500 nm by the electronic high pass filter which must be kept above 1000 Hz to prevent corruption of the downshifted signal by low frequencies of the upshifted signal. The interfacial adhesion studies made with thin polymer films spin coated onto the PVDF will be able to detect only large  $(b_{32}=b_{34}=0.4)$  thermal mismatch due to the thermal filtering effect of the 400 nm depoled layer in the PVDF films.

The results from the inversion study show that the photothermal impulse response can be inverted to obtain the source or thermal flux profile in thermally continuous samples. By casting the problem in terms of the free space Green's Function heat conduction problem. one can create a matrix with arbitrary time and spatial coordinates that serves as the model space or basis for the sample. The problem is ill posed as written due to the matrix being rank deficient and ill conditioned; however, by adding a small amount of random noise to the coefficients of the Green's Function matrix the matrix becomes full rank and the conditioning is greatly improved. By averaging of a large number of inversions, each seeded independently and randomly, the thermal source profile can eventually be recovered. The most significant obstacle to applying the inversion routine is obtaining a basis that accurately describes the sample. When used as described in this thesis the inversion routine is not ill conditioned and is not prone to large errors due to noise on the signal and small errors in measuring the samples' thermal properties. The inversion does not degrade with sample depth and will not generate a fit in the time domain if it cannot obtain a fit between the theoretical and experimental source profiles. Once the thermal flux profile is recovered the optical profile can be reconstructed with a minimum of distortion.

In this thesis we have developed the theoretical tools for advancing photothermal spectroscopy in general as scientific tool and proposed precise protocols for using

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photopyroelectric techniques to obtain reliable quantitative optical and thermal properties of a sample. When used within the guidelines laid out in this work chemists can use photopyroelectric spectroscopy to nondestructively characterize their polymer films and laminates with confidence.

The photothermal images of PVC films are an example of one potential application of photothermal techniques. Future work may include photothermal imaging of photodegradation in drawn polymer films. If degradation is observed to spread with aligned polymer fibers it could be argued that the degradation is due to thermal mechanisms; however, if the degradation spot remains circular in nature, this would suggest that the degradation is dominated by optical effects. The depth dependent spread of the polyene bands may show that the surface optical image may vary significantly from the depth dependent spread of degradation.

It is the opinion of the author that future work on the inversion routine should center around techniques to select a good basis for the inversion. Rather than using discrete delta function source bins, box bins which distribute the energy more uniformly across the bin should be more effective.

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. . Appendix A:

# CONSTRUCTION OF A FREQUENCY DOMAIN PHOTOPROELECTRIC SPECTROMETER FOR THE SPATIAL DEPTH PROFILING OF CHROMOPHORES IN THIN POLYMER FILMS

(hardware and software)

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# INSTRUMENTATION

The spectrometer design described below is illustrated in Figure A-1. The output of a 1000 W Xenon arc lamp (Oriel) or a continuous wave dve laser (Coherent) is focused onto the entrance slit of a monochromator (Jobin Yvon #H.10) and the output beam is mechanically modulated with a variable speed chopper (Ealing Scientific). Focusing optics are used to direct the beam onto a homemade pyroelectric cell. The pyroelectric transducer is a 28 micron thickness, Ni/A1 coated, polyvinylidene difluoride (PVDF) film (Atochem). When heated the pyroelectric transducer material polarizes producing a potential difference across the two metallized surfaces. The incurred voltage change is proportional to the spatially averaged temperature change induced in the pyroelectric. The voltage generated by the pyroelectric is fed into a differential amplifier (Tektronix AM502) before being input to a lock-in amplifier (PAR 5101). The lock-in reference is taken from the chopper and the output is read by a 12 bit analogue to digital converter resident on an IBM data acquisition board. An IBM PC XT compatible equipped with an 8087 math coprocessor, Hercules graphics card, two floppy drives and two parallel ports, is used to control the spectrometer and collect the data. The software was written in ASYST (TM) (ASYST software technologies), output data files are made available in ASCII format for further processing using commercial graphics packages, such as GRAFTOOL (3-D Visions), which has been used to process all of the axonometric (3D) displays presented in this work.

#### PRINCIPLES

#### (i) Hardware Configuration

Printer cards are I/O mapped and are accessed through ASYST's PORT.IN and PORT.OUT commands. Typically, the cards use the default base addresses of 0x378 for LPT1, 0x278 for LPT2 and 0x3BC for LPT3. Our computer is programmed on LPT2 reserving LPT1 for printer use. Pin#2 at I/O base+0 is used to program the stepper motor of the monochromator. Ground is taken from pin#18. A rising edge sent from pin#2 of LPT2 to the stepper motor controller causes the grating to advance by a one-half nanometer division. To prevent the motor from slewing too rapidly and damaging the grating or overshooting the desired wavelength a short delay of about 250 milliseconds between each pulse is inserted. This is shown in the word STEP below.

:STEP\ moves the grating 1 nm n5 0 DO 0 632 PORT.OUT 1 632 PORT.OUT\ rising edge #1 0 632 PORT.OUT 1000 0 DO LOOP\ delay 1 632 PORT.OUT\ rising edge #2 0 632 PORT.OUT 1000 0 DO LOOP LOOP

2 - - -

The lock-in amplifier makes only single phase manual measurements and has no programming capability. To minimize the manual operation a TTL relay was inserted to electronically switch the 0-90° phase quadrant. Initially there were 3 jumper pads, reference Figure A-2a, which controlled the quadrant of the lock-in amplifier. Jumper 1 controlled the 0-90° quadrant and jumper 2 the 180-270° quadrant when used in conjunction with jumper 3 which controlled the 0-180° quadrant. To read 0° lines B and C were closed sending a signal from B to pin 12 of the bottom flip flop while leaving pin 10 open. To read 90° lines A and B were closed energizing pin 10 leaving pin 12 open.

A TTL relay inserted in place of jumper 1 permits keyboard access to the 0 and 90 degrees quadrants when the instrument panel phase controls are pre-set to 0° (ref. Fig A-2b). No longer are the connections (A,B, and C) on jumper 1 directly controlling the quadrant shift. When a TTL low is present at the base of the transistor the relay is deenergized and pin 12 of the bottom flip *i*lop is closed leaving pin 10 open. Subsequently, the 0° quadrant is read. A TTL high at the base energizes the relay causing the switch to change positions energizing pin 10 and opening pin 12. This allows the 90° quadrant to be read. In this manner the operation of the 0-90° phase control is automated. For manual operation of the lock-in the TTL input to the base of the transistor is kept low and the relay is energized by tying its negative terminal to the new ground at line A. This is accomplished by pushing the 90° quadrant button. Line A is no longer the direct 90° control; however, the phase quadrant is still shifted through the effect of the relay.

1

The TTL signal was supplied via LPT2 pin #2 which is located at I/O base+2. The lockin gain and filtering levels must be entered manually but the subsequent timing and data acquisition are automated and under computer control.

The chopper assembly was purchased and used as received from Ealing Electrooptics. A DC output voltage from the digital to analogue converter sets the chopper speed: -10 volts gives full speed and 0 volts stops the wheel. The chopper frequency must be calibrated as the speed is not linear with applied voltage over the entire range. This calibration is performed in-line by directing the output of the reference to a frequency counter (model #3030 Brunelle Instruments).

#### (ii) PPES Cell Design and Equivalent Circuit

The design of the pyroelectric cell is shown in Figure A-3. Brass inlaid electrodes make contact with the PVDF film which is held flush to the bottom of the cell with a thin film of silicone vacuum grease which ensures thermal and mechanical contact of the pyroelectric film to the backing. The sample under study is brought into close thermal contact to the PVDF with optical epoxy, silicone grease or by spin coating samples directly onto the PVDF. The entire cell is contained within a shell of aluminum which acts as an EMI shield. The interior of the shield is painted black to reduce the stray light

striking the PVDF film. The signals are output through shielded coaxial cables and fed into a differential pre-amplifier.

An equivalent electrical circuit of the pyroelectric detector is shown in Figure A-4. The heated pyroelectric functions as a capacitor with a temperature dependent dielectric constant. Such an element is equivalent to a voltage source in series with the PVDF film capacitance (Cp) if temperature changes are small. The resistance, R1, and capacitance, C1, are contributed by the input resistance of the preamplifier and the combined input capacitance of the signal leads and preamplifier. In order to recover the true FD-PPES voltage response the detection system consisting of the pyroelectric cell, pre-amplifier chopper and lock-in must have a flat frequency response. This is obtained by using a high input impedance amplifier (200M $\Omega$ ) and minimizing the use of preamplifier filtering. The results of varying the input impedance and the effects of the frequency response of various preamplifier input filters on the measured photothermal transfer function are shown in Figures A-5 and A-6. Loading the PVDF film with  $1.0k\Omega$ ,  $2.2k\Omega$ ,  $4.7k\Omega$  and 200M $\Omega$  as shown in Figure A-5, produces a trend towards increased uniformity of the magnitude response and increased signal level from the film. The phase response is linear for all input impedance settings. The frequency response of the detection system as a function of preamplifier low pass filter settings is illustrated in Figure A-6. With the low pass filter open to at least 0.1MHz the phase response is flat with frequency above 100Hz and becomes less flat as the low pass filter is reduced. The magnitude plot has been expanded along the intensity axis to show that

setting the low pass filter cutoff frequency below 0.1MHz also causes a slight roll off in the magnitude with frequency. The increased noise that passes through the preamplifier due to the open band pass is filtered out of the signal by the internal filters in the lock-in amplifier. It would also have been possible to use a low pass filter setting of about 10kHz and the correct for the transfer function after the signal has been recorded.

The use of the lock-in amplifier in this spectrometer is to obtain the magnitude and phase of the signal rather than to shift the analytical signal away from a region of spectral noise. The lock-in amplifier output contains a narrowband signal centered around dc, and a second harmonic output which is rejected by means of a lowpass filter. The narrower the bandwidth of the lowpass filter, the longer the settling time and therefore the longer the acquisition time. The advantage is improved rejection of the second harmonic from the dc output. If faster acquisition times are desired, one must settle for a wider bandwidth on the lowpass filter and contend with the transmission of the second harmonic component to the output channel. The second harmonic component is a periodic, well defined interference and subsequently it cannot be averaged out by averaging the output signal with uniform time sampling. In order to make the best compromise we settled for a filter time constant which gives the best trade off between settling time and rejection of the second harmonic. We then used random time sampling of the output channel to average out the interference. This approach works because the use of a random acquisition delay interval (whose probability distribution function (pdf) is uniform) to sample a periodic interference (with a fixed initial phase) gives the same result as randomly varying the initial phase (with uniform pdf) and fixing acquisition the time interval. The net contribution of the interference approaches zero as the number of samples increases to infinity. This is accounted for in the word GET1POINT of the data aquisition program.

We have found experimentally that the magnitude measurement is much less susceptible to the effects of this interference than the phase. The magnitude is calculated as the square root of the sum of the two readings in each quadrature with each squared individually. The phase is calculated as the arctan of the ratio of the quadrature reading over the in phase reading. Subsequently small variations in the quadrature contribution may show up as significant changes in the phase, but are less significant to the measurement of the magnitude.

To obtain one data poinst the computer sends a TTL low to the lock-in to measure 0 degrees, the lock-in is given time to settle proportional to three times the sum of the pre and post filter settings, the lockin signal is sampled up to 500 times (n1) and between each sampling a random delay is set. This delay has a uniform pdf as discussed in the preceding paragraph. The computer then sends a TTL high to measure the 90 degree quadrant and the process is repeated. The n1 points for both quadrants are averaged arithmetically and the magnitude ( $\mu\nu$ ) and phase (radians) of the signal are calculated via the procedure PROCESSPOINT and then saved with the associated wavelength and



chopping frequency in DATASTORE.

# MAIN PROGRAM

To execute the system RUN is typed. The program first INITIALISESs all the data by prompting the user to input the amount of averaging desired, the wavelength range and resolution to be studied, the modulation frequency range and resolution and the initial lock-in amplifier settings. These include gain and pre and post filter time constants. The user is given the opportunity to change any of the settings as often as needed at the start of the experiment or after any point during the scan. These changes are then accounted for in the experiment. It should be noted that the operator must set the monochromator to the starting wavelength manually at the beginning of the scan. The program then STARTs the experiment by sending a DC voltage from the digital to analogue converter to the chopper causing it to modulate the light at the desired frequency via the word SENDDATA. GETISET controls the number of data points taken at each modulation frequency and wavelength. Depending on n2, the number of data points required at each frequency and wavelength, it calls GETIPOINT.

At the end of the run the data can be viewed by plotting the magnitude or phase versus frequency or wavelength.

## RESULTS

The agreement between theory and experiment indicates that the system is capable of measuring photothermal and thermal wave responses without instrumental distortion and that the observed signal is due to the thermal response of the sample rather than the electrical response of the detector and filters. The spectrometer has achieved an adequate signal to noise ratio at low signal levels and the TTL relay inserted into the manual lock-in amplifier provides a low cost semi-automated system.

Results obtained using the broadband Xenon Arc source and a 4 nm monochromator bandpass had a poorer signal to noise figure due to the lower light flux incident on the sample. Improving the signal to noise may be achieved by opening the bandpass of the monochromator to 15 nm; however, the results then may no longer give good agreement with the theoretical response. This is especially true in the neighborhood of rapidly varying spectral features (e.g. band edges) where a lack of monochromaticity is evident. The proposed heat transfer model assumes that the light is absorbed in the sample according to Beer's law and the heat generated in the sample is due to the nonradiative decay of the absorbing species. The 15 nm bandpass sets up the equivalent of a distribution of thermal sources in the sample, over the range of wavelengths passed by the monochromator. The optical deposisiton profile, and therefore the heat flux profile set up in the sample, becomes a quantity weighed over the spectral band. These factors make modelling of the thermal response of the sample much more complex.



Fig. A-1 Hardware configuration for FD-PPES spectrometer.

<u>\_\_</u>



**(a)** 



Fig. A-2 Three tracks from the printed circuit board of the lock-in amplifier were cut (A,B,&C) and a TTL relay was inserted. The relay allows automatic 0-90 degree phase changes to be programmed into the software.



Fig. A-3 The PPES cell design. The cell is made of PMT A with inlaid brass electrodes. Two BNC cables take the electrical signal to the post signal differential amplifier.



Fig. A-4 The equivalent circuit of the thin film PPES detector and associated input electrical network.



Fig. A-5 Frequency response measurement for FD-PPES cell with amplifier input impedance set to (1)  $1k\Omega$ , (2)  $2.2k\Omega$ , (4)  $4.7k\Omega$  and (O) 200 k\Omega. The bandpass was set to 0.1Hz to  $0.1M_{\odot}$ 



Fig. A-6 The phase (a) and magnitude (b) frequency response of the PPES cell as a function of bandpass settings. Pass (\*) 0.1 Hz-3kHz, (#) 0.1Hz-10kHz, (x) 0.1Hz-0.1MHz, (o)0.1Hz-0.3MHz. The amplifier input impedance is 200MΩ.

# VPROGRAM TO ACQUIRE DATA FOR A FREQUENCY DOMAIN VPHOTOPYROELECTRIC SPECTROMETER

# **\\*\*\*\*** PART I: ENTERING THE EXPERIMENTAL PARAMETERS \*\*\*\*

 $\land$  Declare relevant scalars

integer scalar check	\ toggle to excape from the RECHECK		
integer scalar n1	\ #pnts\avg		
integer scalar n2	\ # of avg\frequency		
integer scalar n3	\ starting wavelength		
integer scalar n4	\ finishing wavelength		
integer scalar n5	\ wavelength step		
real scalar n6	\ starting Hz		
real scalar n7	\ finishing Hz		
real scalar n8	\ step Hz		
real scalar n9	\lock-in sensitivity		
real scalar n10	\ prefilter setting		
real scalar n11	\ post filter setting		
integer scalar n12	\ reference phase		
integer scalar n13	\ pre-amp filter		
integer scalar n15	\ random sampling time delay		
integer scalar choice	\ choice at case statement		
integer scalar fit-it	$\$ a curve fitting constant for calibrating $\$ variable speed choper		

#### :WARN

 $\$  this word warns when an invalid frequency parameter is entered.  $\$  called by SETUP

#### screen.clear

cr"The frequency must be a positive number from 1 - 2000" "type cr "If you entera neg number the program will crash" "type #input

#### ;

# :SETUP

\ experimental parameters are input. This word is called by INITIALISE

40 n15 :=  $\$  random sampling dealy is set to less than 40 msec

```
cr " please input the following values
                                                " "type
cr " " "type
cr " number of points read per avg.
                                                " "type
#input nl :=
cr " number of averages per value, min of 3
                                                " "type
#input n2 :=
                                   Nif its true it'll enter the loop
         3 n^2 > if
           screen.clear
            cr " The # of avg.s must be at least 3" "type
            cr " if you enter a # less than 3 the program will crash " "type
              #input n2 :=
          then
screen.clear
cr " with regards to the ** MONOCHROMETER ** please give ..." "type
cr " starting wavelength :
                                    " "type
\#input n3 :=
cr " finishing wavelength :
                                    " "type
#input n4 :=
cr " step size for wavelength :
                                    " "type
\#input n5 :=
screen.clear
cr " with regards to the ** VARIABLE SPEED CHOPPER ** please give ..." "type
ст " " "type
cr " slower Hz" "type
#input n6 :=
0 n6>if
  WARN
  nб :=
    then
cr " faster Hz " "type
#input n7 :=
0 n7 > if
  WARN
  N7 :=
     then
cr " step Hz " "type
#input n8 :=
 0 n8 > if
  WARN
 n8 :=
    then
screen.clear
```

```
cr " with regards to the instrument controls " "type
cr " Lock-in sensitivity (mV) " "type
#input n9 :=
cr " lock-in prefilter # " "type
#input n10 :=
cr " lock-in postfilter # " "type
#input n11 :=
cr " reference phase " "type
#input n12 :=
cr " preamp gain " "type
#input n13 :=
```

;

#### :RECHECK

 $\$  allows any experimental parameter to be changed by the operator  $\$  this word is called by INITIALISE

screen.clear

cr " do you want to change any of these " "type cr " enter the # ... you'll have a chance to change more than one." "type cr " hit 0 if they are all o.k. " "type

cr " 1: #pts/avg ( 500 max)	" "type nl
Cr " 2: # of avg/value (min of 3)	" "type n2.
cr " 3: starting wavelength	" "type n3.
cr " 4: finishing wavelength	" "type n4.
cr " 5: wavelength step	" "type n5.
cr " 6: starting Hz	" "type n6.
cr " 7: finishing Hz	" "type n7.
cr " 8: step Hz	" "type n8
cr "9: lockin sensitivity	" "type n9.
cr " 10: prefilter	" "type n10.
cr " 11: postfilter	" "type n11.
cr " 12: ref. phase	" "type n12.
cr " 13: preamp gain	" "type n13.
cr " 15: sampling delay	" "type n15.
ст	

#input choice := choice

case

1 of ." #pnts/avg	" "type	<pre>#input n1 := endof</pre>
2 of ." # of avgs/value min of 3	**	#input n2 :- endof
3 of ." start wavelength	••	#input n3 := endof
4 of ." finishing wavelength	••	#input n4 := endof
5 of ." step wavelength of	••	#input n5 := endof
6 of ." start Hz	*1	#input n6 := endof
7 of ." finishing Hz	••	#input n7 := endof
8 of ." step Hz	••	#input n8 := endof
9 of ." sensitivity (mV)	••	#input n9 := endof
10 of ." prefilter	10	#input n10 := endof
11 of ." postfilter	17	#input n11 := endof
12 of ." ref phase	**	#input n12 := endof
13 of ." preamp gain	••	#input n13 := endof
15 of ." sampling delay	**	#input n15 := endof
." << all are o.k. >>	••	1 check :=

#### endcase

CT

# ;

#### :INITIALISE

 $\$  all experimental parameters are input and checked  $\$  called by the word RUN

screen.clear 0 check := SETUP begin RECHECK check 1 = until 0 check :=

;

# **\PART II: DATA IS ACQUIRED**

\ delcare all relevant variables \ these are capitalized to emphasize that these variables \ are required for the actual data acquisition REAL DIM[ 4, 200 ] ARRAY STOREAVG REAL SCALAR D1 REAL SCALAR Q1 REAL SCALAR D REAL SCALAR Q REAL SCALAR PHASE REAL SCALAR MAGNITUDE REAL SCALAR FREQUENCY INTEGER DIM[ 1 ] ARRAY WAVELENGTH INTEGER DIM[ 1 ] ARRAY CHOPRATE DP.INTEGER SCALAR CHOPSEG INTEGER DIM[ 500 ] ARRAY DBANK INTEGER DIM[ 500 ] ARRAY QBANK INTEGER SCALAR MS INTEGER SCALAR LS INTEGER SCALAR MSNB INTEGER SCALAR LSNB

DP.INTEGER SCALAR BANKSEG INTEGER SCALAR LB INTEGER SCALAR UB INTEGER SCALAR LWNB INTEGER SCALAR HGNB INTEGER SCALAR ROW INTEGER SCALAR COL DP.INTEGER SCALAR QBANKSEG DP.INTEGER SCALAR WAVESEG INTEGER SCALAR FR INTEGER SCALAR WV INTEGER SCALAR h  $\land$  store the data from each run

\ calculated phase value \ calculated magnitude value \ data to be sent to chopper \ data to be sent to monochromator \ binary value of data sent

\ holds the most sig. byte of data \ holds the lease sig. byte of data \ digital nb. equiv. to MS \ digital nb. equiv. to LS

\ gives the address of DBANK \ least sig. byte of data incoming \ upper byte of data incoming \ digital nb. equiv. to LB \ digital nb. equiv. to UP \ row of storeavg \ col of storeavg

:START

\ called by RUN.

0 Is := 0 dbank := dbank address . bankseg := wavelength address . waveseg := 0 qbank := qbank address . qbankseg := choprate address . chopseg := \ sets counter to 0
\ dbank address is found
\ sets the quadrature array to 0
\ qbank address is found

\ freq address is found

- 0 lb := 0 ub := 0 storeavg :=  $0 \operatorname{col} :=$ 0 row := n3 wavelength := n6 frequency := 9 49890 port.out \ sets up the data acquisition board \ parameter used in plotting data 0 h := : : SENDDATA  $\land$  sets the chopper modulating at the starting frequency \ called by OVER.FREQUENCY.RANGE freque ncy 100 / fit-it := \ offset is added to chopping speed fit-it 8 > if\ to give a linear calibration curge then frquency -2000 / 1 + 2048 5 - \* fit-it - choprate :=  $\setminus$  5 is an offset and the 1.01 alters the slope slightly to \get an accurate frequency setting 1 ls + ms := $\$ ms is greater than 1s by 1 chopseg def.seg ls peek Isnb := ms peek msnb := 0 4835 port.out  $\land$  sets computer to write to channel 0 Isnb 13026 port.out msnb 13027 port.out ; :READ2BIT \ data acquisition board reads the hi bit and low bit from the lock-in \ called by GET1POINT 1 738 port. out 0 739 port.out 0 738 port.out
- 0 739 port.out

```
8930 port.in lwnb :=
8931 port. in hgnb :=
```

# :STORE2BIT

 $\$  data read in READ2BIT after a 0 degree reading is stored  $\$  called by GET1POINT

1 lb + ub := bankseg def.seg 1wnb LB poke hgnb UB poke

2 lb + lb :=

# :QSTORE2BIT

\ data read in READ2BIT after a 90 degree reading is stored \ called by GET1POINT

1 lb + ub := qbankseg def.seg 1wnb 1b poke hgnb ub poke

2 lb + lb := ;

#### :PROCESSPOINT

 $\$  the phase and magnitude values are calculated  $\$  called by GET1POINT

```
dbank 1 - dbank :=

qbank 1 - qbank :=

dbank sub[1, n1, 1] mean d :=

qbank sub[1, n1, 1] mean q :=

d 10 * 4096 /-5 - 2 * d :=

q 10 * 4096 / 5 - 2 * q :=

q d / atan phase :=

q q * q1 :=

d d * d1 :=

q1 d1 + sqrt magnitude :=
```

\ offset correction on the board
\ take the average reading of n1
\ convert bits to volts
\ set output to +- 10V output

 $\land$  find the phase and mag of signal

: DATASTORE

;

 $\$  the data is stored in the array storeavg  $\$  called by GET1POINT

```
1 col + col :=
frequency fr :=
wavelength [ 1 ] wv :=
```

```
1 row :=
fr storeavg [ row , col ] :=
2 row :=
wv storeavg [ row , col ] :=
3 row :=
phase storeavg [ row , col ] :=
4 row :=
magnitude storeavg [ row , col ] :=
```

```
;
```

:

### : SCREEN.POINT

 $\$  data is output to screen as it is recorded to allow changes  $\$  during the experiment

```
cr " frequency " "type fr .
cr " wavelength " "type wv .
cr " phase " "type phase .
cr " magnitude " "type magnitude .
cr " " " "type
```

: GET1POINT

 $\$  one phase and magnitude value is taken  $\$  called by over.frequency.range

cr " toggle switch to 0 degrees on the lock-in " "type

```
\lambda sets the phase to 0 degrees automatically
  0 634 port.out
                                     \ system is allowed to settle
                                     \ pre-filter time constant
   1000 n10 * 3 *
                                     \ plus post filter time constant
   1000 n11 * 3 * + msec.delay
   1 h + h :=
                                     Vincrement h every time a point is taken
                                     Nh is a data plotting parameter
  0 1s :=
   0 1b :=
   nl 0 do
      rand.unif n15 * msec.delay
                                     \ random delay between taking points
                                     \ to minimize sampling error
       READ2BIT
       STORE2BIT
   loop
   cr " toggle switch on lock-in-amplifier to 90 degrees " "type
                                     \ switches the 90 degree button automatically
   1 634 port.out
                                      \ then the system is allowed to stabilize
   1000 N10 * 3 *
                                      \ pre filter setting
   1009 n11 * 3 * + msec.delay
                                      \land post filter setting
    0 1s :=
   0 1b :=
    nl 0 do
       rand.unif n15 * MSEC.delay \random delay between taking points
       READ2BIT
       QSTORE2BIT
loop
   PROCESPOINT
   DATASTORE
   SCREEN.POINT
   ;
   :GET1SET
   \ called by OVER.FREQUENCY.RANGE
    n20 do
       GET1POINT
```

loop 0 634 port.out :

•

•

.

.

 $\land$  set quad button back to 0 degrees

.

# : OVER.FREQUENCY.RANGE

```
\ takes data over the frequency range selected 
\ called by OVER.WAVELENGTHS
```

```
begin
SENDDATA
CR " ***** NEW FREQUENCY LET CHOPPER STABILIZE THEN RETURN
********** " "TYPE
cr "input "drop cr
```

cr " \*\*\* to change a value hit the spacebar else hit return \*\*\* " "type

```
pckey 32 = if

screen.clear

cr " up to wavelength : " "type wavelength .

cr " up to frequency : " "type frequency .

cr " preamp gain " "type n13 .

cr " ref phase " "type n12 .

cr " post filter " "type n11 .

cr " prefilter " "type n10 .
```

```
cr " sensitivity" "type n9.cr " # of pnts/avg" "type n1.cr " # of avg/value" "type n2.
```

```
CT
```

÷

# :STEP

```
\ steps the monochromator n5 namometers
\ called by OVER.WAVELENGTHS
 n5 0 do
 0 632 port.out
 1 632 port.out \ steps grating half a nm
0 632 port.out
  1000 0 do
              \ delay between hafl steps
  loop
 1 632 port.out \ steps grating half a nm
 0 632 port.out
  1000 0 DO
  loop
 loop
;
: OVER.WAVELENGTHS
\ called by RUN
```

```
\ does a frequency scan at every wavelength selected
```

```
begin
OVER.FREQUENCY.RANGE
n6 frequency :=
cr" +++++ LET CHOPPER SETTLE BEFORE HITTING RETURN TO GO ON +++++
" "type
cr "input "drop cr
STEP
n5 wavelength + wavelength :=
wavelength [ 1 ] n4 >
until
```

```
;
```

: RUN

INITIALIZE START OVER.WAVELENGTHS

**:** ;

Appendix B

The theoretical frequency domain voltage response equation

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## Appendix B

N

The theoretical voltage response for each sample was calculated using equation 1 below. The equation was derived assuming that a thermally homogeneous, optically inhomogeneous sample can be divided into N arbitrary layers and the thermal response of each layer determined individually. Using the linear properties of heat transfer each of the N responses are summed giving the thermal response of the entire sample. The 8 thermal transit times represent the time it takes for the downward propagating thermal waves ( $\tau_1$ - $\tau_4$ ) to reach the top and bottom of the pyroelectric detector from the top and bottom of the absorbing layer and the upward propagating thermal waves ( $\tau_5$ - $\tau_8$ ) to pass up to the air sample interface where they are fully reflected back down to the pyroelectric. The following parameters are also required in the model: the pyroelectric thickness (d), the sample thermal diffusivity ( $\alpha_2$ ), the pyroelectric diffusivity ( $\alpha_3$ ), the sample thickness ( $\sigma_N$ ), the distance between the air sample interface to the top of the ith layer ( $\sigma_3$ ).

$$V(s) = \gamma \leq \Delta T_{3}(x,s) > C_{p}$$

$$= \sum_{m=0}^{\infty} \frac{2\pi (-1)^{m} \zeta^{m} \gamma}{\alpha_{2}(b_{32}+1) d q_{2}q_{3}} \sum_{i=1}^{N} \eta_{i}\beta_{i}I_{i-1}$$

$$\left[\frac{(e^{-\sqrt{\tau_{1}s}} - e^{-\beta_{i}\ell_{i}} e^{-\sqrt{\tau_{2}s}})}{(\beta_{i} - q_{2})} + \frac{(e^{-\sqrt{\tau_{5}s}} - e^{-\beta_{i}\ell_{i}} e^{-\sqrt{\tau_{6}s}})}{(\beta_{i} + q_{2})}\right]$$

$$\frac{-(e^{-\sqrt{\tau_{3}s}} - e^{-\beta_{1}\ell_{1}}e^{-\sqrt{\tau_{4}s}})}{(\beta_{1} - q_{2})} - \frac{(e^{-\sqrt{\tau_{7}s}} - e^{-\beta_{1}\ell_{1}}e^{-\sqrt{\tau_{8}s}})}{(\beta_{1} + q_{2})}$$
(1)

Ξ.

where

$$\begin{aligned} \tau_{1} &= ((2m+1)\sigma_{N} - \sigma_{i-1})^{2} / \alpha_{2} \\ \tau_{2} &= ((2m+1)\sigma_{N} - \sigma_{i})^{2} / \alpha_{2} \\ \tau_{3} &= \{((2m+1)\sigma_{N} - \sigma_{i-1})/\alpha_{2}^{1/2}) + d/\alpha_{3}^{1/2}\}^{2} \\ \tau_{4} &= \{((2m+1)\sigma_{N} - \sigma_{i})/\alpha_{2}^{1/2}) + d/\alpha_{3}^{1/2}\}^{2} \\ \tau_{5} &= ((2m+1)\sigma_{N} + \sigma_{i-1})^{2} / \alpha_{2} \\ \tau_{6} &= ((2m+1)\sigma_{N} + \sigma_{i})^{2} / \alpha_{2} \\ \tau_{7} &= \{((2m+1)\sigma_{N} + \sigma_{i-1})/\alpha_{2}^{1/2}) + d/\alpha_{3}^{1/2}\}^{2} \\ \tau_{8} &= \{((2m+1)\sigma_{N} + \sigma_{i})/\alpha_{2}^{1/2}) + d/\alpha_{3}^{1/2}\}^{2} \end{aligned}$$

The nonradiative decay coefficient  $(\eta_i)$ , light absorption  $(\beta_i)$  and incident light intensity  $(I_{i-1})$  must be input for each of the i layers in the sample. The  $\gamma$  term is the pyroelectric coefficient and Cp is the capacitance of the pyroelectric. The voltage response is proportional to the modulation rate where s=jw and w=2\pi f. Other terms calculated are b<sub>32</sub>, a thermal mismatch factor between the sample and pyroelectric and q<sub>i</sub> a second frequency related term  $(q_i = s/\alpha_i)^{1/2})$ . Appendix C

Derivation of the four layer theoretical model.

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## APPENDIX C

Equations (4-9 - 4-13) are derived using the four layer model presented in Fig. 4-2. The heat conduction equation is written for the individual layers of the model as:

gas: 
$$\frac{\partial^2 \Delta T_1}{\partial x^2} - \frac{1}{\alpha_1} \frac{\partial \Delta T_1}{\partial t} = 0$$
 (C1)

sample: 
$$\frac{\partial^2 \Delta T_2}{\partial x^2} - \frac{1}{\alpha_2} \frac{\partial \Delta T_2}{\partial t} = \begin{bmatrix} -\delta(x)\delta(t) & (\text{transmission mode}) \\ 0 & (\text{inverse mode}) \end{bmatrix}$$
(C2)

contact layer: 
$$\frac{\partial^2 \Delta T_3}{\partial x^2} - \frac{1}{\alpha_3} \frac{\partial \Delta T_3}{\partial t} = 0$$
 (C3)

pyroelectric: 
$$\frac{\partial^2 \Delta T_4}{\partial x^2} - \frac{1}{\alpha_4} \frac{\partial \Delta T_4}{\partial t} = \begin{bmatrix} 0 & (\text{tranmission}) \\ -\delta(x+(d+\ell)\delta(t) & (\text{inve } r \text{ se}) \end{bmatrix}$$
 (C4)

These are inverted into the Laplace domain to give the 's' domain solutions:

$$\Delta T_1(\mathbf{x},\mathbf{s}) = \mathbf{A}_1 \, \mathbf{e}^{-\mathbf{q}_1 \mathbf{x}} \tag{C5}$$

$$\Delta T_2(x,s) = A_2 e^{-q_2 x} + A_3 e^{q_2 x} + S_2(x,s)$$
(C6)

$$\Delta T_3(x,s) = A_4 e^{-q_3(x+\ell)} + A_5 e^{q_3(x+\ell)}$$
(C7)

$$\Delta T_4(x,s) = A_6 e^{Q_4(x+\ell+d)} + S_4(x,s)$$
(C8)

Where  $S_2(x,s)$  is the inhomogeneous solution to the transmission mode temperature profile, and  $S_4(x,s)$  is the inverse mode inhomogeneous solution:

$$S_2(x,s) = \frac{1}{2\alpha_2 q_2} e^{-q_2 |x|}$$
(C9)

$$S_4(x,s) = \frac{1}{2\alpha_2 q_2} e^{-q_4 |x + (\ell + d)|}$$
(C10)

The temperature in the pyroelectric is determined by integrating over the thickness of the active pyroelectric medium (which extends from  $-(1+d+d_{ep})$  to  $-(1+d+d_f)$  in Fig. 4-1):

in transmission mode:

$$\langle \Delta T_4(\mathbf{x}, \mathbf{s}) \rangle = \frac{1}{(d_f - d_{ep})} \int_{-(d+\ell+d_f)}^{-(d+\ell+d_{ep})} \left[ A_6(\mathbf{s}) e^{\mathbf{q}_4(\mathbf{x}+\ell+d)} + \frac{1}{2\alpha_4 q_4} e^{-\mathbf{q}_4 |\mathbf{x}+\ell+d|} \right] d\mathbf{x}$$
(C11)

(inverse mode)

$$<\Delta T_4(x,s)> = \frac{1}{(d_f^- - d_{ep})} \int_{-(d+\ell+d_f)}^{-(d+\ell+d_{ep})} A_6(s) e^{q_4(x+\ell+d)} dx$$

(transmission mode)

The  $A_6$  value is determined by solving the four equations using the conventional boundary conditions of temperature and heat flux continuity at each interface.

(C12)

 $A_6$  is evaluated Using Cramer's rule, given the assumption that there is negligible heat conduction from the sample into the gas phase (e.g.  $b_{12} = 0$ ). For the transmission case:

temperature continuity:

$$A_1 - A_2 - A_3 = 1/2\alpha_2 q_2 \tag{C13}$$

$$A_2L + A_3L^{-1} - A_4 - A_5 = L^{-1}/2\alpha_2q_2$$
 (C14)

$$A_4 D + A_5 D^{-1} - A_6 = 0 \tag{C15}$$

heat flux continuity:

$$-b_{12}A_1 + A_2 - A_3 = -1/2\alpha_2 q_2 \tag{C16}$$

$$-A_{2}L + A_{3}L^{-1} + b_{32}A_{4} - b_{32}A_{5} = -(1/2\alpha_{2}q_{2})$$
(C17)

$$b_{34}A_4D - b_{34}A_5D^{-1} + A_6 = 0$$
 (C18)

where:

$$L = e^{q_2 \ell}$$
  $D = e^{q_3 d}$   $q_i = \sqrt{s/\alpha_i}$ 

$$b_{ij} = \frac{k_i}{k_j} \sqrt{\frac{\alpha_i}{\alpha_i}} \qquad \Gamma_{ij} = (1-b_{ij})/(1+b_{ij})$$

Assuming that the pyroelectric layer is approximately thermally matched to the polymer, the reflection coefficients between pyroelectric/interfacial zone and polymer/interfacial zone are very similar. Therefore we write,  $\Gamma_{32} = -\Gamma_{43}$  and:

$$A_{6} = \frac{4b_{34}}{\alpha_{2}q_{2}} \cdot \frac{-1}{LD(b_{34}+1)(b_{32}+1)} \sum_{n=0}^{\infty} \Gamma_{32}^{n} 1^{-2n} D^{-2n} \{1 + \Gamma_{32}L^{2} - D^{2}\}^{n}$$
(C19)

The term  $\{1 + \Gamma_{32}l^2 - D^2\}^n$  is expanded in a binomial series:

$$\{1 + \Gamma_{32}L^2 - D^2\}^n = \sum_{k=0}^n \frac{n!}{(n-k)!k!} (\Gamma_{32}L^2 - D^2)^k$$
(C20)

The terms in the summation are expanded in a second binomial series yielding:

$$A_{6} = \frac{4b_{34}}{\alpha_{2}q_{2}} - \frac{1}{(b_{34}+1)(b_{32}+1)} \sum_{n=0}^{\infty} \sum_{k=0}^{n} \sum_{j=0}^{k} \frac{n!}{(n-k)! (k-j)!j!}$$

$$\Gamma_{32}^{n+k-j} (-1)^{j+1} L^{-2(n-k+j)-1} D^{-2(n-j)-1}$$
(C21)

Evaluation of the spatial integral in equation (C11-12) gives the transform of the temperature in the pyroelectric:

$$\langle \Delta T_{4}(\mathbf{x}, \mathbf{s}) \rangle = \frac{4 \ \mathbf{b}_{12}}{2(\mathbf{d} - \mathbf{d}_{ep})(1 + \mathbf{b}_{34})(1 + \mathbf{b}_{32})} (\alpha_{4}/\alpha_{2})^{1/2}$$

$$\sum_{n=0}^{n} \sum_{k=0}^{k} \sum_{j=0}^{n} \frac{n!}{(\mathbf{n} - \mathbf{k})!(\mathbf{k} - \mathbf{j})!\mathbf{j}!} \Gamma_{32}^{n+k-j} (-1)^{j+1} \frac{1}{s} \left[ e^{-\sqrt{\tau_{1s}}} - e^{-\sqrt{\tau_{2s}}} \right]$$

$$(C22)$$

Terms of the form  $\{\frac{1}{s} e^{-\sqrt{\tau_i s}}\}$  are readily inverted to expressions of the form  $\{\operatorname{erfc}(1/2[\tau/t])\}$  (22), to give a temperature/time profile of the form:

$$\langle \Delta T_{4} | \mathbf{x}, t \rangle = \frac{4}{2(d_{f} - d_{ep})(1 + b_{34})(1 + b_{32})} (\alpha_{4}/\alpha_{2})^{1/2}$$

$$= \frac{n}{2} \sum_{n=0}^{k} \sum_{k=0}^{k} \frac{n!}{(n-k)!(k-j)!j!} \Gamma_{32}^{n+k-j} (-1)^{j+1} \left[ \operatorname{erfc} \{ \frac{1}{2^{j}} \tau_{2}/\tau \} - \operatorname{erfc} \{ \frac{1}{2^{j}} \tau_{2}/\tau \} \right]$$

$$(C23)$$

The same approach is used to invert the expressions obtained for the inverse mode case.

Appendix D

The Asyst software program to calculate the thermal transmission photopyroelectric response of the four layer model.

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\ TRAN4LAY.THR
\ ASYST SOFTWARE
\ CALCULATES THE THERMAL TRANSMISSION RESPONSE FOR THE 4
LAYER
\ MODEL.

## \ DECLARE THE VARIABLES

INTEGER SCALAR MARC SCALAR N \ M TO KK ARE USED IN "SUMMATION" SCALAR M SCALAR K SCALAR L SCALAR NN SCALAR KK

DP.REAL SCALAR E \ E F & G ARE USED IN "FACTORIAL" SCALAR F SCALAR G

DP.REAL DIM[ 256 ] ARRAY TIME DIM[ 256 ] ARRAY T-RESP \ TIME RESPONSE DIM[ 256 ] ARRAY THERM.RESP \ THERMAL RESPONSE SCALAR GAMMA34 SCALAR GAMMA32 SCALAR ALPHA2 SCALAR ALPHA3 SCALAR ALPHA4 SCALAR B32 SCALAR B34 SCALAR DEP SCALAR L2 SCALAR L3 Υ. SCALAR D SCALAR TIME.RESOLUTION

REAL DIM[ 256 ] ARRAY H1 REAL DIM[ 256 ] ARRAY H2 REAL DIM[ 256 ] ARRAY H3 REAL DIM[ 256 ] ARRAY H3 REAL DIM[ 256 ] ARRAY H4 REAL DIM[ 256 ] ARRAY H5 REAL DIM[ 256 ] ARRAY H6 REAL DIM[ 256 ] ARRAY H7 REAL DIM[ 256 ] ARRAY H8 REAL DIM[ 256 ] ARRAY H9 REAL DIM[ 256 ] ARRAY H10

COMPLEX DIM[ 4096 ] ARRAY H(T) 15 STRING FNAME



\ WORDS TO INPUT VALUES

: INPUT.VALUES NORMAL.DISPLAY SCREEN.CLEAR THICKNESS: " "TYPE #INPUT L2 := CR " POLYMER LAYER CR " DIFFUSIVITY: " "TYPE #INPUT ALPHA2 := CR " "TYPE #INPUT L3 := CR " ALIEGNED LAYER THICKNESS: CR " DIFFUSIVITY: " "TYPE #INPUT ALPHA3 := CR CR " PVDF LAYER DEPOLED THICKNESS: " "TYPE #INPUT DEP := CR " DIFFUSIVITY: " "TYPE #INPUT ALPHA4 := CR CR " POLYMER-ALIEGNED INTERFACE B32 : " "TYPE #INPUT B32 := CR " ALIEGNED-PVDF INTERFACE B34 : " "TYPE #INPUT B34 := CR CR " NUMBER OF SUMMATIONS DESIED : " "TYPE #INPUT M := CR " TIME.RESOLUTION : " "TYPE #INPUT TIME.RESOLUTION := : VALUES NORMAL.DISPLAY SCREEN.CLEAR " PROGRAM : TRAN4LAY.THR " "TYPE CR CR -1. 2. FIX.FORMAT CR " POLYMER LAYER THICKNESS: L2 (nm) " "TYPE L2 1.E-9 / CR " DIFFUSIVITY: (ALPHA2 E-7) " "TYPE ALPHA2 1.E-7 / . CR CR " ALIEGNED LAYER THICKNESS: L3 (nm) " "TYPE L3 1.E-9 / CR " DIFFUSIVITY: (ALPHA3 E-7) " "TYPE ALPHA3 1.E-7 / . CR CR " PVDF LAYER DEPOLED THICKNESS: DEP (nm) " "TYPE DEP 1.E-9 / . CR " DIFFUSIVITY: (ALPHA4 E-7) " "TYPE ALPHA4 1.E-7 / . CR CR " TIME.RESOLUTION : (E-9) " "TYPE TIME.RESOLUTION 1.E-9 / . CR -1. 4. FIX.FORMAT CR " POLYMER-ALIEGNED INTERFACE B32 : " "TYPE B32 . CR " ALIEGNED-PVDF INTERFACE B34 : " "TYPE B34 . CR CR " NUMBER OF SUMMATIONS DESIED: (M) " "TYPE M . CR CR " GAMMA34 : " "TYPE GAMMA34 .

```
CR "
            GAMMA32 : " "TYPE GAMMA32 .
;
: FIX.VALUES
1 B34 - 1 B34 + / GAMMA34 :=
1 B32 - 1 B32 + / -1. * GAMMA32 :=
TIME []RAMP
TIME 1. - TIME :=
0.1 TIME [ 1 ] :=
TIME TIME.RESOLUTION * TIME :=
;
\ THERMAL TIME CONSTANTS ARE CACULATED
: Tl
N K - L + 2 * 1 + L2 * ALPHA2 SQRT /
NL - 2 * 1 + L3 * ALPHA3 SQRT / +
DEP ALPHA4 SQRT / +
;
: T2
N K - L + 2 * 1 + L2 * ALPHA2 SQRT /
N L - 2 * 1 + L3 * ALPHA3 SORT / +
9.E-6 ALPHA4 SORT / +
;
: FACTORIAL
F := 1 E :=
F1 > IF
      BEGIN
          F 1 - G :=
          FG*E*E :=
          F 2 - F :=
        F 2 <
      UNTIL
E F :=
ELSE
1 F := \ FOR 0! OR 1!
THEN
F
;
: BI.COEFF
N K - FACTORIAL K L - FACTORIAL * L FACTORIAL * INV
N FACTORIAL *
```

: ERFC ERF 1 SWAP -; DP.REAL DIM[ 256 ] ARRAY CHECK.ARRAY INTEGER SCALAR CHECK \ CHECK FOR ARGUEMENTS THAT WILL BE TOO LARGE FOR THE ERFC \ FUNCTION - PUT A FLAG (\*) ON THE SCREEN IF THIS OCCURS : TEST.THE.ARRAY.VALUES CHECK.ARRAY := 1 CHECK := 10 0 DO CHECK.ARRAY [ CHECK ] 106 > IF 106 CHECK.ARRAY [ CHECK ] := " \* " "TYPE THEN 1 CHECK + CHECK := LOOP " "TYPE CHECK.ARRAY ; : DELAY.TERMS STACK.CLEAR TIME SQRT 2 \* INV T1 \* TEST.THE.ARRAY.VALUES ERFC TIME SQRT 2 \* INV T2 \* TEST.THE.ARRAY.VALUES ERFC -T-RESP := STACK.CLEAR 7 : GUTS STACK CLEAR . DELAY.TERMS BI.COEFF -1 L \*\* \* GAMMA32 N K + L - \*\* \* T-RESP \* ;

: SUMMATIONS

.

;

```
STACK.CLEAR
O THERM.RESP :=
0 N :=
M O DO
N NN :=
        0 K :=
        NN 1 + 0 DO
        К КК :=
                  0 L :=
                  KK 1 + 0 DO
                                GUTS
                                THERM.RESP + THERM.RESP :=
                  L 1 + L :=
                  LOOP
        K 1 + K :=
        LOOP
CR
N 1 + N :=
LOOP
;
: READ.DSET
CR " INPUT FILENAME: " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
H(T) FILE>ARRAY
FILE.CLOSE
7
: READ.P10
CR " IPUT FILENAME *.P10 : " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
1 SUBFILE H1 FILE>ARRAY
2 SUBFILE H2 FILE>ARRAY
3 SUBFILE H3 FILE>ARRAY
4 SUBFILE H4 FILE>ARRAY
5 SUBFILE H5 FILE>ARRAY
6 SUBFILE H6 FILE>ARRAY
7 SUBFILE H7 FILE>ARRAY
8 SUBFILE H8 FILE>ARRAY
9 SUBFILE H9 FILE>ARRAY
10 SUBFILE H10 FILE>ARRAY
FILE.CLOSE
;
```

```
: WRITE.P10
CR " INPUT FILENAME *. P10 : " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
1 SUBFILE H1 ARRAY>FILE
2 SUBFILE H2 ARRAY>FILE
3 SUBFILE H3 ARRAY>FILE
4 SUBFILE H4 ARRAY>FILE
5 SUBFILE H5 ARRAY>FILE
6 SUBFILE H6 ARRAY>FILE
7 SUBFILE H7 ARRAY>FILE
8 SUBFILE H8 ARRAY>FILE
9 SUBFILE H9 ARRAY>FILE
10 SUBFILE H10 ARRAY>FILE
FILE.CLOSE
7
: LINDA
THERM.RESP
H(T) SUB[ 0 , 256 ] ZREAL
CONV.APER
SUB[ 0 , 256 ]
DUP ^MAX [ 256 ] /
;
: LINDA.INV
THERM.RESP
H(T) SUB[ 0 , 256 ] ZREAL
CONV.APER
SUB[ 0 , 256 ]
-1. *
DUP ^MAX [ 256 ] /
;
: DEFAULT
400.E-9 L2 :=
10.E-9 L3 :=
450.E-9 DEP :=
0.5E-7 ALPHA2 :=
0.5E-7 ALPHA3 :=
0.5E-7 ALPHA4 :=
1.1 B32 := 0.9 B34 :=
500.E-9 TIME.RESOLUTION :=
1 M :=
FIX.VALUES
;
: SAVE.HT
H(T) SUB[ 0 , 256 ] ZREAL
```

DUP ^MAX [ 256 ] /

•

;

-

\ INPUT.VALUES
\ VALUES - PRINTS OUT THE VALUES
\ FIX.VALUES

.

\ SUMMATIONS

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Appendix E

The Asyst software program to calculate the thermal inverse mode photopyroelectric response of the four layer model.

\ FOUR LAYER THEORY AUG 30 92 PROGRAM: 4LTHRPVD.LEN (ASYST SOFTWARE) \ V POLYMER BULK LAYER, L2, CONTAINS ALL RELECTIONS ALIENGED LAYER, LAYERS, CONTAINS NO REFLECTIONS INVERSE THEORY ١. \ DECLARE THE VARIABLES INTEGER SCALAR MARC SCALAR M SCALAR N DP.REAL DIM[ 256 ] ARRAY TIME DIM[ 256 ] ARRAY T-RESP \ TIME RESPONSE DIM[ 256 ] ARRAY THERM.RESP \ THERMAL RESPONSE SCALAR GAMMA34 SCALAR GAMMA32 SCALAR XX SCALAR ALPHA2 SCALAR ALPHA3 SCALAR ALPHA4 SCALAR B32 SCALAR B34 SCALAR DEP SCALAR L SCALAR D SCALAR TIME.RESOLUTION REAL DIM[ 256 ] ARRAY H1 REAL DIM[ 256 ] ARRAY H2 REAL DIM[ 256 ] ARRAY H3 REAL DIM[ 256 ] ARRAY H3 REAL DIM[ 256 ] ARRAY H4 REAL DIM[ 256 ] ARRAY H5 REAL DIM[ 256 ] ARRAY H6 REAL DIM[ 256 ] ARRAY H7 REAL DIM[ 256 ] ARRAY H8 REAL DIM[ 256 ] ARRAY H9 REAL DIM[ 256 ] ARRAY H10 COMPLEX DIM[ 4096 ] ARRAY H(T) 15 STRING FNAME \ WORDS TO INPUT THE EXPERIMENTAL PARAMETERS : INPUT.VALUES NORMAL, DISPLAY SCREEN.CLEAR CR " POLYMER LAYER THICKNESS: " "TYPE #INPUT L := CR " DIFFUSIVITY: " "TYPE #INPUT ALPHA2 := CR

THICKNESS: " "TYPE #INPUT D := CR " ALIEGNED LAYER DIFFUSIVITY: " "TYPE #INPUT ALPHA3 := CR " CR CR " PVDF LAYER DEPOLED THICKNESS: " "TYPE #INPUT DEP := DIFFUSIVITY: " "TYPE #INPUT ALPHA4 := CR " CR CR " POLYMER-ALIEGNED INTERFACE B32 : " "TYPE #INPUT B32 := CR " ALIEGNED-PVDF INTERFACE B34 : " "TYPE #INPUT B34 := CR CR " NUMBER OF SUMMATIONS DESIED : " "TYPE #INPUT M := CR " TIME.RESOLUTION : " "TYPE #INPUT TIME.RESOLUTION := : : VALUES NORMAL DISPLAY " PROGRAM : 4LTHRPVD.LEN " "TYPE CR CR SCREEN.CLEAR -1. 2. FIX.FORMAT CR " POLYMER LAYER THICKNESS: L (nm) " "TYPE L 1.E-9 / . CR " DIFFUSIVITY: (ALPHA2 E-7) " "TYPE ALPHA2 1.E-7 / . CR CR " ALIEGNED LAYER THICKNESS: D (nm) " "TYPE D 1.E-9 / . DIFFUSIVITY: (ALPHA3 E-7) " "TYPE ALPHA3 1.E-CR " 7 / . CR CR " PVDF LAYER DEPOLED THICKNESS: DEP (nm) " "TYPE DEP 1.E-9 / . CR " DIFFUSIVITY: (ALPHA4 E-7) " "TYPE ALPHA4 1.E-7 / . CR CR " TIME.RESOLUTION : (E-9) " "TYPE TIME.RESOLUTION 1.E-9/. CR -1. 4. FIX.FORMAT CR " POLYMER-ALIEGNED INTERFACE B32 : " "TYPE B32 . CR " ALIEGNED-PVDF INTERFACE B34 : " "TYPE B34 . CR CR " NUMBER OF SUMMATIONS DESIED: (M) " "TYPE M . CR CR " (1-B34)/(1+B34) = GAMMA34 : "TYPE GAMMA34CR " (1-B32)/(1+B32) -1 \* = GAMMA32 : " "TYPE GAMMA32 CR CR " XX : " "TYPE XX . ; : FIX.VALUES 1 B34 - 1 B34 + / GAMMA34 := 1 B32 - 1 B32 + / -1. \* GAMMA32 := GAMMA34 GAMMA32 \* 1 + INV GAMMA34 GAMMA32 + \* XX := TIME []RAMP TIME 1. - TIME := 0.1 TIME [ 1 ] :=

TIME TIME.RESOLUTION \* TIME := ; \ CALCULATE THE THERMAL TIME CONSTANTS : T1 2 L N \* \* ALPHA2 SQRT / 2. D \* ALPHA3 SQRT / + DEP ALPHA4 SQRT / + ; : T2 2. L \* N \* ALPHA2 SORT / 2. D \* ALPHA3 SQRT / + 9.E-6 ALPHA4 SQRT / + ; : T3 2. L \* N 1 + \* ALPHA2 SQRT / DEP ALPHA4 SQRT / + ; : T4 2 L \* N 1 + \* ALPHA2 SQRT / 9.E-6 ALPHA4 SQRT / + 7 : T5 DEP ALPHA4 SQRT / 2 L N \* \* ALPHA2 SORT / + ; : T6 2 L \* N \* ALPHA2 SQRT / 9.E-6 ALPHA4 SQRT / + 7 : T7 2 L \* N 1 + \* ALPHA2 SQRT / D ALPHA3 SQRT / + DEP ALPHA4 SQRT / + ; : T8 2 L \* N 1 + \* ALPHA2 SQRT /D ALPHA3 SQRT / + 9.E-6 ALPHA4 SQRT / + ; : T9 DEP ALPHA4 SQRT / ;

```
: T10
9.E-6 ALPHA4 SQRT /
:
: ERFC
ERF 1 SWAP -
:
DP.REAL DIM[ 256 ] ARRAY CHECK.ARRAY
INTEGER SCALAR CHECK
\ CHECK THE ARGUEMENTS FOR THE ERFC FUNCTIONS
\ IF THEY ARE TOO LARGE THE PROGRAM WILL CRASH
\ SET THE MAXIMUM VALUE TO 106 AND IF THE
ARGUEMENTS ARE TOO LARGE PUT A FLAG ON THE SCREEN
: TEST. THE. ARRAY. VALUES
CHECK.ARRAY :=
1 CHECK :=
10 0 DO
CHECK.ARRAY [ CHECK ] 106 > IF
106 CHECK.ARRAY [ CHECK ] :=
" * " "TYPE
THEN
1 CHECK + CHECK :=
LOOP
               " "TYPE
11
CHECK.ARRAY
;
: FIRST.TERM
T9 2 TIME SQRT * / TEST. THE. ARRAY. VALUES ERFC
T10 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC -
: SECOND.TERM
0 T-RESP :=
T1 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC
T2 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC - GAMMA32 *
T3 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC
T4 2 TIME SQRT * / TEST. THE. ARRAY. VALUES ERFC - GAMMA34 *
GAMMA32 * +
T-RESP :=
T5 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC
T6 2 TIME SQRT * / TEST. THE. ARRAY. VALUES ERFC - GAMMA34 *
T7 2 TIME SQRT * / TEST.THE.ARRAY.VALUES ERFC
T8 2 TIME SQRT * / TEST. THE. ARRAY. VALUES ERFC - +
T-RESP + T-RESP :=
;
: SUM.SECOND.TERM
0 N :=
```

```
0. THERM.RESP :=
M O DO
SECOND.TERM
-1. N ** XX N ** *
T-RESP * THERM.RESP + THERM.RESP :=
N 1 + N :=
LOOP
;
: GO
FIX.VALUES
                         1
SUM.SECOND.TERM
                         2
FIRST.TERM \ -1. *
                            3
                         4
THERM.RESP +
                             ٠
THERM.RESP :=
                         5
THERM.RESP -1. * THERM.RESP :=
\ FILE HANDELING ROUTINES
: READ.DSET
CR " INPUT FILENAME: " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
H(T) FILE>ARRAY
FILE.CLOSE
;
: READ.P10
CR " IPUT FILENAME *.P10 : " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
1 SUBFILE H1 FILE>ARRAY
2 SUBFILE H2 FILE>ARRAY
3 SUBFILE H3 FILE>ARRAY
4 SUBFILE H4 FILE>ARRAY
5 SUBFILE H5 FILE>ARRAY
6 SUBFILE H6 FILE>ARRAY
7 SUBFILE H7 FILE>ARRAY
8 SUBFILE H8 FILE>ARRAY
9 SUBFILE H9 FILE>ARRAY
10 SUBFILE H10 FILE>ARRAY
FILE. CLOSE
;
: WRITE.P10
CR " IPUT FILENAME *.P10 : " "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE.OPEN
1 SUBFILE H1 ARRAY>FILE
```



2 SUBFILE H2 ARRAY>FILE 3 SUBFILE H3 ARRAY>FILE 4 SUBFILE H4 ARRAY>FILE 5 SUBFILE H5 ARRAY>FILE 6 SUBFILE H6 ARRAY>FILE 7 SUBFILE H7 ARRAY>FILE 8 SUBFILE H8 ARRAY>FILE 9 SUBFILE H9 ARRAY>FILE 10 SUBFILE H10 ARRAY>FILE FILE.CLOSE ; : LINDA THERM.RESP H(T) SUB[ 0 , 256 ] ZREAL CONV.APER SUB[ 0 , 256 ] DUP ^MAX [ 256 ] / ; : LINDA.INV THERM.RESP H(T) SUB[ 0 , 256 ] ZREAL CONV.APER SUB[ 0 , 256 ] -1. \* DUP ^MAX [ 256 ] / ; : DEFAULT 400.E-9 L := 1.E-9 D := 450.E-9 DEP := 0.5E-7 ALPHA2 := 0.5E-7 ALPHA3 := 0.5E-7 ALPHA4 := 1.1 B32 := 0.9 B34 := 500.E-9 TIME.RESOLUTION := 1 M := FIX.VALUES VALUES ; : SAVE.HT H(T) SUB[ 0 , 256 ] ZREAL DUP ^MAX [ 256 ] / ; \ WORDS TO RUN THE PROGRAM





- \ INPUT.VALUES
  \ VALUES PRINTS OUT THE VALUES
  \ FIX.VALUES
  \ GO

Appendix F

Parallel port communication between three computers

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Modifying the parallel for read/write communication.

A PC printer port is designed to be output only as communication between a computer and printer is unidirectional. Fortunately, it is easy to modify a common printer port to allow both input and output, and the modification should not effect normal operation. The standard printer interface uses a 74LS374 (Motorola) to drive the output connector, and an input buffer to read back the state of the output pins is already provided.

According to the IBM Options and Adapters Technical Reference, the '374 is at U41 on the monochrome/printer adapter, at U18 on the AT serial/parallel adapter and at U4 on the plain printer adapter. The '374 is an 8-bit latch with tri-state outputs. In the original design OE (pin #1) is grounded, always enabling the outputs. If you liberate this pin from ground and connect it instead to a spare output bit on the 74LS174 hex D latch that drives miscellaneous printer control lines. You can control the read/write selection of the '374 by controlling this line.

The '174 is located at U39 on the monochrome board, at U4 on the AT serial/parallel card and U7 on the plain printer adapter. The pin from '174 that you want to control the port is the one that latches BD5 from the data bus. On the monochrome card and plain printer adapters this is pin #15, while it is pin 10 on the AT serial/parallel card.

Printer port (plain) is diagrammed in Fig. F-1. To make the port bi-directional the pin #1 from LS374 was cut and attached to pin #1 of the 26 pin printer connector. By writing a TTL low the printer port writes 8 bits from the bus to the parallel port. By writing a TTL high the printer port reads the 8 bits at the parallel port and puts the values on the bus.

The pin out of the printer port is diagrammed in Fig. F-2. Pins 2-9 are located at the base address (BA) and are the lines for writing and reading the data from the parallel ports. Pin #1 (BA+2) is used to control the port being in read mode or write mode. Pin 12 (BA+1) and pin 14 (BA+2) are used for handshaking.

The pin to pin connections for communications between three computers is illustrated in Fig. F-3.



Fig. F-1 Wiring diagram taken from owners manual of printer port. The \* indicates the position the wire was cut and the solid line indicates where the cut line was re-attached. The final connection is from pin 1 of '374 to pin 1 of the printer port.



Fig. F-2. Pin diagram of a printer port showing the base address and offset of each pin.



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APPENDIX G

Construction of a XY-translator

A XY-translator was constructed using two micrometers (Ealing Scientific), two high precision motors (Compumotor #s57-51-mo, Le Groupe Rotalec, St. Laurent, P.Q.), two DB drives ( Compumotor, Le Groupe Rotalec, St. Laurent, P.Q.), and a single 24VDC, 4.8 amps, linear power supply (#55067 Active Electronics Montreal, P.Q.). The DB drives are designed to convert TTL pulses to rotation of the shaft of the drive motor. Jumpers on the DB drives allow the user to select resolution between 200 TTL pulses per shaft resolution to 25,400 TTL pulses per shaft resolution. The exact resolution of the XY-translator depends not only on the step size but on the quality of the micrometer and the hysteris in the connection between the motors and micrometers. In theory the XY-translator can provide nanometer resolution but in practice we used only 100 µm resolution. This was acheived by setting the jumpers to 200 TTL pulses per resolution and moving the axis 40 pulses for each step. The s-motors generate a large amount of heat when they are not translating and should either be shut off when not being used or mounted on a good heat sink.

The owners manuals for the DB drives and s-motors provide a range of wiring options depending on the required torque, the required spatial resolution and load being driven. We needed four signal lines (two to send output pulses and two to set direction of movement of 2 different motors) to run the translator. In practice we found that a single TTL pulse from our data aquisition board did not provide enough current to the DB drives for reliable translation. To solve this problem two output lines from the data aquisition board went to each control point of the DB drives. To do this the digital out lines were used. Writing a binary 1100 0000 was one signal 0011 0000 was a second and so on.

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The software program to run the translator ("Translat.img") is included in this appendix. This particular version is run in conjunction with other computers and is used in generating the 3-D photothermal images. The program operates as follows:

"Low.res.image" runs the program

- the direction is chosen to be vertical and the number of steps between positions 40.

- a 100 msec. delay lets the electronic jitter settle before a new move is initiated

- the data aquisition board is set to output a signal on its binary channel and the translator is moved by outputting the correct number of pulses.

the direction (x and y or forwards and backwards) are always noted so that translator never drives the spindle of the micrometer into the base of the micrometer.

**N FILE: TRANSLAT.IMG** N DATE : NOV 30 92 V program to read in a call from the master computer V and translate the xy micrometers a set distance. Adeclar the scalars INTEGER SCALAR MARC INTEGER SCALAR G INTEGER SCALAR H INTEGER SCALAR CRAM SCALAR LLSNB SCALAR MMSNB SCALAR DIRECTION.VERTICAL SCALAR DIRECTION.HORIZONTAL SCALAR PULSE#.VERTICAL SCALAR PULSE#.HORIZONTAL INTEGER DIM[ 1 ] ARRAY TTLVOLTAGE DP.INTEGER SCALAR TTLSEG TTLVOLTAGE ADDRESS . TTLSEG := REAL SCALAR N **\SEND A STEP** : GGO LLSNB 8930 PORT.OUT MMSNB 8931 PORT.OUT : SCAN.THE.IMAGE.VERTICALLY \THIS MOTOR IS LEFT ON ALL THE TIME 0. MMSNB := **\NO EFFECT HORIZONTALLY** PULSE#.VERTICAL 0 DO \40 STEPS = 0.1 MM FOR 200 STEPS/REV. 0 DIRECTION.VERTICAL + LLSNB := \DOWN 5. MSEC.DELAY GGO 3 DIRECTION.VERTICAL + LLSNB := \UP 5. MSEC.DELAY GGO LOOP : : SCAN.THE.IMAGE.HORIZONTALLY **\MUST TURN ON THE MOTOR BEFORE EXECUTING \TO PREVENT OVER HEATING MOTOR IS SHUT OF WHILE NOT BEING USED \TURN ON THE MOTOR** 9 49890 PORT.OUT \SET BOARD ANALOGUE 1 4835 PORT.OUT \ SETS THE COMPUTER THE WRITE TO A/D CHANNEL #1 **\TURN ON THE XY-TRANSLATION MOTORS** -5. TTLVOLTAGE := TILSEG DEF.SEG 0 PEEK 13026 PORT.OUT \ READ LEAST SIG BIT AND WRITE IT OUT 1 PEEK 13027 PORT.OUT \ MOST **\SET THE BOARD TO DIGITAL CONTROL TO MOVE THE XY-MOUNT** 8 49890 PORT.OUT \BOARD SET BINARY 0 8930 PORT.OUT 0 8931 PORT.OUT

2500. MSEC.DELAY VALLOW TIME FOR THE MOTOR WINDINGS TO ENERGIZE

0. LLSNB := \NO EFFECT IN THE VERTICAL DIRECTION

```
PULSE#.HORIZONTAL 0 DO

0 DIRECTION.HORIZONTAL - MMSNB := \DOWN

5. MSEC.DELAY

GGO

3 DIRECTION.HORIZONTAL - MMSNB := \UP

5. MSEC.DELAY

GGO

LOOP
```

**NTURN OFF MOTOR** 

```
9 49890 PORT.OUT \ SET BOARD ANALOGUE

1 4835 PORT.OUT \ SETS COMPUTER TO WRITE TO A/D CHANNEL #1

\TURN XY-TRANSLATOR MOTOR OFF TO PREVENT

\IT FROM BURNING OUT

2048 TTLVOLTAGE :=

TTLSEG DEF.SEG

0 PEEK 13026 PORT.OUT

1 PEEK 13027 PORT.OUT
```

:

**\PART 4 EXECUTE THE MOVEMENT OF THE TRANSLATOR** 

: SSTART

0 PULSE#.HORIZONTAL < IF SCAN.THE.IMAGE.HORIZONTALLY THEN

-

0 PULSE#.VERTICAL < IF \MUST CHECK FOR THE CASE OF SCAN.THE.IMAGE.VERTICALLY THEN\NO MOVEMENT SELECTED AS ASYST \WILL MOVE AT LEAST 1 STEP MINIMUM

:

;

: TRANSLATE

\SET THE BOARD TO DIGITAL CONTROL TO MOVE THE XY-MOUNT 8 49890 PORT.OUT \BOARD SET BINARY 0 8930 PORT.OUT 0 8931 PORT.OUT

SSTART VUSER INPUTS THE MOVES & THE STEPPER MOTER THEN MOVES

9 49890 PORT.OUT \ BOARD SET TO ANALOGUE 0 4835 PORT.OUT \ SETS COMPUTER TO WRITE TO A/D CHANNEL #0

: HANDSHAKE

0 632 PORT.OUT NIM READY, SEND 1 BYTE

```
SAMPLE HAND TILL BYTE IS SENT
   begin
    stack.clear
    633 portin 8 / \sample handshake line
    18 =
          Nif 18 is on the stack then ready to move
   until
 1 632 PORT, OUT IN GOT IT, DON'T SEND ANY MORE DATA
 NG+G :=
 TRANSLATE
   begin
          WAIT TILL THEY ARE READY WITH ANOTHER BYTE
    stack.clear
    633 port in 8 / \ sample handshake line
    20 =
             Nif 9 is on the stack then fresh byte was sent.
   until
0.632 PORT.OUT
:
: TRANSSHAKE
0.632 PORT.OUT NIM READY, SEND 1 BYTE
         \SAMPLE HAND TILL BYTE IS SENT
   begin
   stack.clear
    633 portin 8 / \sample handshake line
   18 =
          Nif 18 is on the stack then ready to move
   until
1 632 PORT.OUT IN GOT IT, DON'T SEND ANY MORE DATA
 TRANSLATE
          WAIT TILL THEY ARE READY WITH ANOTHER BYTE
  begin
   stack.clear
    633 port.in 8 / \sample handshake line
    20 =
             Nif 9 is on the stack then fresh byte was sent
  until
0 632 PORT.OUT
;
: LOW RES.IMAGE
CR CR " .....SYSTEM IS INITIALISED" "TYPE
CR CR " THE COMPUTER TO CONTROL THE TRANSLATOR IS READY ... " "TYPE
40 PULSE#.VERTICAL := 0 PULSE#.HORIZONTAL :=
12 DIRECTION.VERTICAL := 0 DIRECTION.HORIZONTAL :=
1 H := \HORIZONTAL
1 G := \VERTICAL
1 N :=
500 DO
 49 0 DO
   HANDSHAKE
 LOOP
0 PULSE#.VERTICAL := \MOVE HORIZONTALLY I UNIT
```

40 PULSE#.HORIZONTAL := TRANSSHAKE 0 PULSE#.HORIZONTAL := DIRECTION.VERTICAL CASE 12 OF ." " 0 DIRECTION.VERTICAL := -1. N := 50 G := ENDOF 0 OF ." 12 DIRECTION.VERTICAL := 1, N := 1 G := ENDOFENDCASE 40 PULSE#.VERTICAL := H. H1+H:= LOOP CR CR CR CR - ----- TURN OFF MOTORS AT SWITCH ------ " "TYPE CR CR CR CR
\_\_\_\_\_ ALL DONE \_\_\_\_\_ "TYPE CR 

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Appendix H

Construction of the spectrophotometer

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A spectrophotometer was constructed as shown in Fig. H-1. The incident light beam is split into two components. The first is directed onto a reference photodiode (Hamamatsu s1226-44kb) to record fluctuations in the source. The second component is directed onto the sample. Collection optics collect the transmitted light and direct it onto the photodiode detection surface. The strongly degraded samples scattered light and large refractive index changes which made collection of all transmitted light difficult. The two outputs were directed into a electronic switching mechanism which allowed the computer to read one signal at a time. The transmitted light in the clear undegraded region of the film was taken as the light directed onto the sample.



Fig. H-1 Schematic of the spectrophotometer. The wavelengist of interest is split into two beams. The first component is directed onto photodiode #1 (Hamamatsu s1226-44kb) which records fluctuations in the light source. The second component is directed onto the sample and the transmitted component is recorded by photodiode #2. The two photodiodes are read sequentially by switching the signal using a ADG201A electronic switch.

\OPT-DENS.DOC \A PROGRAM TO RECORD THE SPECTROPHOTOMETRIC IMAGE OF POLYMER \SAMPLES \THE PROGRAM USES THE IBM DATA AQUISITION BOARD \NO SERIAL NUMBER IS ON THE BOARD AND NO INDENTIFYING NAME

**\DECLARE THE VARIABLES** 

INTEGER SCALAR MARC REAL DIM[ 50, 50, 2 ] ARRAY STOREAVG \store the data from each run REAL SCALAR D REAL SCALAR Q REAL SCALAR BKGD REAL SCALAR SAMPLE INTEGER DIM[ 50 ] ARRAY DBANK INTEGER SCALAR MS \holds the most sig. byte of data INTEGER SCALAR LS \holds the least sig. byte of data INTEGER SCALAR MSNB \digital nb. equiv. to MS INTEGER SCALAR LSNB \digital nb. equiv. to LS

DP.INTEGER SCALAR BANKSEG INTEGER SCALAR LB INTEGER SCALAR UB INTEGER SCALAR LWNB INTEGER SCALAR HGNB INTEGER SCALAR G INTEGER SCALAR H

25 STRING FILENAME 40 STRING SPECIFICS1 40 STRING SPECIFICS2 40 STRING SPECIFICS3 40 STRING SPECIFICS4 40 STRING SPECIFICS5

REAL SCALAR N9 SCALAR N1 SCALAR N15 \ comments to attach to the files

Nleast sig, byte of data incoming

Nupper byte of data incoming

\ digital nb. equiv. to LB

\ digital nb. equiv. to UP

Ngives the address of DBANK

INTEGER DIM[ 50 ] ARRAY DBANK2 DP.INTEGER SCALAR BANKSEG2 INTEGER SCALAR LB2 INTEGER SCALAR UB2

: INPUT-VALUES \allows the user to input relevant parameters NORMAL.DISPLAY SCREEN.CLEAR CR " SET XY-TRANSLATOR TO STARTING POSITION MANUALLY " "TYPE CR CR CR CR " # OF AVGS AT EACH POINT ? " "TYPE #INPUT N1 := CR " RANDOM SAMPLING DELAY ?" "TYPE #INPUT N15 := CR CR CR " NB \*\*\* THIS IS A LOW RESOLUTION PLOT [ 50 X 50 ] " "TYPE CR CR : : : START

 Vects up the data aquisition board

 0 LS =
 VETS COUNTER TO ZERO

 0 DBANK :=
 VETS THE INFO ARRAY TO ZERO

 DBANK ADDRESS . BANKSEG :=
 Value address is found



```
0 LB :=
0 UB :=
0 STOREAVG :=
9 49890 PORT.OUT
          A HAND GARE CO-ORDS FOR THE DATA ARRAY
1 h :=
1 G :=
0 DBANK2 :=
DBANK2 ADDRESS . BANKSEG2 :=
0 LB2 :=
0 UB2 :=
:
: READ2BIT
1 738 PORT.OUT
0 739 PORT.OUT
0 738 PORT.OUT
0 739 PORT.OUT
 8930 PORT.IN LWNB :=
 8931 PORT.IN HGNB :=
:
: STORE2BIT
1 LB + UB :=
BANKSEG def.seg
LWNB LB poke
HGNB UB poke
2LB+LB:=
;
: STORE2BIT2
1 LB + UB :=
BANKSEG2 def.seg
LWNB LB poke
HGNB UB poke
2LB+LB ==
:
: PROCESSPOINT
\ process the binary data and convert to volts
DBANK 4. - DBANK := \OFFSET CORRECTION ON THE BOARD
 DBANK SUB[1,n1,1] MEAN D =
 D 10 * 4096 / 5 - D = \CONVERT BITS TO VOLTS
 D SAMPLE := \NOT USING A REVERSED BIAED DIODE -1
 DBANK2 1 - DBANK2 :=
                         \OFFSET CORRECTION ON THE BOARD
DBANK2 SUB[1, n1, 1] MEAN D =
 D 10 * 4096 / 5 - D := \CONVERT BITS TO VOLTS
D BKGD =
:
: DATASTORE
N NEED TO USE 51 H - OR THE IMAGE COMES OUT BACKWARDS
SAMPLE STOREAVG[51H-,G,1] =
BKGD STOREAVG[51H-,G,2] :=
SAMPLE.
:
```



: OPTIMIZE

 $\$  type this word to optimize the positions of the photodetectors  $\$  the photodiode readings are output to the screen

NORMAL DISPLAY " WE WILL NOW OPTIMIZE THE TWO POSITIONS OF THE PHOTODIODES WITH " "TYPE " RESPECT TO THE INCOMING LIGHT SOURCE - "TYPE CR CR " ... FIRST THE SAMPLE PHOTODIODE (MARKED PVDF ON SWITCH) " "TYPE CR " HIT SPACE BAR TO START ..... THEN AGAIN WHEN YOU ARE DONE " "TYPE 0.632 PORT.OUT BEGIN **PCKEY 32 =** UNTIL STACK.CLEAR BEGIN 0 LB := 10 0 DO RAND.UNIF 30. • MSEC.DELAY READ2BIT STORE2BIT LOOP DBANK 4. - DBANK := \3 = .0095 4.0.0018 DBANK SUB[ 1, 10, 1 ] MEAN D := D 10. \* 4096 / 5 - D == D. CR\USING A REVERSED BIASED P.D. STACK.CLEAR ?KEY UNTIL STACK.CLEAR " ... SECOND THE BACKGROUND PHOTODIODE (MARKED P.D. ON SWITCH) " "TYPE CR " HIT SPACE BAR TO START .... THEN AGAIN WHEN YOU ARE DONE " "TYPE 1 632 PORT.OUT BEGIN PCKEY 32 = UNTIL STACK CLEAR BEGIN 0 LB :=-100 DO RAND.UNIF 30. \* MSEC.DELAY READ2BIT STORE2BIT LOOP DBANK 4. - DBANK := DBANK SUB[ 1, 10, 1 ] MEAN D := D 10. \* 4096/5- D := D. CR ?KEY UNTIL STACK CLEAR :

: GETIPOINT 200. N15 • 2. • MSEC.DELAY 0632 PORT.OUT \SET SWITCH TO THE PVDF

```
0LS :=
0 LB :=
nl 0 do
  RAND.UNIF n15 * MSEC.DELAY \random delay between taking points
 READ2BIT
                     A to minimize sampling error
  STORE2BIT
loop
1 632 PORT.OUT \ SET SWITCH TO THE PHOTODIODE
0LS :=
0 LB :=
n1 0 do
  RAND.UNIF n15 * MSEC.DELAY Nrandom delay between taking points
  READ28IT
                    \ to minimize sampling error
  STORE2BIT2
loop
PROCESSPOINT
DATASTORE
:
: SAVECOPY
          \*.LRI = LOW RESOLN IMAGE
CR * INPUT FILENAME •.LRI * * TYPE
 "INPUT FILENAME ":=
FILENAME DEFERS FILE OPEN
CR " INPUT FREQUENCY, WAVELENGTH AND OTHER SPECIFICS " "TYPE
CR " 1 " "TYPE "INPUT SPECIFICS1 ":=
CR "2" TYPE "INPUT SPECIFICS2 "=
CR "3" TYPE "INPUT SPECIFICS3 "=
CR "4" TYPE "INPUT SPECIFICS4 "=
CR " 5 " "TYPE "INPUT SPECIFICSS "=
SPECIFICS1 1 >COMMENT
SPECIFICS2 2 >COMMENT
SPECIFICS3 3 >COMMENT
SPECIFICS4 4 >COMMENT
SPECIFICS5 5 >COMMENT
I SUBFILE STOREAVG ARRAY>FILE
FILE.CLOSE
:
: READDISK
CR " INPUT FILENAME - . LRI " "TYPE
 "INPUT FILENAME ":=
FILENAME DEFERS FILE.OPEN
?COMMENTS
1 SUBFILE STOREAVG FILE>ARRAY
FILE.CLOSE
```

:

: TEXTIT.4FILES \saves the optical density image as a text file



READDISK STACK.CLEAR CR "INPUT THE TEXT FILENAME FOR THE OD IMAGE" "TYPE "INPUT DEFER> OUT>FILE 1 H := 40 0 DO 1 G := 40 0 DO STOREAVG [ G , H , 1 ] . ", " "TYPE 1 G + G := LOOP CR 1 H + H := LOOP OUT>FILE.CLOSE

:

: MAKEFILE FILE.TEMPLATE 5 COMMENTS • REAL DIM( 50, 50, 2 ) SUBFILE END ;

## **\\*\*\*** SUBROUTINE TO MOVE THE TRANSLATOR \*\*\*\*\*

## **\ PART 1 DEFINE VARIABLES**

INTEGER SCALAR CRAM SCALAR LLSNB SCALAR MMSNB SCALAR DIRECTION.VERTICAL SCALAR DIRECTION.HORIZONTAL SCALAR PULSE#.VERTICAL SCALAR PULSE#.HORIZONTAL

INTEGER DIM[1] ARRAY TTLVOLTAGE DP.INTEGER SCALAR TTLSEG TTLVOLTAGE ADDRESS.TTLSEG = REAL SCALAR N

: GGO LLSNB 8930 PORT.OUT MMSNB 8931 PORT.OUT :

: SCAN.THE.IMAGE.VERTICALLY \THIS MOTOR IS LEFT ON ALL THE TIME 0. MMSNB = \NO EFFECT HORIZONTALLY

PULSE#.VERTICAL 0 DO \40 STEPS = 0.1 MM FOR 200 STEPS/REV.

```
0 DIRECTION.VERTICAL + LLSNB := \DOWN

5. MSEC.DELAY

GGO

3 DIRECTION.VERTICAL + LLSNB := \UP

5. MSEC.DELAY

GGO

LOOP
```



```
:
: SCAN.THE.IMAGE.HORIZONTALLY
MUST TURN ON THE MOTOR BEFORE EXECUTING TO PREVENT OVER HEATING
NTURN ON THE MOTOR
9 49890 PORT OUT \ SET BOARD ANALOGUE
1 4835 PORTOUT \ SETS THE COMPUTER THE WRITE TO A/D CHANNEL #1
      VITURN ON THE XY-TRANSLATION MOTORS
-5. TTLVOLTAGE :=
TTLSEG DEF.SEG
0 PEEK 13026 PORT.OUT \ READ LEAST SIG BIT AND WRITE IT OUT
1 PEEK 13027 PORT.OUT \ _____MOST _____
\SET THE BOARD TO DIGITAL CONTROL TO MOVE THE XY-MOUNT
8 49890 PORT.OUT \BOARD SET BINARY
0 8930 PORT.OUT
0 8931 PORT.OUT
2500. MSEC, DELAY VALLOW TIME FOR THE MOTOR WINDINGS TO ENERGIZE
0. LLSNB := \NO EFFECT IN THE VERTICAL DIRECTION
PLLSE#.HORIZONTAL 0 DO
 0 DIRECTION.HORIZONTAL + MMSNB := \DOWN
 5. MSEC.DELAY
   GGO
 3 DIRECTION.HORIZONTAL + MMSNB = \UP
 5. MSEC.DELAY
  GGO
LOOP
\TURN OFF MOTORS
9 49890 PORT.OUT\SET BOARD ANALOGUE
1 4835 PORT.OUT \ SETS COMPUTER TO WRITE TO A/D CHANNEL #1
       \TURN XY-TRANSLATOR MOTORS OFF TO PREVENT
       NTHEM FROM BURNING OUT
2048 TTLVOLTAGE :=
TTLSEG DEF.SEG
0 PEEK 13026 PORT.OUT
1 PEEK 13027 PORT.OUT
;
\PART 4 EXECUTE THE MOVEMENT OF THE TRANSLATOR
:SSTART
0 PULSE# HORIZONTAL < IF
SCAN.THE.IMAGE.HORIZONTALLY THEN
0 PULSE#.VERTICAL < IF \MUST CHECK FOR THE CASE OF
SCAN.THE.IMAGE.VERTICALLY THEN \NO MOVEMENT SELECTED AS ASYST
             WILL MOVE AT LEAST 1 STEP MINIMUM
:
```

: TRANSLATE \SET THE BOARD TO DIGITAL CONTROL TO MOVE THE XY-MOUNT 8 49890 PORT.OUT \BOARD SET BINARY 0 8930 PORT.OUT 0 8931 PORT.OUT

SSTART VUSER INPUTS THE MOVES & THE STEPPER MOTER THEN MOVES

9 49890 PORT.OUT \ BOARD SET TO ANALOGUE 0 4835 PORT.OUT \ SETS COMPUTER TO WRITE TO A/D CHANNEL #0 FOR \ THE LOCK-IN

:

: LOW.RES.IMAGE

START INPUT-VALUES

CR CR " SET TRANSLATION STAGE TO START OF THE IMAGE POSITION " "TYPE " THEN HIT THE SPACE BAR TO CONTINUE " "TYPE CR

BEGIN PCKEY 32 = UNTIL STACK.CLEAR

CR CR " \*\*\* PLUG IN THE XY-TRANSLATOR AND TURN ON THE SWITCH " "TYPE " ON TOP ..... THEN HIT THE SPACE BAR TO CONTINUE " "TYPE CR

BEGIN PCKEY 32 = UNTIL STACK.CLEAR

CR CR "PLUG A LINE FROM PIN #2 OF PARALLEL PORT TO SIGNAL SWITCH " "TYPE CR " THEN HIT THE SPACE BAR TO CONTINUE " "TYPE

BEGIN PCKEY 52 = UNTIL STACK.CLEAR

CR CR " LAST CHANCE TO QUIT BEFORE WE START... " "TYPE

BEGIN PCKEY 32 = UNTIL STACK.CLEAR

CR CR " GETTING THE IMAGE ... GO SIT DOWN FOR A WHILE " "TYPE

•.

40 PULSE#.VERTICAL := 0 PULSE#.HORIZONTAL := 12 DIRECTION.VERTICAL := 0 DIRECTION.HORIZONTAL :=

1 H := \HORIZONTAL 1 G := \VERTICAL 1 N :=

500 DO

49 0 DO

500. MSEC.DELAY GETIPOINT NG+G:= TRANSLATE / VERTICAL TRANSLATE UP I UNIT \ ------2KEY IF BEGIN PCKEY 32 = UNTIL STACK.CLEAR THEN / -----LOOP GET1POINT \ SOTH POINT APRINT 19 93 0 PULSE#, VERTICAL := \ MOVE HORIZONTALLY 1 UNIT 40 PULSE#.HORIZONTAL := TRANSLATE 0 PULSE#.HORIZONTAL := DIRECTION.VERTICAL CASE 12 OF." " 0 DIRECTION.VERTICAL := -1. N := 50 G := ENDOF 0 OF ." " 12 DIRECTION.VERTICAL := 1. N := 1 G := ENDOF ENDCASE 40 PULSE#. VERTICAL := CR H. CR H1+H:= LOOP CRCRCRCR ---- TURN OFF MOTORS AT SWITCH ------ " "TYPE CR - \_ CRCRCR \_\_\_\_\_ " "TYPE CR \_ ALL DONE \_ . \_\_\_\_ ;

" NOTE TO USER: \*\*\* TYPE LOW.RES.IMAGE TO START \*\*\* "



Appendix I

Assembler language routines to transmit and receive a 4096 point array through a parallel port and a Asyst language program that does the signal processing and file management for the 3-D photothermal movies. This appendix contains three programs.

The first is the program that did all the signal processing of the time domain waveforms and generates the photopyroelectric impulse response. After processing the data it has file handling algorithms to store the data.

The second is an assembler language program that transmits a 4096 point array from the parallel port of one computer.

The third is an assembler language program that receives a 4096 point array from the parallel port of a computer.

The second and third programs are designed to work together and have handshaking routines to prevent the data from becoming lost or shuffled in the transfer process. A 4096 point array can be transferred in under 2 seconds. \File: PHOT2CAL.DOC
\ DATE OF LATEST VERSION: FEB.2 93
\ (1) TAKES IN THE 40% POINT TIME RESPONSE FROM THE LPT2
\ (2) CALCULATES THE IMPULSE RESPONSE
\ (3) SAVES THE FILES TO DISK

HORIZONTAL GRID.OFF VERTICAL GRID.OFF Vsctup of data arrays for analysis INTEGER SCALAR MARC DP.INTEGER DIM[ 2048 ] ARRAY X1 DP.INTEGER DIM[ 2048 ] ARRAY Y1

INTEGER DIM[ 512 ] ARRAY RX

REAL DIM[ 4096 ] ARRAY X(T) \x channel data array REAL DIM[ 4096 ] ARRAY Y(T) \y channel data array

\define arrays for FFT results

COMPLEX DIM[ 4096 ] ARRAY H(F) \frequency response COMPLEX DIM[ 4096 ] ARRAY GXY(F) \cross spectrum REAL DIM[ 4096 ] ARRAY GXX(F) \input autospectrum

REAL DIM[ 4096 ] ARRAY H(T) \impulse response COMPLEX DIM[ 4096 ] ARRAY W(T) \time domain window COMPLEX DIM[ 4096 ] ARRAY W(F) \frequency domain window REAL DIM[ 4096 ] ARRAY RXY(T) \cross correlation function REAL DIM[ 1600 ] ARRAY FREQ \measured frequencies in run \lower bandwidth limit is FREQ1 REAL SCALAR FREQ2\upper bandwidth limit REAL SCALAR GMAX

INTEGER SCALAR XSEG INTEGER SCALAR YSEG INTEGER SCALAR RXOFS INTEGER SCALAR RXSEG INTEGER SCALAR OFS INTEGER SCALAR NAVG INTEGER SCALAR M INTEGER SCALAR N INTEGER SCALAR COUNTER

**NINITALISE THE SYSTEM TO INTERFACE BETWEEN THE COMPUTERS** 

: INIT FILE-OPEN C:RX.IMG \CALL UP THE ASSEMBLER LANGUAGE ROUTINE RX FILE-ARRAY \STORE THE ASSEMBLER FILE IN THE ARRAY SPACE FILE.CLOSE X1 ADDRESS OFS = XSEG := Y1 ADDRESS OFS = YSEG := XSEG RX [ 143 ] :=



< 2.

```
YSEG RX [ 145 ] :=
RX ADDRESS RXOFS := RXSEG :=
:
RECVR
0 X1 := 0 Y1 :=
CALLI RXSEG, RXOFS ]
0.0 X(T) = 0.0 Y(T) =
X1_X(T) SUB[ 0 , 2048 ] :=
Y1 Y(T) SUB[ 0, 2048 ] :=
:
: DC.CORRECT
Nde correct the incoming signal for Fourier analysis
STACK.CLEAR
Xm
X(T) SUB[ 0 , 2048 ] MEAN -
X(T) :=
0 X(T) SUB[ 2049 , 2048 ] :=
X(T) NAVG / 409.6 / X(T) :=
0 X(T) [1] :=
STACK_CLEAR
YΠ
Y(T) SUB[ 0 , 2048 ] MEAN -
Y(T) :=
0 Y(T) SUB[ 2049 , 2048 ] :=
Y(T) NAVG / 409.6 / Y(T) :=
0 Y(T) [ 1 ] :=
STACK.CLEAR
;
:GXX
Ninput autospectral calculation
STACK.CLEAR
0. 0. Z=X+IY
X(T) FFT H(F) :=
H(F) ZMAG GXX(F) :=
GXX(F) DUP . GXX(F) :=
;
:GYY
Noutput autospectral calculation
STACK.CLEAR
Y(T) FFT
ZMAG DUP •
:
:GXY
```

STACK.CLEAR X(T) FFT H(F) := H(F) CONJ GXY(F) := 0. 0. Z=X+IY H(F) := Y(T) FFT H(F) := STACK.CLEAR H(F) GXY(F) • GXY(F) :=

٠

•

```
:
: RXX
STACK.CLEAR
GXX(F) IFFT ZREAL
:
:RYY
STACK.CLEAR
GYY IFFT ZREAL
٠
:RXY
STACK.CLEAR
GXY(F) IFFT ZREAL
RXY(T) :=
STACK.CLEAR
;
: FREQUENCY RESPONSE
0. 0. Z=X+IY H(F) :=
STACK.CLEAR
1 GXX(F) [1] ==
1 GXX(F) SUB[ 1602 , 895 ] :=
GXY(F) GXX(F) / H(F) :=
W(F) H(F) * H(F) :=
\002=X+IY H(F)[1]:=
;
                   H(F) IS LOST NEED IT TO PREVENT CRASHING
Vimpulse response
: IMPULSE RESPONSE
STACK CLEAR
0. H(T) :=
00Z=X+IY W(T) :=
H(F) IFFT W(T) := STACK.CLEAR
W(T) ZREAL H(T) :=
:
15 STRING FNAME
: READ.DSET
CR * Enter filename (b:7char.ext): * "TYPE
"INPUT FNAME ":=
FNAME DEFER> FILE OPEN
1 SUBFILE X(T) SUB[ 0, 2048 ] FILE>ARRAY
2 SUBFILE Y(T) SUB[ 0, 2048 ] FILE>ARRAY
FILE.CLOSE
;
: WRITE.DSET
\word to save a single files frequency response
CR " Enter filename (B:7char.ext) : " "TYPE
 "INPUT FNAME ":=
FNAME DEFERS FILE OPEN
 1 SUBFILE X(T) SUB[ 0, 2048 ] ARRAY>FILE
 2 SUBFILE Y(T) SUB[ 0, 2048 ] ARRAY>FILE
 FILE.CLOSE
 :
```

REAL DIM[ 256 ] ARRAY IMPLS



REAL DIM( 256 | ARRAY IMPLS2 REAL DIM( 256 , 50 ) ARRAY 1-IMAGE

: MAKEFILE \file template to store the image ; each impulse response \is saved (256 points) S0x50x256

HLE.TEMPLATE REAL DIMI 256 , 50 | SUBFILE REAL DIMI 256 , 50 | SUBFILE REAL DIM( 256 , 50 | SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIMI 256 , 50 | SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIM( 256, 50 | SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIM[ 256, 50 ] SUBFILE REAL DIM( 256, 50 | SUBFILE REAL DIMI 256, 501 SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256, 50 ] SUBFILE REAL DIMI 256 . 50 | SUBFILE REAL DIM[ 256 . 50 ] SUBFILE REAL DIMI 256 . 50 | SUBFILE REAL DIMI 256, 50 ] SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIMI 256 . 50 ] SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIM[ 256, 50 ] SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256, 50 | SUBFILE REAL DIMI 256 , 50 ) SUBFILE REAL DIM[ 256, 50 ] SUBFILE REAL DIM( 256 , 50 ) SUBFILE REAL DIM[ 256 , 50 ] SUBFILE REAL DIM[ 256, 50 ] SUBFILE REAL DIM( 256, 50 ] SUBFILE REAL DIM[ 256, 50 ] SUBFILE REAL DIM( 256, 50 ) SUBFILE REAL DIM[ 256, 50 ] SUBFILE END

:

: GRAPH.IT \plots the impulse response on the screen as they are calculated VUPORT.CLEAR 1. DMPLS2 :=



```
CR CR "WAITING FOR DATA ... " "TYPE CR
۱.
250 DO
             \VERTICAL
  GRAPHLIT
              \CLEAR SCREEN
\FIRST LINE GOING 1 DIRECTION
  50 0 DO
    RECVR
              \BRING OVER THE ARRAYS, PUT THEM INTO X & Y
    H(T).ANALYSIS
    N 20 MODULO 0 = IF GRAPHLIT THEN
    IMPLS Y.DATA.PLOT
    1 COUNTER := \TRANSFER 256 POINTS INTO 1-IMAGE ARRAY
    256 0 DO
    IMPLS [ COUNTER ]
     1-IMAGE [ COUNTER , N ] =
     COUNTER 1 + COUNTER :=
    LOOP
```

V GET THE IMAGE ... REMEMBER THAT YOU SCAN I WAY THEN SCAN BACK THE OTHER

"FNAME : " "TYPE FNAME "TYPE CR "NAVGS : " "TYPE NAVG . CR

1 M := 1 N := 0.1-IMAGE := GRAPHICS.DISPLAY

CR CR " INPUT # OF AVG'S AT EACH POINT " "TYPE #INPUT NAVG := CR CR " INPUT THE FILENAME FOR THIS IMAGE " "TYPE CR .... D:HOLD1.IMG D:HOLD2.IMG OR D:HOLD3.IMG \*\* TYPE "INPUT FNAME ":=

INIT

IMPLS2 [JRAMP \SET UP THE TEMPLATE TO SHOW THE IMAGE IMPLS2 DUP ^MAX [ 256 ] / IMPLS2 := -0.3 IMPLS2 [ 1 ] := IMPLS2 Y.AUTO.PLOT NORMAL DISPLAY

:GO \word that runs the entire porgram

10Z=X+IY W(F) :=

:

```
DC.CORRECT \REMOVE THE DC OFFSET
GXX
GXY
          \CALC THE AUTO & CROSS COREL. SPECTRAL FUNCTIONS
FREQUENCY RESPONSE
0.0 Z=X+IY H(F) SUB[ 1601 , 897 ] := \ SET THE BANDSTOP
00Z=X+IY H(F)SUB[0,3]:=
00Z=X+IY H(F)SUB[4095,2]:=
IMPULSE.RESPONSE \ GET H(T)
H(T) SUB[ 0, 256 ] IMPLS :=
IMPLS -1. * IMPLS := \NINVERT IMPLS RESP
IMPLS DUP ^MAX [ 256 ] / IMPLS :=
```

: H(T).ANALYSIS N word that processes the data and generates the impulse response

0 IMPLS2 [ 256 ] := XY.AXIS.PLOT

:

**\" GO " RUNS THE PROGRAM** 

: CLEARFILE CR " 11111 MAKE SURE THE FILE IS BACKED UP BEFORE DELETING 11111 " TYPE CR CR " INPUT THE FNAME YOU WANT TO ZERO " "TYPE "INPUT FNAME" := CR 0. 1-IMAGE := 50 0 DO  $1N \approx$ FNAME DEFERS FILE.OPEN N SUBFILE 1-IMAGE ARRAY>FILE FILECLOSE 1N+N =LOOP

:

LOOP N 25 0 DO LOOP

0. 1-IMAGE := 1 M + M := VINCREMENT M 1 N := **\SET N BACK TO 1 AS WE ARE GOING TO SCAN BACK NTHE FIRST DIRECTION** 

**\SAVE THE SECOND LINE** FNAME DEFERS FILE OPEN M SUBFILE 1-IMAGE ARRAY>FILE FILE.CLOSE

RECVR **\BRING OVER THE ARRAYS, PUT THEM INTO X & Y** H(T).ANALYSIS N 20 MODULO 0 = IF GRAPH.IT THEN IMPLS Y.DATA.PLOT 1 COUNTER := \\TRANSFER 256 POINTS INTO 1-IMAGE ARRAY 256 0 DO IMPLS [ COUNTER ] 1-IMAGE [ COUNTER , N ] := COUNTER 1 + COUNTER := LOOP N1-N:= LOOP

GRAPH.IT **\CLEAR SCREEN** 50 0 DO

0. 1-IMAGE := 1 M + M := 50 N := **NSTART AT 50 AND WORK DOWN** 

NNOW DO SECOND LINE GOING BACK THE OTHER WAY

FNAME DEFERS FILE.OPEN SAVE ONE LINE M SUBFILE 1-IMAGE ARRAY>FILE FILE.CLOSE

1 N + N := LOOP

TITLE TRNS.ASM COMMENT\* Transmitter module routine called by PHOTOS (2.01) to dump XBUFFER data from a PC-XT to a 486 via a 8522 (Centronix type) printer port Version Date: 02-Nov-1992 PARMSEG SEGMENT PAGE PUBLIC 'PARAMETERS' STACKAREA DW 0045H STACKPOINTER DW 00FEH STACKOFFSET DW 0013H ; offset of internal stack segment into ASEG ; stackoffset to be checked in .MAP/.EXE files PARMOFFSET DW 0010H ; offset of parameter segment into ASEG ; final assignment must be checked prior to final link TEMPDS DW 0000 TEMPAX DW 0000 TEMPRET DW 0000 TEMPCS DW 0000 NADA DW 0000 DW 0378H ; printer card base address PBASE PBASE1 DW 0379H ;printer card BASE+1 PBASE2 DW 037AH ;printer card BASE+2 TREADY DW 0002H ; Tx ready status RMASK DW 0020H ; Rx ansbk DW 1000 XSEG ; address of Asyst integer data as offset DW 0000 XOFS ; into IMAGE array DW 2000 ; as per XBUFFER address is passed by YSEG ASYST YOFS DW 0000 ; as IMAGE offset DW 8192 ; size in bytes of x and y buffers BUFR PARMSEG ENDS WRITE\_DATA MACRO MOV DX, PBASE MOV AL, ES: [BX] OUT DX,AL ENDM READ RX MACRO MOV DX, PBASE1 IN AL,DX ENDM WRITE TX MACRO MOV DX, PBASE2 DX,AL OUT ENDM 'STACK' SEGMENT PAGE STACK STACK DB 256 DUP('S') STACK ENDS

; Macro definitions BYTE PUBLIC 'ASYST' ASEG SEGMENT ASSUME CS:ASEG, DS:PARMSEG, ES:ASEG, SS:STACK PUBLIC TLINK TLINK PROC FAR ; Enter from Asyst with no parameters passed directly ; return with all registers and PSW restored. ;disable all further interrupts CLI PUSH AX ; save most volatile registers on Asyst stack PUSH DS PUSHF MOV AX,CS ;set up parmseg in DS for access to stack info. ADD AX,0010H ; this is Parmseg offset into ASEG - check MAP ; before final link MOV DS, AX MOV [STACKPOINTER], SP ; save Asyst stack address in Parmseg MOV [STACKAREA], SS ;reserved space for Asyst stack address MOV AX,CS ADD AX, STACKOFFSET ; internl stack segment is given as offset MOV SS,AX MOV SP,00FEH ; internal stack addressing is now set up. The remainder of Asyst ; registers is now saved. PUSH BX PUSH CX PUSH DX PUSH ES PUSH BP PUSH SI PUSH DI CALL TRANSMITTER ; exit sequence below MOV AX,CS ADD AX,0010H MOV DS,AX ; Parmseg is reset in DS ; warning! be sure to verify above 00140h offest from map! POP DI POP SI POP BP

POP ES POP DX POP СХ ; restore Asyst stack pointer for return POP BX MOV SP, [STACKPOINTER] SS,[STACKAREA] MOV ; the sequence outlined below removes the top five entries ; from Asyst stack: in sequence: DS,AX,IP,CS, and NADA. ; Nada is a parameter passed by Asyst indicating the number ; of parameters which were passed by the calling routine. In ; this case it is zero ('nada'). This parameter must be ; removed from the Asyst stack otherwisw an error message ; is observed on return to Asyst. The five parameters are ; temporarily stored in Parmseg, pushed back onto Asyst's ; stack. and then restored in correct sequence. POPF POP [TEMPDS] POP [TEMPAX] POP [TEMPRET] POP [TEMPCS] POP [NADA] PUSH [TEMPCS] PUSH [TEMPRET] PUSH [TEMPAX] PUSH [TEMPDS] POP DS POP AX STI RET TLINK ENDP PUBLIC TRANSMITTER TRANSMITTER PROC NEAR MOV ES, YSEG MOV CX, BUFR MOV BX, YOFS ; set up y address buffer in ES:BX buffer size in CX YTRANS: WRITE DATA MOV AX,0002 WRITE\_TX ; all tx writes are complementary READ1: READ RX AND AX, RMASK JNZ READ1 ; wait for low bit ind. rx has read lines MOV AX,0000 WRITE TX ; signal rx that write is complete

READ2: READ RX AND \_ AX, RMASK READ2 ; check ansbk form rx, ind. ready for read JZ INC BX LOOP YTRANS MOV ES,XSEG MOV CX, BUFR MOV BX, XOFS ; set up x address buffer in ES:BX buffer size in CX XTRANS: WRITE DATA MOV AX,0002 ; write lines are complementary, drive low WRITE TX ; write low bit to transmitter ; wait for low from receiver ind. read over READ3: READ\_RX AX, RMASK AND JNZ READ3 MOV AX,0000 WRITE TX ; send high to rx ind. roger READ4: ; ready to start next cycle READ\_RX AX, RMASK AND JZ READ4 ; check to see of rx is also ready INC BX ; in address, dec count if yes LOOP YTRANS RET TRANSMITTER ENDP ASEG ENDS END

TITLE RECVR.ASM COMMENT\* Transmitter module routine called by PHOTOS (2.01) to dump XBUFFER data from a PC-XT to a 486 via a 8522 (Centronix type) printer port Version Date: 02-Nov-1992 ÷ PARMSEG SEGMENT PAGE PUBLIC 'PARAMETERS' STACKAREA DW 0045H STACKPOINTER DW 00FEH STACKOFFSET DW 0013H ; offset of internal stack segment into ASEG ; stackoffset to be checked in .MAP/.EXE files PARMOFFSET DW 0100H ; offset of parameter segment into ASEG ; final assignment must be checked prior to final link TEMPDS DW 0000 TEMPAX DW 0000 TEMPRET DW 0000 TEMPCS DW 0000 NADA DW 0000 ; printer card base address (suppl) DW 0278H PBASE DW 0279H ;supp printer card DW 027AH ; supp printer card BASE+2 PBASE1 PBASE2 RREADY DW 0002H ; Tx ready status TMASK DW 0020H ; tX ansbk XSEG DW 9000 ; address of X1 (segment) DW 0000 XOFS ; into IMAGE array DW 8000 ; as per XSEG above YSEG YOFS DW 0000 ; as IMAGE offset DW 8192 ; size in bytes of x and y buffers BUFR PARMSEG ENDS ; Macro definitions READ DATA MACRO ; macro to read data from printer port MOV DX, PBASE IN AL, DX MOV ES:[BX],AL ENDM READ TX MACRO ; macro to read transmitter status MOV DX, PBASE1 IN AL, DX ENDM



MACRO WRITE RX ; macro to output rx status to tx MOV DX, PBASE2 OUT DX,AL ENDM PAGE STACK 'STACK' STACK SEGMENT DB 256 DUP('S') STACK ENDS ASEG SEGMENT BYTE PUBLIC 'ASYST' ASSUME CS:ASEG, DS:PARMSEG, ES:ASEG, SS:STACK PUBLIC RLINK RLINK PROC FAR ; Enter from Asyst with no parameters passed directly ; return with all registers and PSW restored. ;disable all further interrupts CLI PUSH AX ; save most volatile registers on Asyst stack PUSH DS PUSHF MOV AX,CS ;set up parmseg in DS for access to stack info. ADD AX,0010H ; this is Parmseg offset into ASEG - check MAP ; before final link MOV DS,AX MOV [STACKPOINTER], SP ; save Asyst stack address in Parmseg MOV [STACKAREA], SS ; reserved space for Asyst stack address MOV AX.CS ADD AX, STACKOFFSET ; internal stack segment is given as offset MOV SS,AX MOV SP,00FEH ; internal stack addressing is now set up. The remainder of Asyst ; registers is now saved. PUSH BX PUSH CX PUSH DX PUSH ES PUSH BP PUSH SI PUSH DI CALL RECEIVER

; exit sequence below MOV AX,CS ADD AX,0010H DS,AX ;Parmseg is reset in DS MOV ; warning! be sure to verify above 0010h offset from map! POP DI SI POP POP BP ES POP POP DX POP CX ; restore Asyst stack pointer for return POP BX SP, [STACKPOINTER] MOV MOV SS, [STACKAREA] ; the sequence outlined below removes the top five entries ; from Asyst stack: in sequence: DS,AX,IP,CS, and NADA. ; Nada is a parameter passed by Asyst indicating the number ; of parameters which were passed by the calling routine. In ; this case it is zero ('nada'). This parameter must be ; removed from the Asyst stack otherwisw an error message ; is observed on return to Asyst. The five parameters are ; temporarily stored in Parmseg, pushed back onto Asyst's ; stack. and then restored in correct sequence. POPF POP [TEMPDS] POP [TEMPAX] POP [TEMPRET] POP [TEMPCS] POP [NADA] PUSH [TEMPCS] PUSH [TEMPRET] PUSH [TEMPAX] PUSH [TEMPDS] POP DS POP AX STI RET RLINK ENDP PUBLIC RECEIVER RECEIVER NEAR PROC MOV ES, YSEG MOV CX, BUFR MOV BX,YOFS ; set up y address buffer in ES:[BX], buffer size in CX

YTRANS:

; check tx status for valid data READ1: READ\_TX AND 🗌 AX, TMASK JNZ READ1 READ DATA ; input data from printer lines MOV AX,0002H WRITE\_RX READ2: READ\_TX AND AX, TMASK READ2 JZ MOV AX,0000H WRITE\_RX INC BX LOOP YTRANS ES,XSEG MOV MOV CX, BUFR BX,XOFS MOV

## XTRANS:

; check tx status for valid data READ3: READ\_TX AND AX,TMASK JNZ READ3 READ\_DATA ; input data from printer lines MOV AX,0002H WRITE\_RX

READ4: READ\_TX AND AX,TMASK JZ READ4 MOV AX,0000H WRITE\_RX INC BX

LOOP XTRANS





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Appendix J

Software Routines for inversion of photothermal impulse response

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All code for the inversion of the photothermal impulse response was written in the Matlab software package (Mathworks, MA). The software is designed so that individual functions or commands can be written and then used as needed in software routines or from the keyboard. The code for important functions used in the inversion algorithms commands are presented here.

The pseudoinverse function {pinv(A,tol)} was supplied by Matlab.

The non-negative least squares algorithm {nnls(E,f,tol)} was taken form the reference: Lawson and Hanson, "Solving Least Squares Problems", Prentice-Hall, 1974. The basic code was supplied in the Matlab manual and new versions of Matlab have the code included in the Optimization Tool Kit.

The function {erfc\_g(x\_dim, t\_dim, l, dt)} generates the photopyroelectric free space Green's Function for accounting for the front surface reflections.

The function {one\_g(m,n,l,dt,x\_o)} generates the conventional free space Green's Function for the parameters supplies.

The function {avgtnnls( T, ht, l, dt, noise, loopno, hh)} calculates the average of an ensemble of nnls inversions. Inside the function the user can select the method of generating the Green's Function and select whether to include the effect of electrical convolution or not.

```
function X = pinv(A, tol)
      Pseudoinverse. X = PINV(A) produces a matrix X of the
VPINV
       same dimensions as A' so that A^*X^*A = A, X^*A^*X = X and
٩.
       AX and XA are Hermitian. The computation is based on
١
       SVD(A) and any singular values less than a tolerance are
٩
                               The
                                       default
٩.
       treated as zero.
                                                  tolerance
                                                               is
۲
       MAX(SIZE(A)) * NORM(A) * EPS.
                                        This tolerance may be
       overridden with X = PINV(A,tol). See RANK.
٩.
% Pseudo-inverse, ignore singular values <= tol.</pre>
> Default tol = max(size(A)) * s(1) * eps.
[U,S,V] = svd(A);
if min(size(S)) == 1
  S = S(1);
else
  S = diag(S);
end
if (nargin == 1)
  tol = max(size(A)) * S(1) * eps;
end
r = sum(S > tol);
if (r == 0)
 X = zeros(A');
else
  S = diag(ones(r,1)./S(1:r));
  X = V(:,l:r)*S*U(:,l:r)';
```

end

```
function [x,w] = nnls(E,f,tol)
INNLS
      Non-negative least-squares.
٩.
       X = NNLS(A,b) returns the vector X that solves A^*x = b
٩
        in a least squares sense, subject to x \ge 0.
٩.
        A default tolerance of TOL = MAX(SIZE(A)) * NORM(A,1) * EPS
٩.
        is used for deciding when elements of X are less than zero.
٩
       This can be overridden with X = NNLS(A, b, TOL).
٩
٩
        [X,W] = NNLS(A,b) also returns dual vector W where
٩.
٤
        w(i) < 0 where x(i) = 0 and w(i) = 0 where x(i) > 0.
N Reference:
Lawson and Hanson, "Solving Least Squares Problems", Prentice-Hall, 1974.
code suggestion obtained from Matlab reference manual
1 initialize variables
if nargin < 3
        tol = 10*eps*norm(E,1)*max(size(E));
end
[m,n] = size(E);
P = zeros(1,n);
Z = 1:n;
x = P';
2Z=Z;
w = E'^*(f - E^*x);
set up iteration criterion
iter = 0;
itmax = 3*n;
% outer loop to put variables into set to hold positive coefficients
while any(Z) \in any(w(ZZ) > tol)
        [wt,t] = max(w(ZZ));
        t = 22(t);
        P(1,t) = t;
        Z(t) = 0;
        PP = find(P);
        ZZ = find(Z);
        nzz = size(ZZ);
        EP(1:m, PP) = E(:, PP);
        EP(:,ZZ) = zeros(m,nzz(2));
        z = pinv(EP) * f;
        z(ZZ) = zeros(nzz(2), nzz(1));
% inner loop to remove elements from the positive set which no longer belong
        while any((z(PP) <= tol))
                iter = iter + 1;
                if iter > itmax
                         error(['NNLS quitting because iteration count is exceeded.', ...
' Try raising the tolerance.'])
                end
                QQ = find((z \le tol) \in P');
                alpha = min(x(QQ)./(x(QQ) - z(QQ)));
                x = x + alpha^{+}(z - x);
                ij = find(abs(x) < tol \in P' \rightarrow 0);
                Z(1j)=1j';
                P(ij)=zeros(l,max(size(ij)));
                                                     PP = find(P);
                ZZ = find(Z);
                                                                                       ÷.
```

```
nzz = size(ZZ);
EP(1:m,PP) = E(:,PP);
EP(:,ZZ) = zeros(m,nzz(2));
z = pinv(EP)*f;
z(ZZ) = zeros(nzz(2),nzz(1));
end
x = z;
w = E'*(f-E*x);
end
```

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```
Gl(t,x)=(l-(x-1)*dx) /sqrt(4*1.0e-7*t*dt);
G2(t,x)=(l-(x-1)*dx+9e-6) /sqrt(4*1.0e-7*t*dt);
G3(t,x)=(l+(x-1)*dx) /sqrt(4*1.0e-7*t*dt);
G4(t,x)=(l+(x-1)*dx+9.e-6) /sqrt(4*1.0e-7*t*dt);
```

end

end;

G2=erf(G2,inf); G3=erf(G3,inf); G4=erf(G4,inf); G1=erf(G1,inf); G=G1-G2+G3-G4;

```
function g_array = one_g(m,n,l,dt,x_0)
% syntax is one_g(time_dim, space_dim, sample_thickness, timeresolution,x(0))
% i.e. one_g( 16 , 16 , 50.e=6, 5.e=4, 55.e=6);
% x(0) = at what position to record temp: x(0) is multiplies by =1 in
% the program.
% returns the calculated greens function, not normalized
dx=1/n;
for j=1:m
   for i=1:n
   g_array(j,i)=(exp(-1* (((-1)*x_0+(i=1)*dx)^2) /(4*1.e=7*j*dt))) ...
        /sqrt(4*3.14*1.e=7*j*dt);
   end
end
% g_array=g_array/max(max(g_array));
```

```
2 -
```

-;

```
function [HT,H,T,q]=avgtnnls( T, ht, l, dt, noise, loopno, hh);
$ syntax [HT,H,T,q]=avgtnnls( G, ht, sample thickness, time resolution,...
                        noise in G, no of loops to avg, sample, impls.resp)
٩.
% ex HT=avgt( rand(32), fname of elect impls resp, 50.e-6, 5.e-4, 0.01, 3, hh)
                  % will become T-the Greens Function
[w,p]=size(T);
                   will become H-the transfer function matrix of [nxn]
[n,q]=size(ht);
if n -= w error('arrays sizes do not match'), return; else; end
                 % fill the transfer function array
H=zeros(n);
M=zeros(n,1);
k=n;
for i=1:n
 M(k:n)=ht(l:(n-k+1));
 H(:,k)=M;
 k=k-1;
end
                   t calculate 10 Greens Functions
\ offset=0:
♦ for i=1:10
T=one g(w, p, l, dt, offset) + T;
$ offset=offset + 0.9e-6; $ 9 um pvdf
$ offset=offset + 2.8e-6; $ 28 um PVDF
t end
T=T/max(max(T));
                  t call the erfc_g routine
                  % generates the spatially averaged GF across PVDF
  T=erfc g(w,p,l,dt);
  T=T/max(max(T));
[m,n]=size(H*T);
                 t zero fill HT
HT=zeros(m,n);
[m,n]=size(pinv(H*T)*hh);
q=zeros(m,n);
                t zero fill q
format +
rand('normal'); % put noise on Greens function avg
for i=1:loopno
z=rand(w,p);
z=z*noise;
TT=T+z;
% q=nnls((H*TT),hh) + q; % ***** will do nnls on T only for deconv data
     q=nnls(TT,hh) + q;
end
```

1.5