Leona C. Rudinskas Ph.D. Chemistry

Role of Energy Transfer in Photoprotection of Polystyrene

Ph.D. CHEMISTRY

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THE ROLE OF ENERGY TRANSFER IN THE PHOTOPROTECTION OF POLYSTYRENE

Abstract

This thesis demonstrates that when polystyrene containing anthracene dissolved in the polymer matrix is excited electronically (by ultraviolet radiation e.g.), at high enough solute concentrations, an efficient process of resonance energy transfer takes place from the first excited singlet state of polystyrene to anthracene raising the latter to its first singlet state. This process causes a decrease in the singlet population of polystyrene (as well as in the triplet population which is derived by intersystem crossing from the singlet state).

Polystyrene-anthracene samples were irradiated in vacuum by ultraviolet light (2700 Å) so that only polystyrene was the absorbing species. It was shown that crosslinking is decreased in an amount proportional to the efficiency of energy transfer. With gamma radiation crosslinking was also suppressed as well as polystyrene radical formation. However, the hydrogen gas yield remained constant regardless of the amount of solute present, indicating that with ionizing radiation the upper excited states play a role in the degradation process at a rate that is higher than the rate of energy transfer by the Forster mechanism.

THE ROLE OF ENERGY TRANSFER IN THE PHOTOPROTECTION OF POLYSTYRENE

by

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To my parents

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FOREWORD

An investigation of the role of energy transfer in the photoprotection of polystyrene is presented in five chapters.

CHAPTER I	General Introduction: A brief description of the various modes of energy transfer is given as well as their application to the present investigation.
CHAPTER II	Experimental Techniques: These are all presented in one chapter to allow discussion of the experimental results without interruption.
CHAPTER III	Primary Photophysical Processes: Experimental data showing the efficiency of energy transfer for the solvent-solute systems chosen for this work are given.
CHAPTER IV	Degradation of Polysytrene: A description of the amount of radiation protection from ultra-violet and gamma rays afforded by the additives is presented.
CHAPTER V	Claims to Originality of Research Work and Suggestions for Further Work

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CHAPTER I

GENERAL INTRODUCTION

CHAPTER I

GENERAL INTRODUCTION

I-1 INTRODUCTION

All matter has the ability to absorb some form of energy, whether it be gamma radiation consisting of very high-energy photons on the one hand, or very low-energy photons such as radio waves on the other hand. Table I-1 lists the conventional names given to the various regions in the electromagnetic spectrum along with their wavelengths and energies.(1) The type of energy absorbed by a molecule determines the course of events that occur to its physical and/or electron configurations.

Organic substances almost always absorb visible or ultraviolet light with the latter being a region that possesses quanta of sufficient energy to initiate chemical reactions. In the jargon of the photochemist, when a molecule has absorbed a quantum of ultraviolet energy, it is said to be in an electronically excited state from which it can often undergo chemical reaction. However, since not every quantum of energy absorbed results in reaction, the molecule is also capable of dissipating the energy without undergoing a net change itself. If one desires to predict which of the two events is more likely to occur or to alter the natural course of events, one must

TABLE I-1

FORMS OF ENERGY

Radiation Classification	Wavelength(Å)	Kcal/Mole of Quanta
Cosmic Rays	10^{-4}-10^{-3}	10^{9}-10^{8}
Gamma Rays	10^{-2}-10^{-1}	10^{7}-10^{6}
X-Rays	1-10	10^{6}-10^{4}
Ultraviolet	10^{2}-4×10^{3}	10^{3}-10^{2}
Visible	4×10^{3}-10^{4}	10^{2}-1
Infrared	10^{4}-10^{6}	1-10^{-1}
Microwave	10^{7}-10^{8}	10^{-2}-10^{-3}
Radar	10^{8}-10^{9}	10^{-3}-10^{-4}
Television	10^{10}-10^{11}	10^{-4}-10^{-5}
Nuclear Magnetic Resonance	10^{12}	10^{-6}
Radio Waves	10^{12}-10^{13}	10^{-6}-10^{-7}

Useful Identities

1 electron volt (e.v.) = 1.6×10^{-12} erg
= 12.398 Å
= 23.06 Kcal/mole

first understand the nature of the interaction between the molecule and the quantum of energy. The various steps that the molecule can go through prior to a chemical reaction or reemission of the energy are called the primary photophysical processes.

I-2 PRIMARY PHOTOPHYSICAL PROCESSES

I-2.1 Absorption

The first step in the interaction between a quantum of electromagnetic radiation and a molecule is the absorption of the quantum of (ultraviolet, for our purposes) energy. This is described by the Einstein relation:

$$E_2 - E_1 = h\gamma \qquad \text{(I-1)}$$

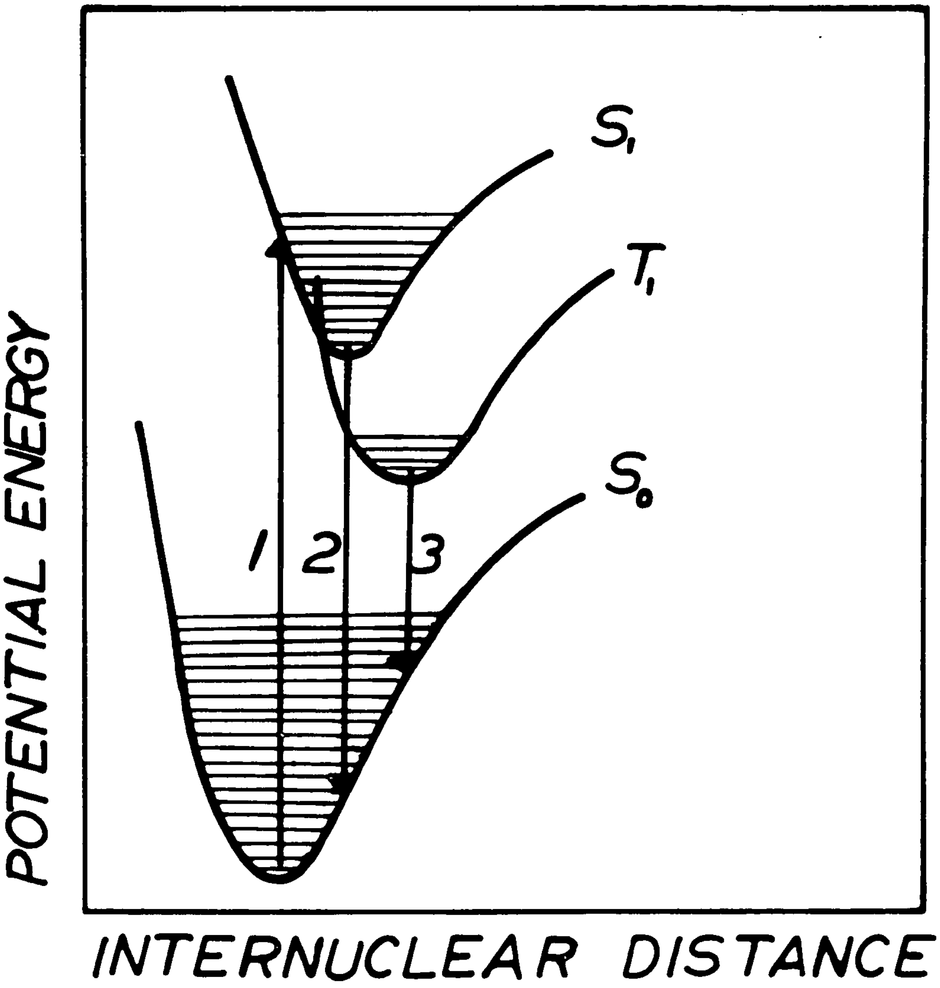
where E_1, E_2 are the initial and final energies of the molecule, h is Planck's constant and γ is the frequency of the quantum.

When a quantum of light is absorbed by a molecule, one of the electrons is raised to some higher excited state. The excited molecule is then in an unstable condition and can be stabilized by the loss of this excess energy. The events which can then occur can be understood by referring to Figure I-1.(2)

The most important electronic state for most organic molecules are the ground state, S_0, which

FIGURE I-1

Potential Energy of the Various Electronic States of a Simple Molecule Versus Internuclear Distance



[1] ABSORPTION
[2] FLUORESCENCE
[3] PHOSPHORESCENCE

is a singlet state, the first excited singlet state, S_1, and the first triplet state, T_1. In the singlet state the electrons occupying that state have their spins paired, whereas in the triplet state the spins are unpaired.

In Figure I-1 the potential energies of a hypothetical diatomic molecule versus internuclear distances are plotted for each electronic state. The allowed vibrational energy levels are shown. It should be remembered in the discussion which follows that for most molecules, Figure I-1 is an oversimplification that is not rigidly valid. In the energy region above the ground state there will normally be many electronic arrangements having potential energy curves that cross one another. For example, a hypersurface of 66 dimensions would be necessary to represent completely the vibrational motions of the anthracene molecule.(2)

When a photon with an appropriate energy is absorbed by a molecule, an electron is raised from the zero vibrational level of the ground state to one of several vibrational levels of the first excited singlet state ($S_0 \rightarrow S_1$). The singlet-singlet transition occurs in accordance with the Franck-Condon Principle which states that electronic transitions are so fast (10^{-15}sec.) in comparison to nuclear motion (10^{-12}sec.) that immediately after the transition, the nuclei have nearly the same relative positions and velocities as they did before the transition.(2)

It should be noted here that photochemical activation of a molecule is a very selective process in contrast to thermal excitation. Absorption of a quantum of light can specifically excite a particular bond (such as the carbonyl carbon-oxygen bond) in a molecule. Use of the proper frequency of exciting light allows activation of a solute molecule in the presence of a large excess of transparent solvent. Thermal activation of the same molecule or a particular bond can only be achieved by an increase in the over-all molecular energy of the environment.

I-2.2 Internal Conversion and Intersystem Crossing(2-5)

In the upper excited singlet state the molecule can lose its excess energy as heat by small vibrational steps taking it down through the vibrational levels of the excited electronic state to the point where the potential energy curve of the state crosses that of another state. At this point both electronic arrangements have the same geometry and the same potential energy facilitating a change from one state to another. Hence in Figure I-1, the overlapping of S_1 with T_1 makes it possible for a singlet to triplet transition to occur. In this transition, in which a change of spin occurs, the process is called intersystem crossing. If on the other hand, the transition had been of the type $S_2 \rightarrow S_1$ (or $T_2 \rightarrow T_1$) where there is no change of spin, it is called internal conversion. Thus internal conversion and intersystem crossing are transitions whereby excess energy in the molecule is dissipated as heat. They are both radiationless transitions.

For aromatic hydrocarbon compounds, conversion to the lowest excited state (T_1) from a higher state (singlet or triplet) is much more rapid than conversion from the first excited singlet state (S_1) to the ground state (S_0). In the latter process, since the potential energy curves of S_1 and S_0 generally do not cross at any point, it is believed that the important step involves a jump from the lowest vibrational level of the S_1 state to a very high vibrational level of the ground state (of about the same energy).(3) However classical mechanics requires momentum to be conserved in the process. Now the transition $S_1 \rightarrow S_0$ is a large one step process not involving small vibrational-sized steps and it is thus usually the longest one of the nonradiative processes, making the most stringent demands on the conservation requirements and therefore is the least probable. Thus the assumption is made in photochemistry that most molecules with low fluorescence yields, upon electronic excitation enter the triplet state T_1.(4)
In molecules such as aromatic hydrocarbons, radiationless crossings from the upper singlet state S_1 to the triplet state T_1 occurs with a rate constant which is typically of the order of 10^8 sec.$^{-1}$ in rigid media.(5)

I-2.3 Fluorescence and Phosphorescence(4,6)

Fluorescence is a property of those molecules which do not have an easy degradatory path for losing energy as heat between levels S_1 and S_0. The Franck-Condon Principle indicates that for rigid structures the radiationless conversions $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ will be difficult because of the restraints placed on the molecule tending to hold the nuclei together. Thus as an alternative the molecule will emit the remaining energy as light. If emission occurs from the singlet state, then the process is called fluorescence and if it occurs from the triplet state, it is called phosphorescence.

Since thermal relaxation is very fast to the first excited electronic state S_1, it may be stated, in general, that fluorescence occurs from the first excited singlet state of a molecule. Proof of this can be seen from the fact that in most cases, the fluorescence spectrum of a molecule is independent of the wavelength of excitation. Moreover since the transition leading to fluorescence takes place from the zero vibrational level of S_1 to one of the vibrational levels of the ground state, the quanta emitted have less energy than the absorbed quanta resulting in the occurrence of the fluorescence spectrum at longer wavelengths than the absorption spectrum. For similar reasons the phosphorescence spectrum occurs at even longer wavelengths, emission occurring from the triplet level, a level much lower in energy than the corresponding singlet state.

The average lifetime of fluorescence is 10^{-9}-10^{-6} sec., so that fluorescence can be observed with conventional apparatus only while the excitation source is on. The lifetime of phosphorescence varies from 10^{-2}-10 sec., so that in some cases phosphorescence may still be observed for some time after the excitation source has been removed.

I-2.4 Summary

All of the primary photophysical processes can be summarized in a modified Jablonski diagram(7) shown in Figure I-2. The processes are represented by the following equations:

Step	Rate	
$S_o + h\gamma \rightarrow S_1$	$I(nh\gamma)$	(I-2)
$S_1 \rightarrow S_o$ + heat	$k_s(S_1)$	(I-3)
$S_1 \rightarrow T_1$ + heat	$k_{st}(S_1)$	(I-4)
$T_1 \rightarrow S_o$ + heat	$k_t(T_1)$	(I-5)
$S_1 \rightarrow S_o + h\gamma'$	$k_f(S_1)$	(I-6)
$T_1 \rightarrow S_o + h\gamma''$	$k_p(T_1)$	(I-7)

From many photochemical experiments the following four photochemical laws have been deduced:

1. Only the light absorbed by a system is effective in producing a photochemical change.
2. Each photon or quantum absorbed activates one molecule

FIGURE I-2

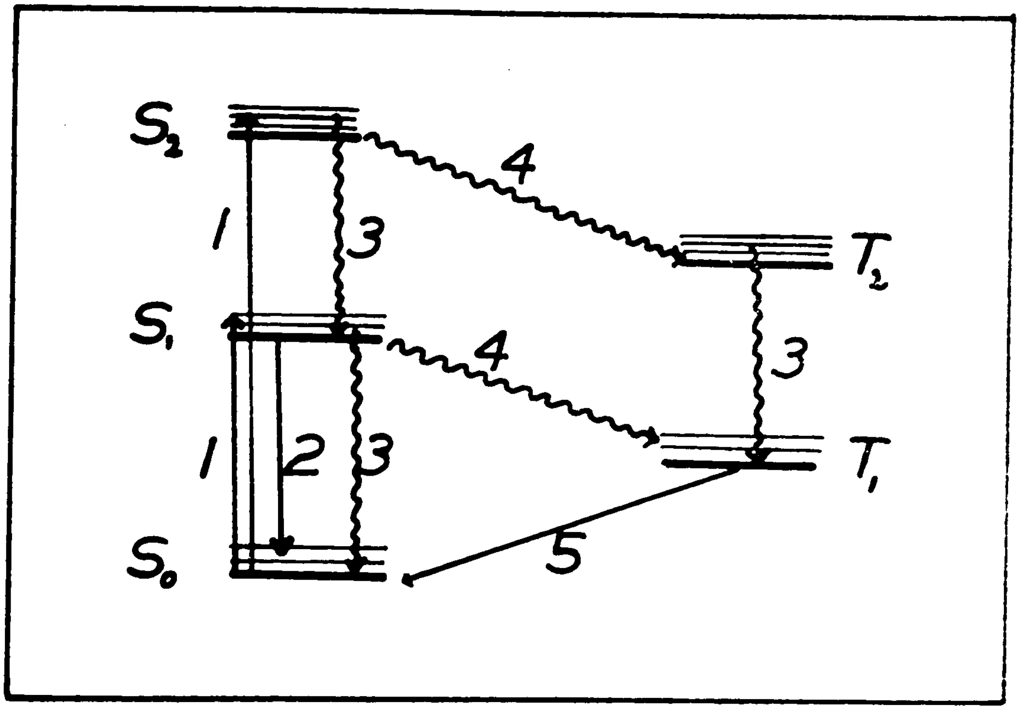
Jablonski Diagram

Radiative processes are indicated by a solid arrow.

Radiationless processes are indicated by a wavy arrow.

Figure is taken from ref. (7).

JABLONSKI DIAGRAM



APPROXIMATE TIMES
FOR EVENTS TO OCCUR

1	ABSORPTION	10^{-15} SEC.
2	FLUORESCENCE	$10^{-9} - 10^{-6}$ "
3	INTERNAL CONVERSION	$10^{-13} - 10^{-11}$ "
4	INTERSYSTEM CROSSING	10^{-8} "
5	PHOSPHORESCENCE	$10^{-3} - 10$ "

in the primary excitation step of a photochemical sequence.

3. Each photon or quantum absorbed by a molecule has a certain probability of populating either the lowest singlet state S_1, or lowest triplet state T_1.
4. Since only molecules in the lowest vibrational levels of the lowest excited states persist long enough to be important photochemically, the lowest excited singlet and triplet states are the starting points of most organic chemical reactions.

I-3 THE TRIPLET STATE

The triplet state is invariably of lower energy than the corresponding singlet state. The lower energy of the triplet results from operation of the Pauli Principle which demands that if the orbitally unpaired electrons have parallel spin, they cannot occupy the same space simultaneously. In the triplet state, therefore, the electrons stay away from one another as far as possible and electron repulsion is reduced. This is not so for the corresponding singlet state. The electrons are paired, i.e. have opposite spins and can occupy the same state resulting in greater electron repulsion so that this state has a higher energy than the corresponding triplet state.

It is now known that many chemical reactions occur from the triplet state.(2,4) The reasons for this are associated with the properties which the triplet state possesses:(5)

a) It is the lowest excited electronic state of the molecule.
b) It has a lifetime, even in fluid solutions of the order of 10^{-4} to 0.1 sec., i.e. a lifetime several orders of magnitude greater than that of the singlet state and hence it is far more susceptible to chemical reaction.
c) Its chemical behavior is usually characteristic of a biradical.

Since the chief mechanism for population of the triplet states of organic molecules is intersystem crossing from the excited singlet state,(4) a good way to photo-protect the molecule should be by a mechanism whereby the singlet states are prevented from passing into the triplet state. This can be accomplished by energy transfer to another molecule through a resonance mechanism.

I-4 ENERGY TRANSFER PROCESSES

Radiationless resonance transfer of electronic energy occurs in the gas phase, in liquids, in solid solutions and in crystals.(8) The course of many reactions in radiation- and photochemistry as well as certain biological processes depends upon the role of energy transfer. It is important then, to familiarize oneself with some of the more important modes of energy transfer. For the most part we shall confine ourselves to the solid state where diffusion and collisional deactivation are negligible, that is, the accepting and donating molecules are considered to be stationary.

I-4.1 Singlet-Singlet Energy Transfer

Consider two molecules B and C where B has its first singlet state above the first excited singlet state of C. When B is electronically excited, thermal relaxation to the first vibrational level of S_1 will occur. B* (* indicates excited state) will now remain in this level until it is deactivated by photoemission or some nonradiative process. However if C is brought into the vicinity of B*, then we have the classical situation in physics where the electronic systems of B and C can be approximated by mechanical oscillators (such as two tuning forks) both of which are capable of oscillating with the common frequency γ. The oscillating charges of B* and C will interact with one another as two dipoles, that is, with an interaction energy which falls off as the inverse third power of the distance separating the interacting centers. Thus when C is in the vicinity of B*, there is the probability that the excitation energy will be transferred from B* to C before either intersystem crossing or emission can occur.

J. Perrin(9) formulated the first theory of excitation transfer by such a resonance mechanism between molecules in solution based on the principles of classical physics. This theory as well as its later quantum-mechanical refinement by F. Perrin(10) predicted transfer distances of more than 100 Å, far greater than those observed experimentally.

Th. Forster(11-15) later developed a theory that predicts energy transfer distances that are closer to experimental values. He was able to derive an equation which relates the probability of energy transfer to the emission spectrum of B (donor) and the absorption spectrum of C (acceptor). His equation predicts the number of intermolecular dipole-dipole transitions per second, where the transfer rate constant is:(15)

$$k_{B^{*} \rightarrow C} = \frac{9000\ k^{2}\ (\ln 10)}{128\ \pi^{5}\ n^{4}\ N\ R_{BC}^{6}\ T^{\circ}} \int_{0}^{\infty} f_{B}(\gamma)\ \varepsilon_{C}(\gamma)\ \frac{d\gamma}{\gamma^{4}} \qquad \text{(I-8)}$$

k : orientation factor, its value being 0.816 for fast Brownian rotation of both molecules and 0.690 for random but rigid orientations

n : solvent refractive index

N : Avogadro's number

R_{BC}: intermolecular distance between donor and acceptor in cm.

T°: intrinsic lifetime of the donor (sec.)

γ : frequency in cm^{-1} of absorption or fluorescence

$f_{B}(\gamma)$: spectral distribution of the fluorescence of the donor (in quanta normalized to unity)

$\varepsilon_{C}(\gamma)$: molar extinction coefficient of the acceptor as a function of γ

The transfer probability depends on the magnitude of the individual transitions and the energy overlap of the emission band of the donor and the absorption band of the acceptor. Now(4)

$$T = T^{\circ} \times \phi_f \qquad (I\text{-}9)$$

where T is the natural lifetime of the molecule in the excited state, T° the intrinsic lifetime, and ϕ_f is the quantum yield of fluorescence (number of quanta emitted divided by the number of quanta absorbed). Also(15)

$$k_{B^* C} = (1/T)(R_o/R)^6 \qquad (I\text{-}10)$$

where R_o is defined as the critical distance between donor and acceptor where emission or energy transfer from the donor can occur with equal probability. With equations (I-9) and (I-10) we can rewrite equation (I-8) as follows:

$$R_o^6 = \frac{9000\ k^2\ (\ln 10)\ \phi_f}{128\ \pi^5\ n^4\ N} \int_0^{\infty} f_B(\gamma)\ \epsilon_C(\gamma) \frac{d\gamma}{\gamma} \qquad (I\text{-}11)$$

Thus from equation (I-11) we see that the lifetime of the donor state is not too important for the efficiency of energy transfer. No matter how forbidden the radiative transition, it is only necessary that the state have a significant emissive yield ϕ_f. For the acceptor there must be an overlap region where the donor transition is isoenergetic with the acceptor transition. Further, the molar extinction coefficient of the acceptor transition should be large. While the donor transition may be strongly forbidden, the acceptor transition cannot.

Another mechanism by which C can be excited when B* is deactivated is when B* fluoresces and C absorbs the fluorescence. This mechanism is sometimes called the "trivial" mechanism. It is an unimportant process once resonance energy transfer begins to occur. At high concentrations of the donor, energy transfer is faster than fluorescence of the donor and hence the trivial mechanism causes negligible excitation of the acceptor.

Table I-2 compares the properties of energy transfer mechanisms such as collisional, formation of complexes, reabsorption (trivial), and resonance energy transfer.

I-4.2 Triplet-Triplet Energy Transfer (16,17)

This type of energy transfer will be efficient when the possibility of singlet-singlet transfer does not occur. In other words, the donor and acceptor molecule would have their energy levels such that S_1 of B lies below the S_1 level of C while the T_1 state of B lies above the T_1 state of C. Triplet-triplet transfer is unlikely by the resonance mechanism because forbidden transitions (unpairing of electron spins) in both the donor and acceptor are involved. However the transfer can take place by the exchange mechanism. Thus when B* and C are close enough for overlap

TABLE I-2

PROPERTIES OF VARIOUS MECHANISMS OF ENERGY TRANSFER (11)

	Collisional	Formation of Complexes	Reabsorption (Trivial)	Resonance Energy Transfer
Absorption Spectrum	does not change	changes	does not change	does not change
Donor Fluorescence Spectrum	does not change	does not change	changes	does not change
Donor Lifetime	decreases	does not change	does not change	decreases
Dependence on Viscosity	energy transfer decreases	independent	independent	independent
Dependence on Volume	independent	independent	increases reabsorption	independent

of their electron clouds, in the region of overlap the electrons are indistinguishable so that an excited electon on B* may also appear on C, that is, an exchange mechanism for energy transfer operates. Both singlet-singlet and triplet-triplet transfer are possible by such an exchange mechanism. However, the transfer requires proximity of the molecules and hence would not be efficient in photoprotection because of the extremely short transfer distance required.

I-4.3 Triplet-Singlet Energy Transfer

In this case the phosphorescence spectrum of the donor must overlap with the absorption spectrum of the acceptor. One might expect that since the process involves a spin-flip, the energy transfer will occur with low probability. Although the rate for energy transfer is small, as can be deduced from equation (I-8), the radiative lifetime of the triplet state of the molecule is so long that energy transfer from a long-lived triplet donor to the singlet level of an acceptor may compete with triplet deactivation by other processes under certain circumstances.(2,4)

I-5 PHOTODEGRADATION OF POLYMERS

Many polymers which are clear transparent plastics could be put to many more commercial uses than is possible at present. Their limited use arises from their short lifetimes when exposed to outdoor conditions. Chemical reactions resulting in unsaturation and oxidation usually initiated by sunlight, a source of ultraviolet radiation, cause the polymer to lose its transparency and become yellow with age. Industry has devised a number of ways to minimize the effects of ultraviolet radiation. These methods do not inhibit the effects of constant radiation permamently, but they do prolong the lifetime of the plastic.

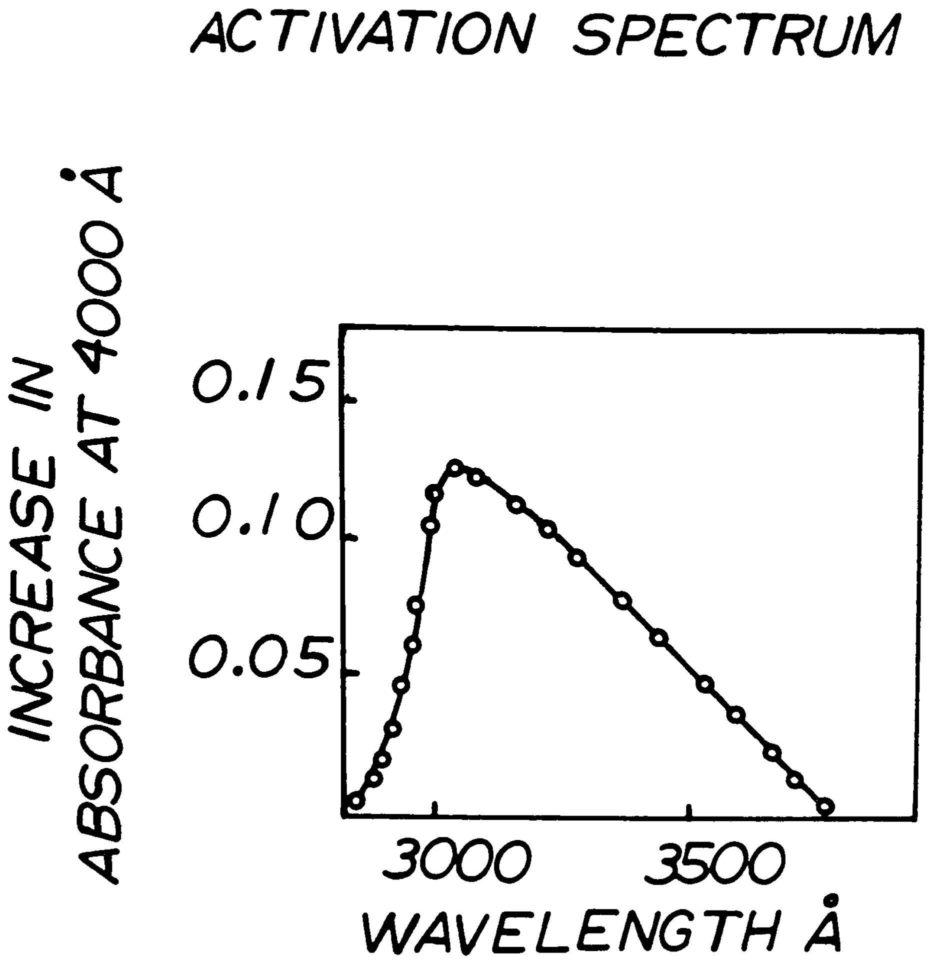
One method is reflection of ultraviolet light by metallizing the polymer.(18) Metals are excellent reflectors of ultraviolet light and therefore, in addition to their value as decorative aids for plastic fittings they confer good protection. However metal powders are not always satisfactory since their incorporation into a polymer matrix may merely mean that they perform as randomly placed mirrors so that repeated reflections throughout the polymer may occur, increasing the distance the light must travel through the matrix and thus increasing the extent of absorption. One must thus experiment with concentration of metal powder and particle size to obtain a polymer composite sufficiently opaque to ultraviolet light to confine its effects to the immediate surface.

Another method is to use pigments or other organic compounds as screening agents. The 'activation' spectrum of the polymer is first determined.(19) An example is given in Figure I-3. The spectrum shows the peak damaging

FIGURE I-3

Activation Spectrum of Polystyrene in Air

Spectrum is taken from ref.(19).


ACTIVATION SPECTRUM
INCREASE IN ABSORBANCE AT 4000 Å
0.15
0.10
0.05
3000
3500
WAVELENGTH Å

wavelengths for the polymer and is not meant to imply that other wavelengths are not detrimental to the polymer. A compound that is stable to ultraviolet light is then selected such that it has a high extinction coefficient in the region of the maximum of the activation spectrum. The outstanding pigment with respect to ultraviolet light absorption is undoubtedly carbon black, which is opaque to u.v. light at a pigment thickness of only 0.0006 mm.(18) Phthalocyanine blues, phthalocyanine greens, quinacridone reds, carbazole violet and indanthrone blue are some of the organic pigments used by industry. The limitation in using pigments as screening agents is that the color they impart to the polymer may not be of the desired shade for the use to which the polymer will be put. Moreover most modern plastics, particularly thermoplastics, are essentially colorless and there are many applications where it is desirable to take advantage of this property. The greatest disadvantage to the screening method however, is that the first few layers of the polymer are not protected. With time these layers become yellow and brittle. Flaking occurs uncovering fresh surfaces to be degraded in like manner so that in a long enough period of time all of the polymer could be degraded layer by layer.

Perhaps the earliest publication on polymer durability was a paper by A. W. Hoffman(20) in 1860 on the deterioration of gutta-percha cables. In the intervening 110 years, a veritable torrent of papers related to polymer degradation, and in particular to polymer weatherability have appeared. A bibliography compiled by Searle and Hirt (21) for a period of only 40 months in 1957-1960 lists over 1000 references. Several examples of polymer degradation are cited in the following paragraphs.

Polyolefins react readily with oxygen during weathering, often becoming brittle long before visual evidence of breakdown appears. Since pure paraffins are transparent to ultraviolet radiation which penetrates the atmosphere, Burgess (22) has proposed that occasional carbonyl groups or other defects in molecular structure absorb the energy required for the photoreaction.

V. R. Regil and N. N. Chernyi (23) studied the life of polymer fibres and films under stress while exposed to ultraviolet radiation by measuring the decay of stress necessary to maintain a constant strain in the fibres and films as a function of time. When the fibres and films are not irradiated and the stress is plotted versus log time, a linear relation is found and is such that the stress decays by 30-50% in 10^6 sec. When the fibers and films under stress are simultaneously strained and irradiated with u.v. light (2300-2700 Å) and the stress again plotted versus log time, the resulting curve is linear and coincident with the first (not irradiated curve) until an elapsed time of about 10^3 sec. is reached, but after this time the curve bends away from the straight line indicating a rapid decay in stress, which at about 10^5 sec. approaches zero. The u.v. irradiation is evidently responsible for much loss in strength. The stress initially applied in the fibers and films was considerable, and approached their breaking load. Thus that imposed on poly(vinyalcohol) fibers was 55 kg./mm.^{2}, on cellulose triacetate fibers 25 kg./mm.^{2}, and on poly(methylmethacrylate) film 7 kg./mm.^{2}

Halogen containing polymers such as chlorinated rubber, polyvinylchloride and polyvinylidene chloride when exposed to ultraviolet light become light yellow at first, gradually turning to dark yellow and then shifting to the red with time and uder extreme exposure eventually approach blackness.(24) Discoloration of polyvinylchloride results from a zip reaction eliminating successive hydrogen chloride units to form a polyene chain structure(25) represented by the following general equation:

$$-(CH_2\text{-}CHCl)_{\bar{n}} \xrightarrow{h\gamma} -(CH{=}CH)_{\bar{n}} \qquad (I\text{-}12)$$

Polymer specimens darken long before HCl loss reaches 0.1% by weight and well before embrittlement is detectable.

Crosslinking and chain-scission reactions occur simultaneously when polyacrylonitrile is subjected to 2537 Å radiation in vacuum.(26) Hydrocyanic acid and hydrogen have been described as the principle volatile product of photolysis.(27)

Polystyrene turns yellow and eventually forms surface crazes in sunlight. Achhammer and co-workers(28) proposed that the color change was associated with gradual conversion of phenyl groups to quinoid structures, but Grassie and Weir(29) concluded instead that conjugated unsaturation developed along the polymer backbone. The latter workers noted that the rate of yellowing under 2537 Å was unaffected by the presence or absence of oxygen. Since the color intensified while the hue remained unchanged, and since the irradiated polymer darkened rapidly on melting, Grassie and Weir suggested that the immobility of molecular chains in the rigid polymer film prevented formation of coplanar sequences of double bonds.

Finally the outdoor service of nylon and cellulosic polymers is less than 3 years.(30) Sunlight generally discolors nylons,(31) bleaches cellulose(32) and destroys its mechanical properties. In short all polymers appear to be vulnerable to ultraviolet light.

I-6 STATEMENT OF PROBLEM

We propose to investigate the possibility of using a different method to protect the polymer from radiation damage, a method that lacks a number of the disadvantages of the techniques described earlier.

For this project we have chosen an amorphous transparent solid polymer, polystyrene. If we select a suitable compound such that its singlet level is below the singlet level of polystyrene, and such that the absorption spectrum of the compound overlaps the fluorescence spectrum of the polymer, then we should see energy transfer from polymer to solute by the Forster mechanism. Now if the assumption that chemical reaction occurs mainly from the triplet state(4) is correct, then we should see a decrease in the degradation of the polymer. This is because resonance energy transfer deactivates the excited singlet states of the polymer preventing it from populating the triplet state by intersystem crossing. However if chemical reaction occurs from the short-lived singlet state of the polymer, then energy transfer will have to occur quickly if any photoprotection is to be observed.

In our method even the very first layer of the material will be protected since upon absorption of ultraviolet energy, the first layer can transfer this energy over a distance of perhaps 30 Å to an acceptor molecule inside the matrix. If we add the requirement that the acceptor molecule have a high fluorescence yield, then we have a system wherein the energy transferred from the polymer to the acceptor molecule is reemitted harmlessly as light. Anthracene and 9,10-diphenylanthracene were chosen as acceptors for this work.

CHAPTER II

EXPERIMENTAL TECHNIQUES

CHAPTER II

EXPERIMENTAL TECHNIQUES

II-1 PREPARATION OF SAMPLES

Styrene monomer(Matheson, Coleman and Bell) was washed with a 10% aqueous solution of potassium hydroxide to remove the inhibitor. The styrene was then washed several times with distilled water and finally dried over anhydrous magnesium sulphate.

Distillation of the purified monomer was carried out twice under reduced pressure. The distilled styrene was then outgassed under high vacuum by the freeze-thaw method. The outgassed styrene was distilled under high vacuum into preweighed ampoules containing a known amount of anthracene (blue-violet fluorescence type) or 9,10-diphenylanthracene. Both solutes were used as received without further purification. The ampoules were sealed off. The ampoule and glass-joint remaining after sealing off the sample were weighed and the difference between the latter value and the empty vial + anthracene gave the amount of styrene distilled into the ampoule. This was of the order of 20 grams.

The ampoules were placed in an oil bath at 120°C., the samples containing large amounts of anthracene (2-5%) were taken out of the oil bath repeatedly and shaken until it was clear that all of the solute had dissolved. The samples were kept in the oil bath for a period of ten days so that there would be little residual styrene monomer. After this interval of time the temperature of the oil bath was slowly lowered to allow annealing of the polymer samples. The solid polymer cylinders were removed by breaking the glass vials.(33)

The samples used for the fluorescence work were 22 mm. in diameter and were machined on a lathe to a thickness of 12 mm.

Preparation of polystyrene film was accomplished by dissolving the appropriate amount of sample (chips obtained by turning the solid cylindrical sample on a lathe) in reagent grade benzene and pouring the solution over a mercury surface in a petri dish. Upon evaporation of the benzene a thin transparent film was left, and this was easily removed. The thickness of the films was 0.02 to 0.03 mm. The measurement was made by cutting the film out to a known area, weighing it, and then dividing the weight of the film by the density of polystyrene.

II-2 APPARATUS FOR FLUORESCENCE MEASUREMENTS

The excitation source was a Bausch and Lomb high intensity monochromator equipped with a 150 watt xenon lamp and a grating of 2700 grooves/mm. for a range of 2000-

4000 Å. A quartz achromatic condenser lens was used to project the image of the exit slit onto the sample. The detection unit for fluorescence was a Beckman DU-2 Spectrophotometer equipped with a quartz prism and a 1P28 phototube. The sample was placed at the entrance slit of the Beckman unit at the position that is normally occupied by the hydrogen or tungsten lamp housing that comes with the unit.

Since the Bausch and Lomb monochromator has only one grating instead of two as in a regular spectrophotometer, there was some scattering of the visible light which emerged with the selected ultraviolet region. Thus a Dow-Corning 7-54 filter which does not transmit visible light was placed at the exit slit of the excitation monochromator. A schematic diagram of the set-up of the equipment is given in Figure II-1.

II-3 MEASUREMENT OF FLUORESCENCE SPECTRA(33-40)

There are three geometrical arrangements which can be used to study the fluorescence from the sample. These are:

a) Front-surface....... the fluorescence is observed on the same side of the sample where the excitation light falls.

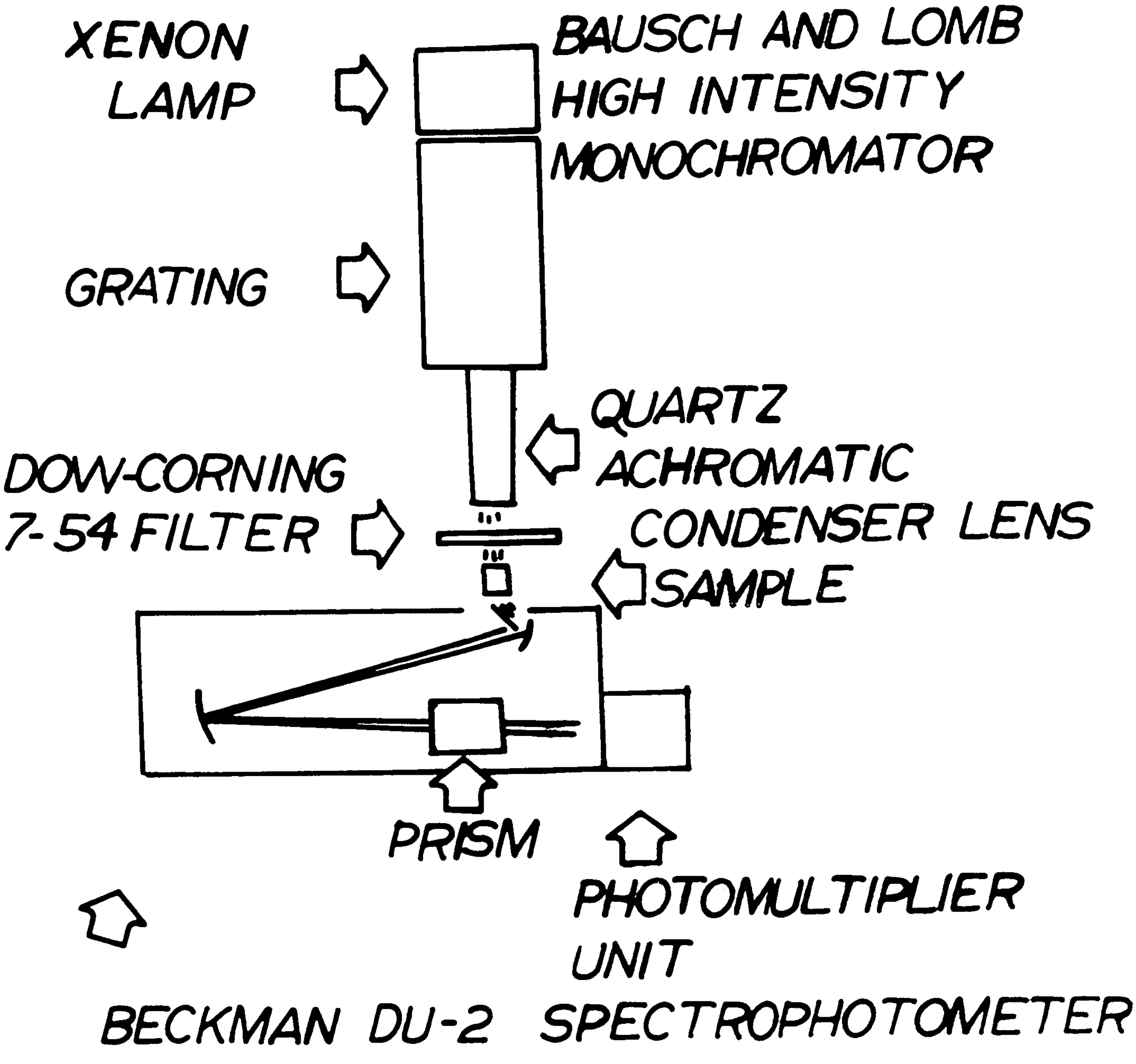
b) Right-angle......... the fluorescence is observed at 90° to the excitation light.

c) Transmission........ the fluorescence is observed on the

FIGURE II-1

Schematic Diagram of Spectrophotofluorometer

SCHEMATIC DIAGRAM OF SPECTROPHOTOFLUOROMETER



opposite side from that where the excitation light falls.

For the particular equipment we have, the transmission method is the most convenient. The front-surface method is best when one does not want to observe any self-absorption effects.

For indirect excitation whereby the polymer absorbs all the light, 2700 Å was used as the excitation wavelength for the polystyrene-anthracene system and 2900 Å for the polystyrene-9,10-diphenylanthracene system. For direct excitation where only the solute absorbs, 3340 Å was used in both cases. The samples were thick enough to absorb all of the radiation.

The fluorescence spectra were measured by setting the Beckman slit width so that the peak of the fluorescence spectrum registered as 100% transmission on the absorbance dial. In so doing the slit width had to be narrowed as one went to higher concentrations of anthracene in the samples. The Beckman instrument was operated at its maximum sensitivity for all of the fluorescence work.

In order to compare the relative fluorescence from sample to sample the amount of incident excitation light had to be normalized for all samples. To do this one takes a sample and with the excitation source on, one makes a plot of intensity of fluorescence (I) at a particular wavelength (4200 Å in this case) versus slit width (SW). The ratios of I_1/I_2 and SW_1/SW_2 are then computed and plotted as shown in Figure II-2.(41) For example, after measuring the fluorescence spectra of two samples it was found that the slit width was open four times wider for sample A than for sample B. The areas of the fluorescence spectra would then be divided by the appropriate value so that the results so obtained are fluorescence intensities for constant excitation intensity. Thus as seen from Figure II-2, the area for sample A would be divided by 10 before comparing its value to that of sample B.

The 1P28 phototube has a very high sensitivity in the region of 5000 Å, a region where fluorescence from the sample is lowest. For this reason the fluorescence spectra had to be corrected for photomultiplier sensitivity. From the manufacturer's data the maximum sensitivity was given a value of one, and the other points on the graph were then assigned a value that is a fraction of one. The correction curve used is shown in Figure II-3. These values were used to divide the relative intensity values of fluorescence, giving the true fluorescence value.

II-4 MEASUREMENT OF EFFICIENCY OF ENERGY TRANSFER

For direct excitation of anthracene, 3340 Å, the maximum of polystyrene fluorescence, was used. The slit width of the Beckman was adjusted to give a reading of 100% transmission at 4200 Å , the peak of the fluorescence spectrum

FIGURE II-2

Ratio of Fluorescence Intensities at 4200 Å for the Same Sample Versus the Ratio of Their Respective Slit Widths on the Beckman Unit

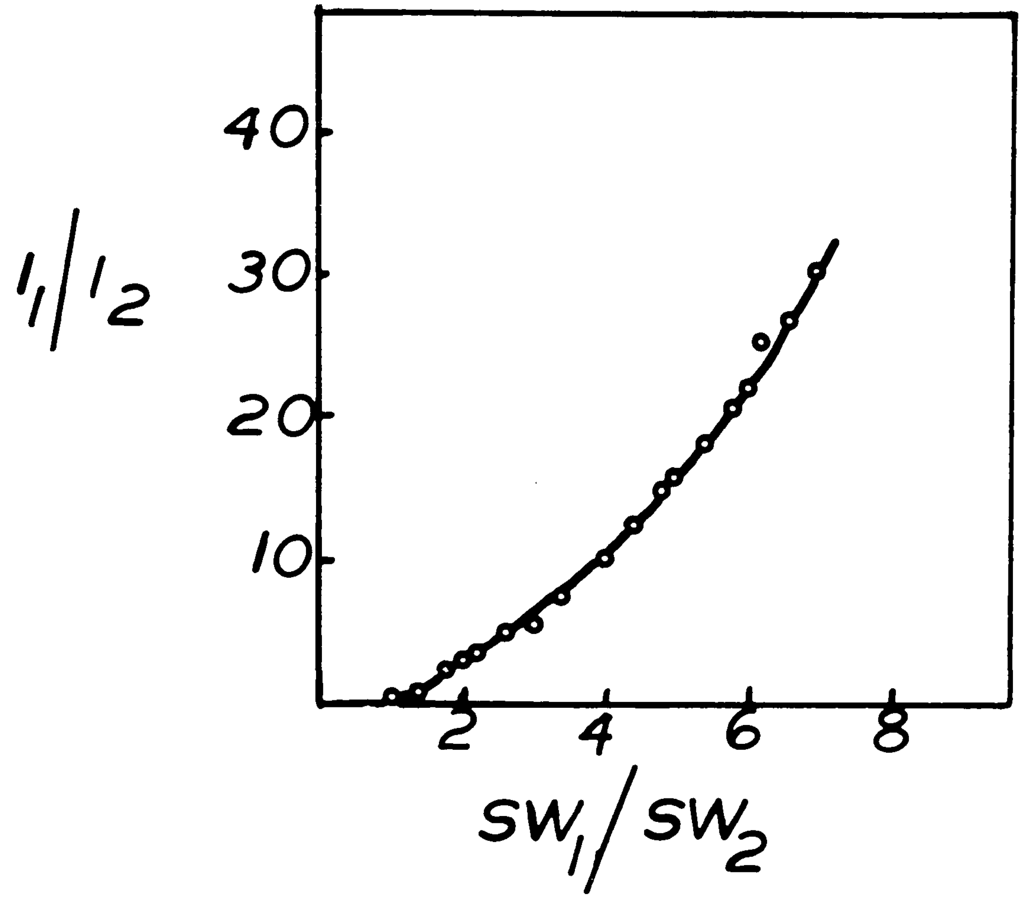
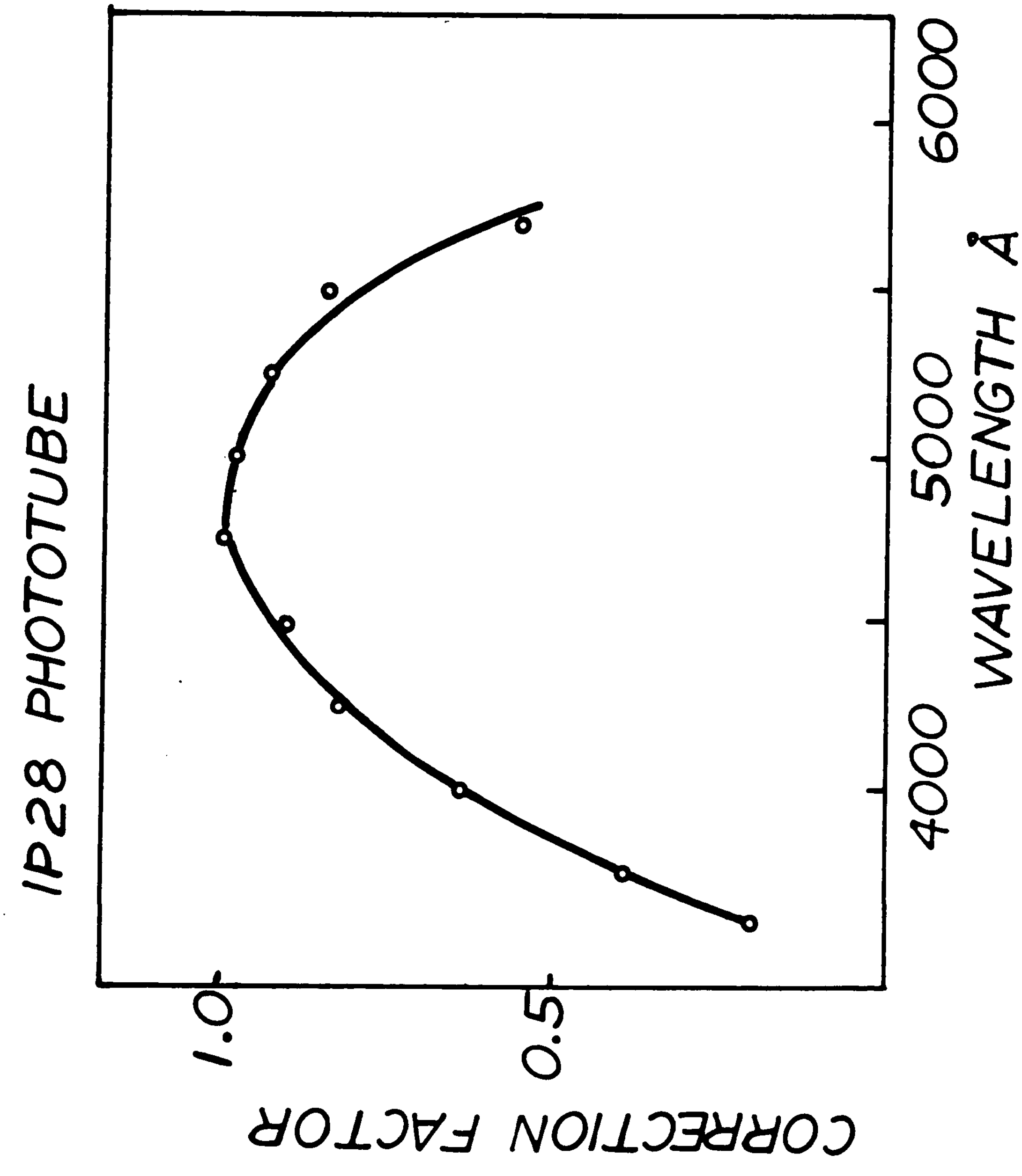

40
30
20
10
I1/I2
2
4
6
8
SW1/SW2

FIGURE II-3

Correction Factor for 1P28 Phototube Versus Wavelength


1P28 PHOTOTUBE
1.0
0.5
CORRECTION FACTOR
4000
5000
6000
WAVELENGTH Å

for most samples. The excitation wavelength was then changed to 2700 Å (for the polystyrene-anthracene system) on the Bausch and Lomb monochromator. The intensity of fluorescence was now measured by using the transmittance dial which will give a value below 100% depending on the amount of energy transfer that has taken place. Since the slit width has remained open to the same extent for both measurements, the fluorescence intensities obtained at 2700 Å and 3340 Å can be compared directly to one another. The xenon lamp does not, however, emit 2700 and 3340 Å in equal intensity. The intensities of the two exciting wavelengths were determined by ferrioxalate actinometry.(42,43) Thus the fluorescence intensities of the acceptor F_{2700} and F_{3340}could be normalized for equal amount of excitation. The efficiency of energy transfer is then defined as (F_{2700}/F_{3340}) x 100.

For 9,10-diphenylanthracene 2900 Å was used for indirect excitation of the solute while 3340 Å was used for direct excitation.

II-5 FERRIOXALATE ACTINOMETRY(42,43)

The potassium ferrioxalate actinometer is a very sensitive actinometer, in fact, it is about one thousand times more sensitive than the uranyl oxalate actinometer, the traditional substance used to determine quantum output. Moreover the ferrioxalate actinometer is as precise for measuring low intensities. Thus it is ideally suited to measuring light intensities in a monochromator. The quantum yield is 1.24. The main reaction is reduction of the ferric ion to the ferrous ion.

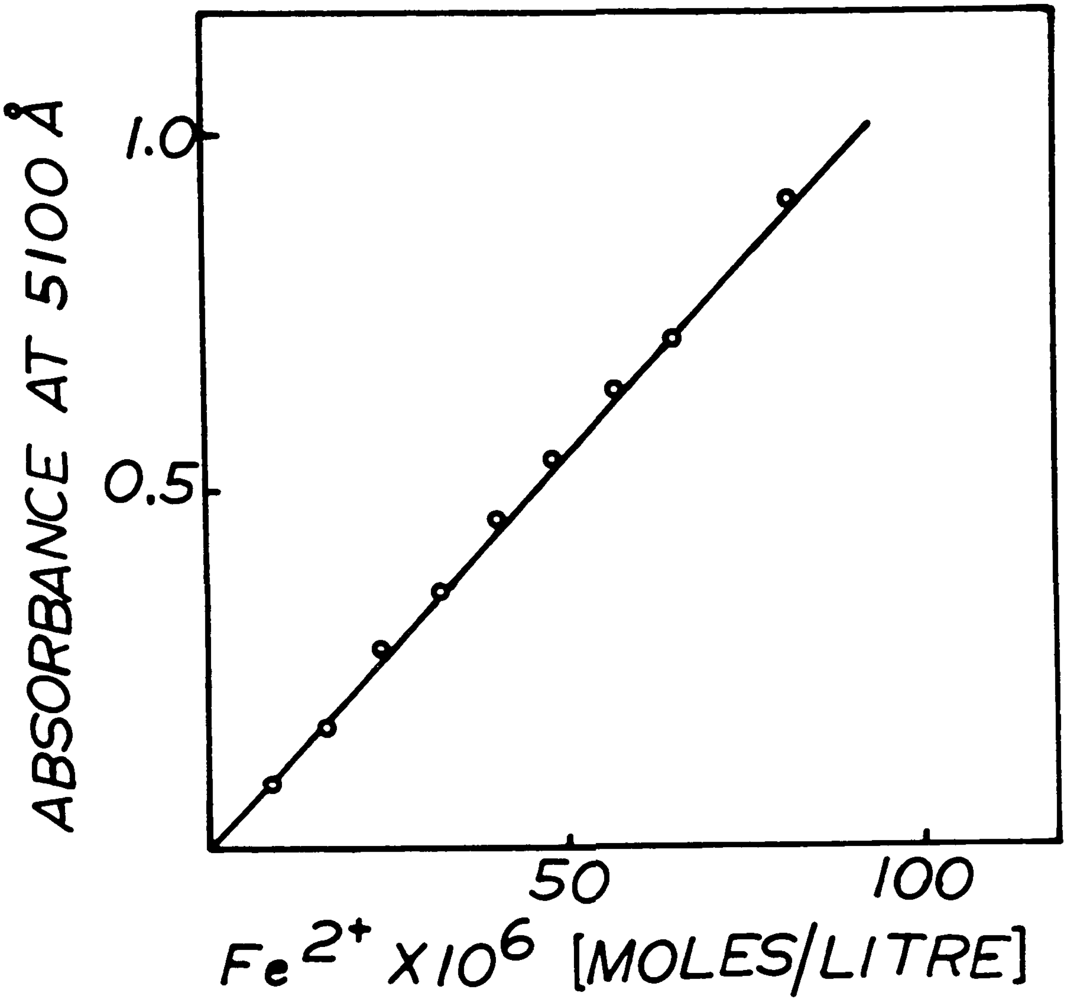
The experimental procedure in using the actinometer is to prepare a calibration graph for analysis of the Fe^{2+} complex. A standard solution of 0.4 x 10^{-6} mole of Fe^{2+}/ml., 0.1N in H_2SO_4, is freshly prepared from a standardized 0.1M $FeSO_4$ solution (0.1N H_2SO_4). To a series of volumetric flasks (25 ml.) 0.0, 0.05, 1.0, 1.5, ...4.5, 5.0 ml. of the standard solutions are pipetted in. Sufficient 0.1N H_2SO_4 is added to bring it to the needed level in the volumetric flask after 5 ml. of the buffer solution of sodium acetate (600 ml. 1N NaO_2CCH_3 and 360 ml. 1N H_2SO_4 diluted to one litre) and 2 ml. of a solution of 1,10-phenanthroline in water (0.1% by weight) have been added. The solutions are allowed to stand for one hour and then the transmittance of each solution is determined at 5100 Å in a one cm. cell using the blank iron-free solution in the reference beam. A linear plot of optical density versus molar concentration is then made. The results can be seen in Figure II-4. The slope of the line is 1.12 x 10^4 litres/mole-$cm.^{-1}$

The reactant ferrioxalate was prepared by mixing 3 volumes of 1.5M $K_2C_2O_4$ solution and 1 volume of 1.5M $FeCl_3$ solution (reagent grade chemicals). The pure green crystals were dried and stored in the dark when not used.

FIGURE II-4

Standard Calibration Graph for Potassium Ferrioxalate Actinometry

STANDARD CALIBRATION GRAPH FOR POTASSIUM FERRIOXALATE ACTINOMETRY



The number of ferrous ions formed during irradiation of an aqueous solution of ferrioxalate is found by using the following equation:

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20} V_1 V_3 \log(I_0/I)}{V_2 L \varepsilon} \qquad (II\text{-}1)$$

V_1 : the volume of actinometer solution irradiated (ml.)

V_2 : the volume of aliquot taken for analysis (ml.)

V_3 : the final volume to which V_2 is diluted (ml.)

$\log(I_0/I)$: the measured optical density of the solution at 5100 Å

L : the path length of the cell used (cm.)

ε : the experimental value of the molar extinction coefficient of the Fe^{2+} complex as determined from the slope of the calibration plot (1.12×10^4 litres/mole-$cm.^{-1}$). Then

$$n_{Fe^{2+}}/1.24t = \text{quanta/unit time} \qquad (II\text{-}2)$$

where t is the time of irradiation.

II-6 ULTRAVIOLET ABSORBANCE MEASUREMENTS

The measurements for ferrioxalate actinometry were made on the Beckman DU-2 spectrophotometer. All other u.v. spectra were taken on a Unicam S.P. 800 recording spectrophotometer.

II-7 DETERMINATION OF RESIDUAL STYRENE MONOMER CONCENTRATION(44)

According to the method described by J. E. Newell(44) the amount of residual styrene monomer in the pure polymer was determined by the use of the equation:

$$X = \frac{100\ (\varepsilon - \varepsilon_p)}{(\varepsilon_m - \varepsilon_p)} \qquad \text{(II-3)}$$

X : the % residual styrene monomer

ε, ε_p, ε_m : the specific extinction coefficients of the sample, monomer-free polymer, and monomer respectively

The sample to be studied was dissolved in chloroform. The optical density of the solution was then measured at three different wavelengths: 2500, 2550, 2600 Å.

$$X = 0.743(\varepsilon_{2500} - 1.34) \qquad \text{(II-4)}$$

$$X = 0.876(\varepsilon_{2550} - 1.80) \qquad \text{(II-5)}$$

$$X = 1.178(\varepsilon_{2600} - 2.12) \qquad \text{(II-6)}$$

II-8 VISCOSITY MEASUREMENTS

Viscosity measurements were made in an Ubbelohde dilution viscometer with a flow time of 24.8 sec. for pure benzene. The solutions contained 1% polymer by weight, the flow time for the solutions varying from 120 to 200 sec. The ratios of the flow times of the solutions at different dilutions to that of the pure solvent (η/η_o) is found. A linear plot is obtained for η_{sp}/c $[\eta_{sp} = (\eta/\eta_o - 1]$ versus c (c is the concentration of polymer in grams per 100 ml.). The extrapolation of this line to c = 0 gives the intrinsic viscosity.

II-9 GAMMA RADIATION

The irradiation source was a Co^{60} Gammacell 220 device with a dose rate that ranged from 0.35 to 0.32 megarad per hour for this work.

II-9.1 Gas Yields

The solid cylindrical sample obtained after polymerization was cut into chips on the lathe. About 0.8 gram of sample was weighed into a glass ampoule provided with a break-seal. Upon evacuation of the ampoule to 10^{-6} mm. Hg the sample was sealed off and placed in the gamma cell. After the required period of irradiation, the seal on the ampoule was broken and the evolved gases were then released into a Toepler pump equipped with a McLeod Gauge.

II-9.2 Gelation Dose

A plot of intrinsic viscosity versus dose in megarads is made. The point at which the intrinsic viscosity increases sharply (i.e. exponentially) is taken as the gelation dose.(45) For comparative purposes samples with the same intrinsic viscosity were used.

II-9.3 Electron Spin Resonance Measurements

The polystyrene chips were ground to a course powder on a Wiley Mill. The powder was packed as uniformly as possible in pyrex tubing (o.d. 4mm.) and evacuated to 10^{-6} mm. Hg before sealing off the vials. The unirradiated samples were checked for any signal for radicals that might have been created by the mechanical grinding. None were found.

The vials were placed in the gamma cell for periods of three hours. One end of the pyrex tubing was heated in a Bunsen flame to eliminate radicals created in the glass by gamma radiation. After the heated end had cooled, the polymer was tapped down into that end and the e.s.r. spectra measured with a Varian V4502 spectrometer which has a 100 kHz modulated cavity and operates in the X band. The spectra consisted of the first derivative of the absorption curve. A mechanical planimeter was used to find the first moment of the spectra. DPPH (1,1-diphenyl-2-picrylhydrazyl) was used as the standard reference compound. Between irradiation periods and recording of the spectra the samples were stored in liquid nitrogen.

The low power configuration of the e.s.r. spectrometer was used with the attenuation dial at 5.9 (20 db) and the cryostat dial at 3.5 (15 db) for a total attenuation of 35 db. The amount of power absorbed by the samples was about 30 microwatts. Polystyrene begins to saturate at 40 microwatts.(46)

For the determination of the e.s.r. spectrum of anthracene radicals in a transparent polymer matrix, anthracene (or 9,10-diphenylanthracene) was dissolved in styrene monomer which had been purified as described in Section II-1 of this chapter. The solution was poured into a pyrex vial (o.d. 4mm.), evacuated and outgassed by the freeze-thaw method before sealing it off. It was placed in an oil bath at 120°C for seven days. The polystyrene samples were removed by breaking the glass vials. The samples were heated very slightly to anneal them and therby obtain very transparent samples. The samples were now placed in pyrex vials (o.d. 5mm.), evacuated and sealed off. The samples were then placed between two pieces of Corning filters 7-60 (having a transmission band from 3000-4200 Å, the maximum transmission occurring at 3500 Å) held together with aluminum foil around the edges of the filters. In this way the samples did not receive any short wavelengths of ultraviolet radiation while exposed to the full intensity of a Hanovia high pressure mercury source.

II-10 ULTRAVIOLET RADIATION

II-10.1 Degradation of Polystyrene Films

A Hanovia 450 watt high pressure mercury lamp (arc 4.5 in.) was used. The filter for isolating the 2700-3000 Å region of the ultraviolet spectrum consisted of an aluminum cylinder divided horizontally into two compartments of 2 cm.depth by quartz plates of optical quality. Copper sulphate (3 gm./l.) was circulated through the upper compartment and in the bottom compartment acridinium chloride (0.0035 gm./l.) together with Cation X (0.022 gm./l.) whose chemical name and synthesis are described below. The filter solutions were kept on ice and circulated by means of two pumps. The mercury lamp and the filter apparatus were enclosed in a box lined with asbestos. One side of the box was open, but covered with a heavy fiberglass curtain to allow the hot air to pass out into the room. In the bottom of the box a hole was cut to the size which allowed an area needed for irradiation of the films.

The quartz apparatus used in the irradiation of the polymer films was a cylinder 2.5 cm. in depth and having quartz windows of optical quality, 7 cm. in diameter. The polymer film was supported near the face toward the u.v. lamp by filling the apparatus with glass beads. The experimental set-up is shown in Figure II-5.

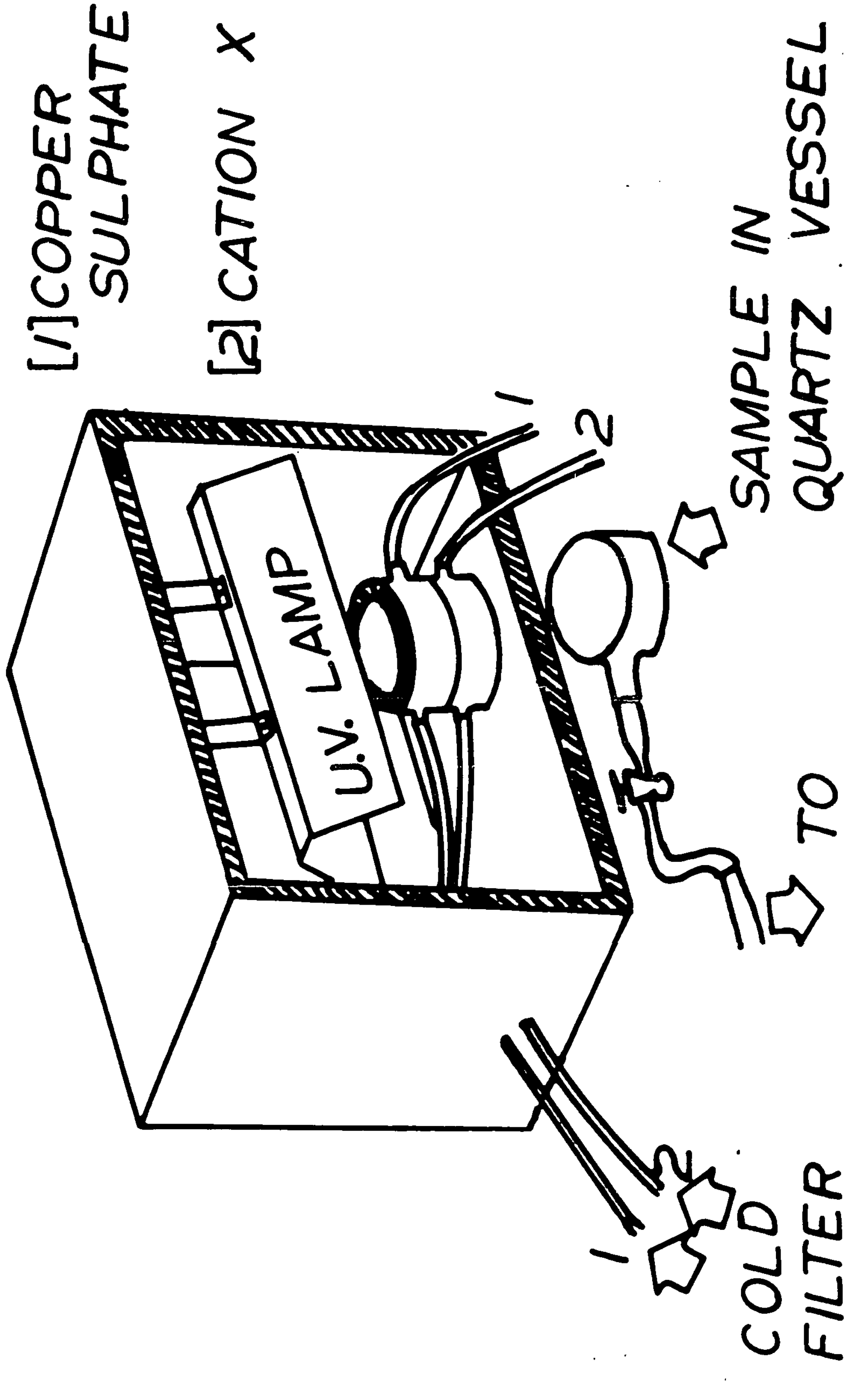
II-10.2 Synthesis of Cation X (2,7-dimethyl-diazo-(3,6)-cycloheptadiene-(1,6)-perchlorate)(47)

One c.c. of 2,4-pentanedione(Eastman Organic Chemicals) and one c.c. of anhydrous ethylenediamine (Matheson,

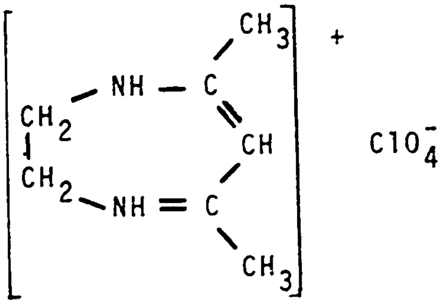
FIGURE II-5

Schematic Diagram of the Experimental Set-up for the Ultraviolet Decomposition of Polystyrene Films

EXPERIMENTAL SET-UP



Coleman and Bell) were warmed in a test tube for two minutes at 120°C in an oil bath. One c.c. of glacial acetic acid was then added in small portions and the mixture held in the oil bath for ten minutes. The mixture was cooled, dissolved in twenty c.c. of water and six c.c. of 20% perchloric acid added. The perchlorate crystallized out of solution into nearly colorless crystals having a light yellow color with a melting point 146-7°C. The crystals were used without any further purification. The formula for the compound is written as:



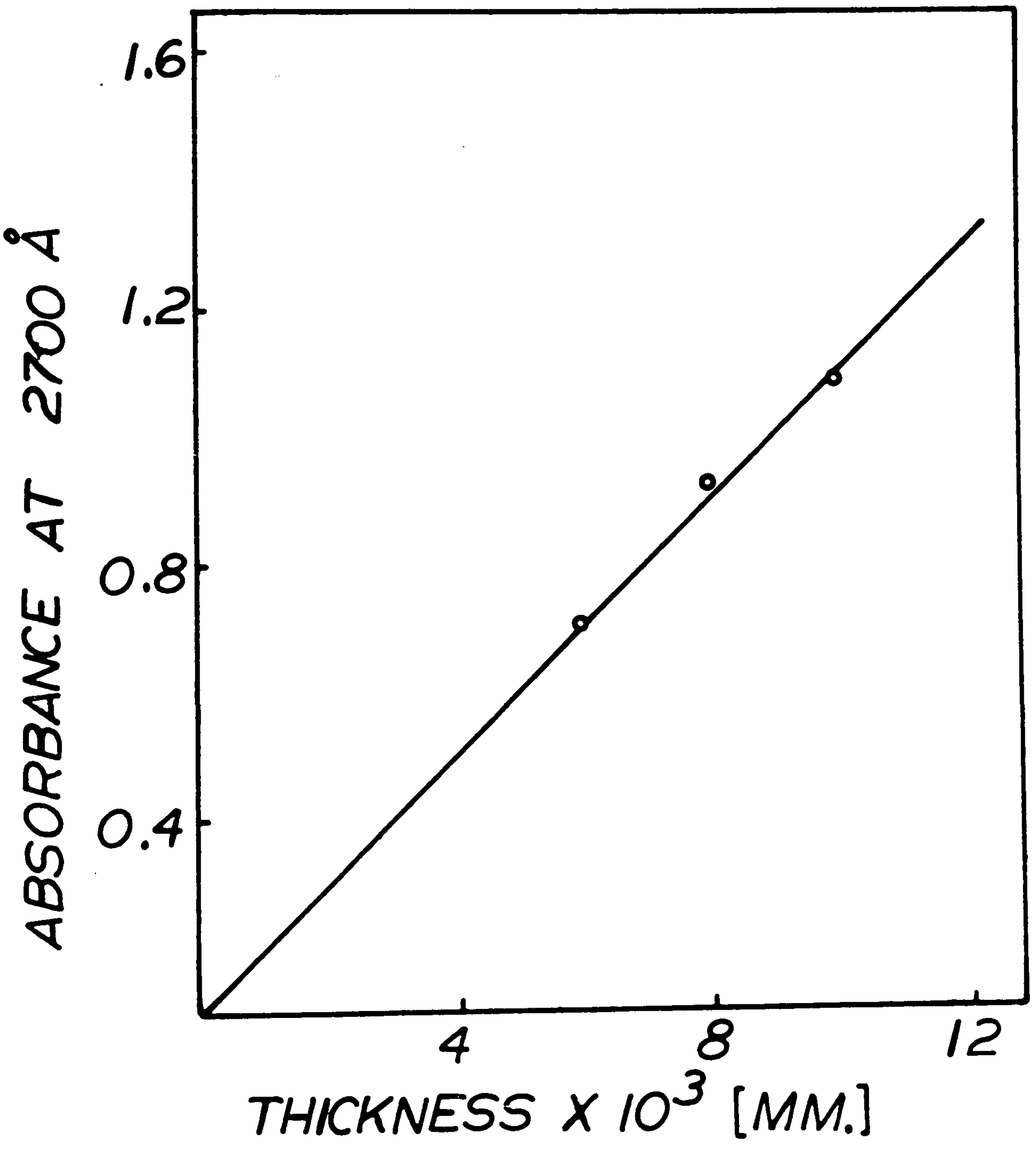
II-10.3 Determination of % Insolubility of Polystyrene After Ultraviolet Irradiation

From a plot of absorbance versus thickness of polystyrene film in Figure II-6, it is seen that for 2700 Å, 95% (absorbance 1.3) of the ultraviolet radiation is absorbed by a thickness of 0.012 mm. and the remaining 5% is absorbed by a thickness of 0.011 mm. Therefore it was decided to assign the weight of insoluble material formed to the first 0.012 mm. of the film. Since most of the films were 0.02 mm. thick or more no correction had to be made for unabsorbed light.

FIGURE II-6

Absorbance at 2700 Å of Thin Pure Polystyrene Films Versus Wavelength

PURE POLYSTYRENE FILM



The films were cut to a constant area with a metal cutter made for this purpose, weighed, and from the known density of polystyrene the thickness calculated. A semicircle of pure polystyrene was placed alongside a semicircle of polymer containing solute. The two films were irradiated at the same time, side by side thus receiving the same amount of radiation. The films were dissolved in tetrahydrofuran (THF) and filtered.

The filter papers used were first wetted with THF and dried under vacuum. They were then used in filtering out the insoluble crosslinked polymer. This pretreatment of the filter paper with THF gives reproducible results upon weighing since these filter papers seem to absorb water vapour more uniformly than untreated filter papers. Since the amount of insoluble material for pure polystyrene varies from 0.0080 to 0.0060 gm., the nonuniform absorption of water vapour can have a large effect on the results.

Whenever a set of polymer films were filtered, three extra filter papers were weighed and used for blanks. After filtering the films, washing the blank filter papers with THF as well, drying, the filter papers were put in the air-conditioned balance room and allowed to come to equilibrium with the air of the room. The blank filter papers were then weighed and it was always found that they either gained or lost weight to the same extent when compared to their first weights. The weight difference was used to correct for the true weight of insoluble material.

The polymer films were irradiated for three and a half hours. The difference in weight of insoluble material for the solute-containing polymer and pure polymer yielded the % protection.

II-11 SYNTHESIS OF DIELS-ALDER ADDUCT OF STYRENE AND ANTHRACENE

About 4 gm. of anthracene were dissolved in 20 c.c. of styrene. The sample was evacuated and outgassed by the freeze-thaw cycle. After sealing the sample off, it was placed in an oil bath at 120°C. The sample was removed repeatedly from the bath and the hot styrene monomer vigorously shaken until the anthracene had all dissolved. The sample was left in the bath for two days. The sample was then dissolved in benzene and precipitated with methanol. The Diels-Alder adduct, being soluble in methanol, can be retrieved by filtering out the polymer and evaporating the methanol.(48) To free the adduct from residual anthracene it was recrystallized from cold methanol and then run through an alumina column using a 3:2 mixture of low-boiling petroleum ether and chloroform. The adduct eluted first, u.v. spectroscopy being used to determine which fractions contained the pure adduct. The styrene-anthracene adduct was found to have a melting point of 87-90°C before purification and 103-4°C after purification. The value reported by Cherkasov and Voldaikina(48) is 95-96.5°C.

II-12 SYNTHESIS OF DIANTHRACENE(49)

A saturated solution of anthracene in methanol was prepared, outgassed in a pyrex vial and sealed off under high vacuum. The sample was then placed in a photochemical reactor having a u.v. range of 3300-4000 Å with a maximum at 3600 Å and irradiated for a period of twelve hours. The dianthracene precipiated out of solution upon formation. The vial was broken and the crystals filtered off and washed. The u.v. spectrum showed the crystals to be pure and needed no further purification. The melting point of the crystals was 260-2 °C

CHAPTER III

PRIMARY PHOTOPHYSICAL PROCESSES

CHAPTER III

PRIMARY PHOTOPHYSICAL PROCESSES

III-1 INTRODUCTION

Schorr and Torney(50) were the first to discover the 'phosphor-plastics'. They reported that solid solutions of p-terphenyl in polystyrene produced scintillations upon excitation with ionizing radiation. Since then many systems have been studied using polystyrene or polyvinyltoluene as the solvent for a number of fluorescent solutes.

The system polystyrene-anthracene was first described by Koski(51) who polymerized dilute solutions of anthracene in styrene using a mixed catalyst of benzoyl peroxide and tricresyl phosphate. The intensity of anthracene fluorescence was much greater than could be attributed to anthracene molecules being directly excited by X-rays; hence he concluded that some mode of energy transfer between polystyrene and anthracene was taking place. He suggested, incorrectly as we shall see later, a radiative transfer mechanism where the fluorescence of the polymer is absorbed by anthracene, the excited anthracene then emitting its characteristic radiation.

Swank and Buck(52) investigated a number of solutes in polystyrene. They concluded that, while radiative transfer does contribute to the overall process, the major fraction of energy is transferred by some nonradiative process.

Krenz(53) also studied the polystyrene-anthracene system and found that the trivial mechanism operated below 5×10^{-4}M, but that a different type of energy transfer started to occur at higher concentrations. He also found that polymerizing styrene in the presence of anthracene resulted in the polymer having a lower viscosity relative to that of styrene polymerized in the absence of anthracene under the same conditions. Krenz proposed that some compound is formed between anthracene and polystyrene, the anthracene most probably acting as a chain terminating agent.

As more information was collected, not only on the polystyrene-anthracene system but also on other polymers such as polyvinyltoluene and fluorescent solutes such as pyrene, tetraphenylbutadiene, diphenyloxazole, to name a few, it became apparent that the most important mechanism for energy transfer in these systems was by dipole-dipole interaction(54) as had been described by Forster.(11-15)

III-2 EXPERIMENTAL SYSTEM

III-2.1 Description

Polystyrene, when prepared by thermal polymerization of the monomer, is an amorphous solid material composed of randomly oriented chains with essentially no crosslinks between them. The polymer has a fluorescence spectrum from 2900-4000 Å. Anthracene, a crystalline compound, has an absorption spectrum which overlaps the fluorescence spectrum of the polymer as shown in Figure III-1. (There is no relationship between the two curves with respect to intensity of emission or absorption, the spectral curves being drawn in such a manner as to emphasize the extent of overlap along the X-axis.) Polystyrene has a fluorescence efficiency (number of quanta emitted/number of quanta absorbed) of 0.16(52) whereas the value for anthracene is 0.26.(6) Therefore if there were no other mode of energy transfer occurring but only a reabsorption of polystyrene fluorescence by the anthracene, with subsequent emission, the maximum fluorescence reached by the sample would be (o.16x0.26) 4.2% of the initial excitation energy. Since the polystyrene matrix is rigid, Brownian motions of the molecules is very limited and energy transfer by diffusion and collision of accepting and donating molecules can be neglected. However as can be seen from Figure III-1, the system satisfies the spectral conditions required for dipole-dipole transfer.

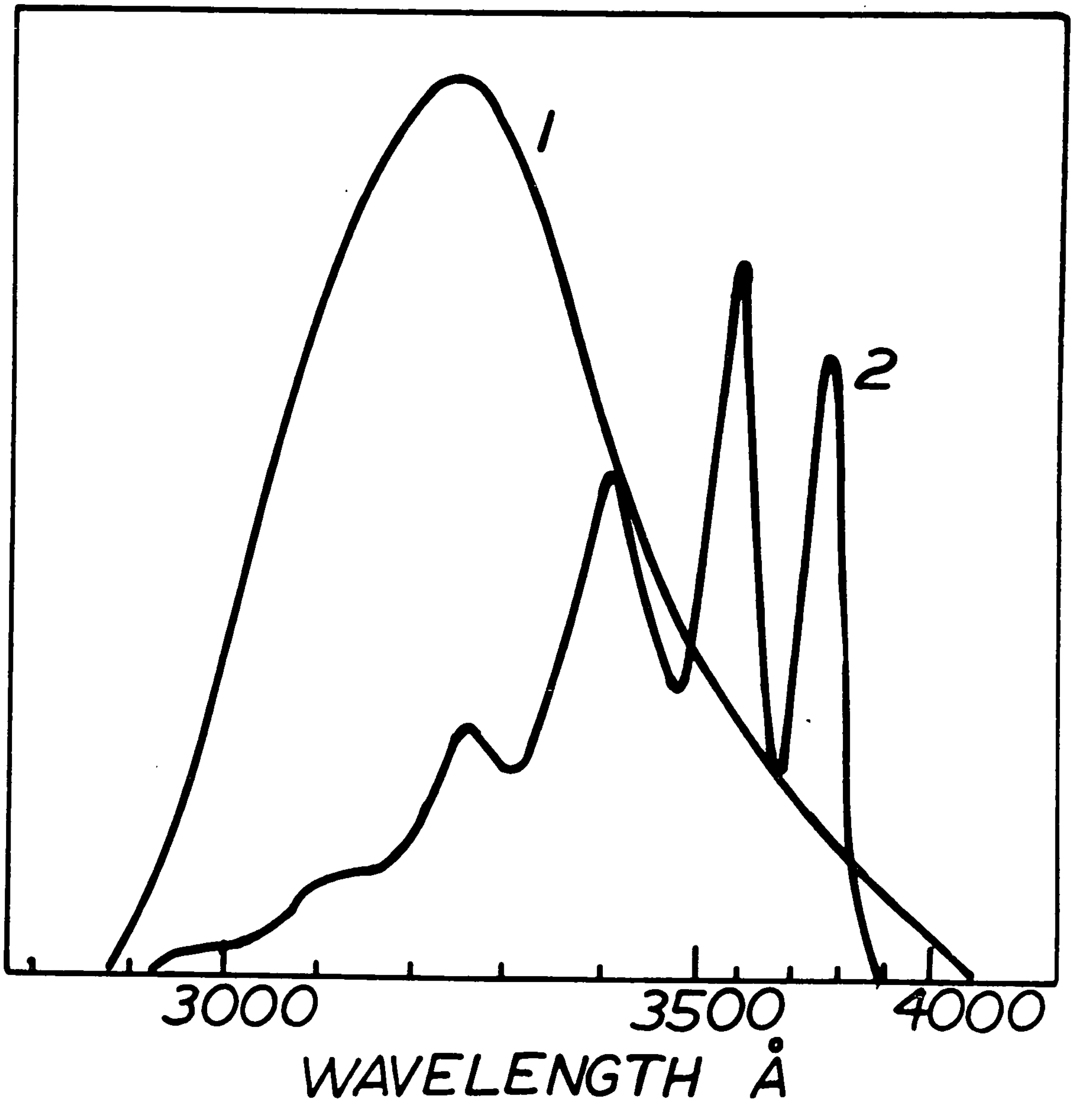
A few samples containing 9,10-diphenylanthracene were also studied since 9,10-diphenylanthracene does not form any compound with styrene during the polymerization process.(55)

It has been shown by Krenz(53) that the

FIGURE III-1

Illustration of the Overlap of the Polystyrene Fluorescence Spectrum with the Absorption Spectrum of Anthracene

(There is no relationship between the two curves with respect to intensity of emission or absorption, the spectral curves being drawn in such a manner as to emphasize the extent of overlap along the X-axis.)



[1] FLUORESCENCE SPECTRUM OF POLYSTYRENE

[2] ABSORPTION SPECTRUM OF ANTHRACENE

presence of anthracene in sytrene during polymeriztion results in a decrease in molecular weight of the polymer normally obtained under the same conditions in the absence of this solute. It was assumed that anthracene was consumed in such a manner that it retained its aromaticity in all three rings and therefore was still functional in the energy transfer process. If anthracene loses its aromaticity in the center ring, then it no longer absorbs in the region 3000-4000 Å,(56-8) and it is then questionable as to whether the compound is capable of dipole-dipole interaction with polystyrene. Thus one must check for the amount of anthracene present in the polymer.

III-2.2 Determination of Final Percent Concentration of Anthracene in Polystyrene After Polymerization

Although Krenz,(53) Basile and Weinreb(55) did a very thorough study on the fluorescence efficiency of the polystyrene-anthracene system, these investigators assumed that although some of the added anthracene was chemically changed, it was changed in such a way that it still functioned as an acceptor molecule. This would be possible if substitution occurs at the 9- or 10- positions of anthracene leaving conjugation intact in the center ring. Cherkasov and and Voldaikina(48) published a paper reporting that anthracene was consumed in several ways during polymerization of styrene, the greatest amount (up to 80% of the initial concentration) forming a Diels-Alder adduct with styrene. The ultraviolet spectrum of the Diels-Alder adduct together with the ultraviolet spectrum of polystyrene are shown in Figure III-2. As can be seen the Diels-Alder adduct has lost the long wavelength band 3000-4000 Å that is needed for the dipole-dipole mechanism of energy transfer to operate, i.e. it can be assumed that the adduct does not enter into singlet-singlet energy transfer.

About 2 to 5% of the initial amount of anthracene forms a compound, styrylanthracene where the anthracene retains its aromaticity in all three rings, and therefore the long wavelength band structure is present but it has an extra absorption band at about 3900 Å.

To check on the results of the previous work,(48) a few milligrams of the polystyrene-anthracene samples were dissolved in a small amount of a 3:2 mixture of low-boiling petroleum ether and chloroform and run through an alumina column. The eluent was collected in 5 c.c. fractions. Ultraviolet spectroscopy was used to identify the components. The order of elution and structural formulae of the compounds are as follows:

1. Diels-Alder adduct

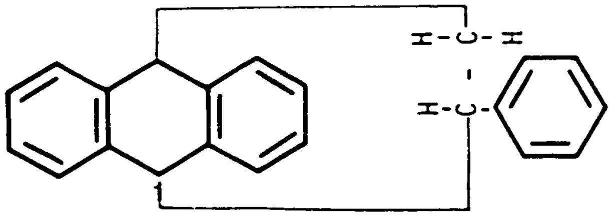
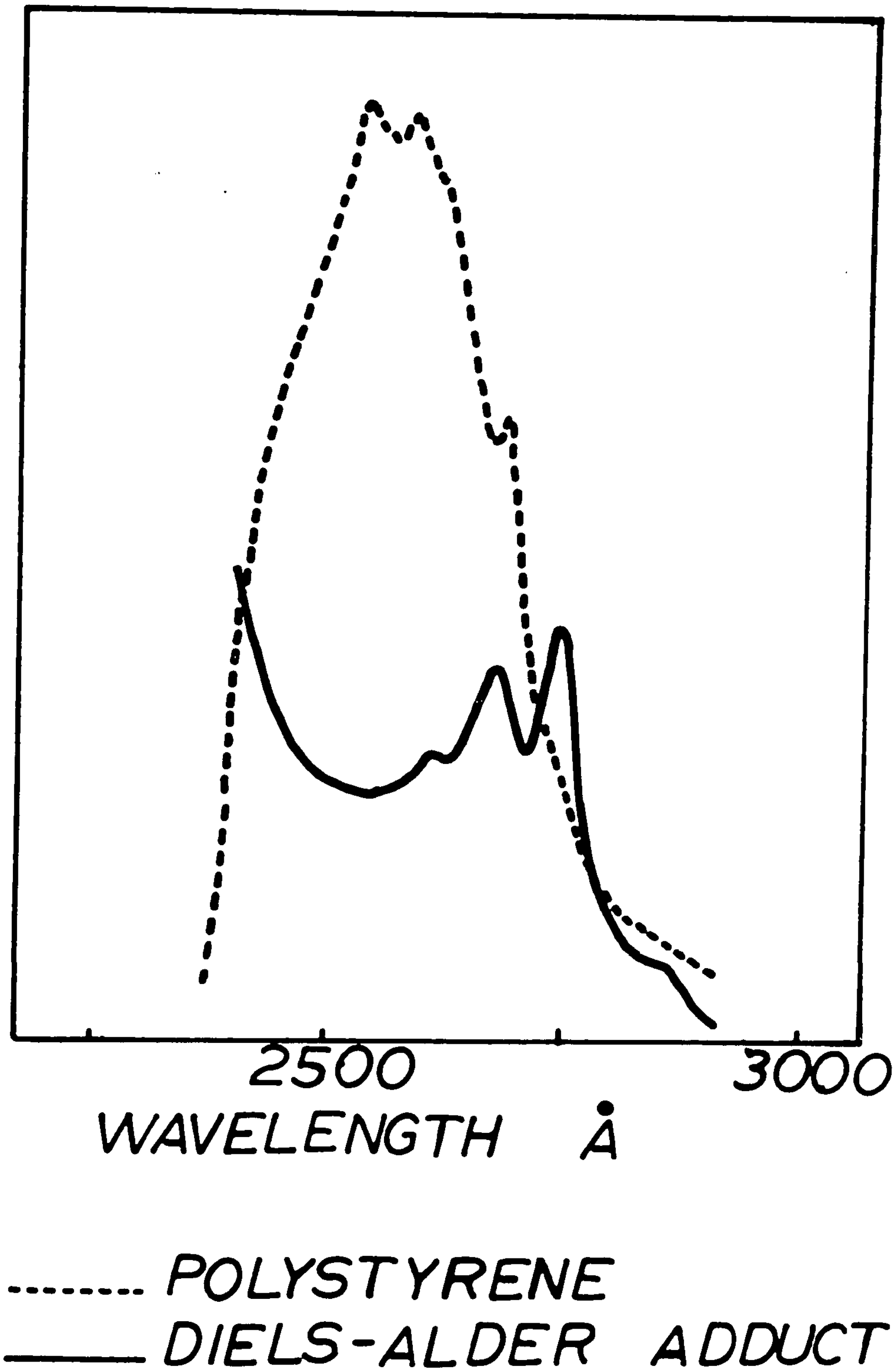


FIGURE III-2

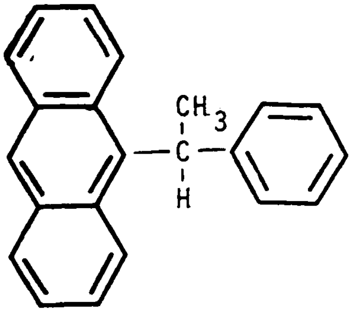
Absorption Spectra of Polystyrene and of the Diels-Alder Adduct of Anthracene and Polystyrene

(There is no relationship between the two curves for intensity of absorption. Since both compounds have about the same extinction coefficient, they were drawn as shown for clarity)

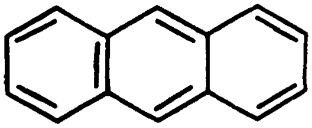
ABSORPTION SPECTRA



2. Styrylanthracene



3. Anthracene



The polymer was strongly absorbed and did not elute out.

A very small amount of anthracene (less than 1% of the initial amount) does become incorporated into the polymer chain. If the polymer is reprecipitated many times in methanol so that it no longer shows an ultraviolet spectrum for anthracene, one still obtains a fluorescence spectrum characteristic for anthracene. (Fluorescence spectroscopy is much more sensitive than ultraviolet spectroscopy when a sensitive phototube is used to detect the fluorescence.)

We were unable to detect any fluorescence from the Diels-Alder adduct in a solution of methanol. Thus there can be no energy transfer from the adduct to anthracene. In short the adduct is inert to energy transfer in the polystyrene-anthracene system.

In all of the present work, the true value, that is the final % concentration of anthracene (unless otherwise mentioned) shall be used in reporting or discussing any of the results. The true value was found by measuring the optical density of anthracene in the samples dissolved in chloroform, and using the extinction coefficient to determine the concentration. The final % concentration is plotted versus the initial % concentration by weight of anthracene in Figure III-3.

III-2.3 Effect of Anthracene on the Viscosity of the Polymer

In Figure III-4 are plotted the intrinsic viscosities of the samples as a function of the initial % concentration of anthracene (by weight). The viscosity decreases sharply at first and then levels out.

III-2.4 Energy Levels of the System

Figure III-5 shows the energy levels for the singlet and triplet states of anthracene, 9,10-diphenylanthracene and polystyrene. The data for the anthracenes come from a paper published by Yildiz and Reilley.(59) The levels for polystyrene have been drawn in from our own estimation of the blue edge of the fluorescence and phosphorescence spectra of the polymer. It can be seen that polystyrene has its singlet level above those of the two anthracenes.

FIGURE III-3

Final Weight Percent of Anthracene in Polystyrene Versus Initial Weight Percent of Anthracene in Styrene (Before Polymerization)

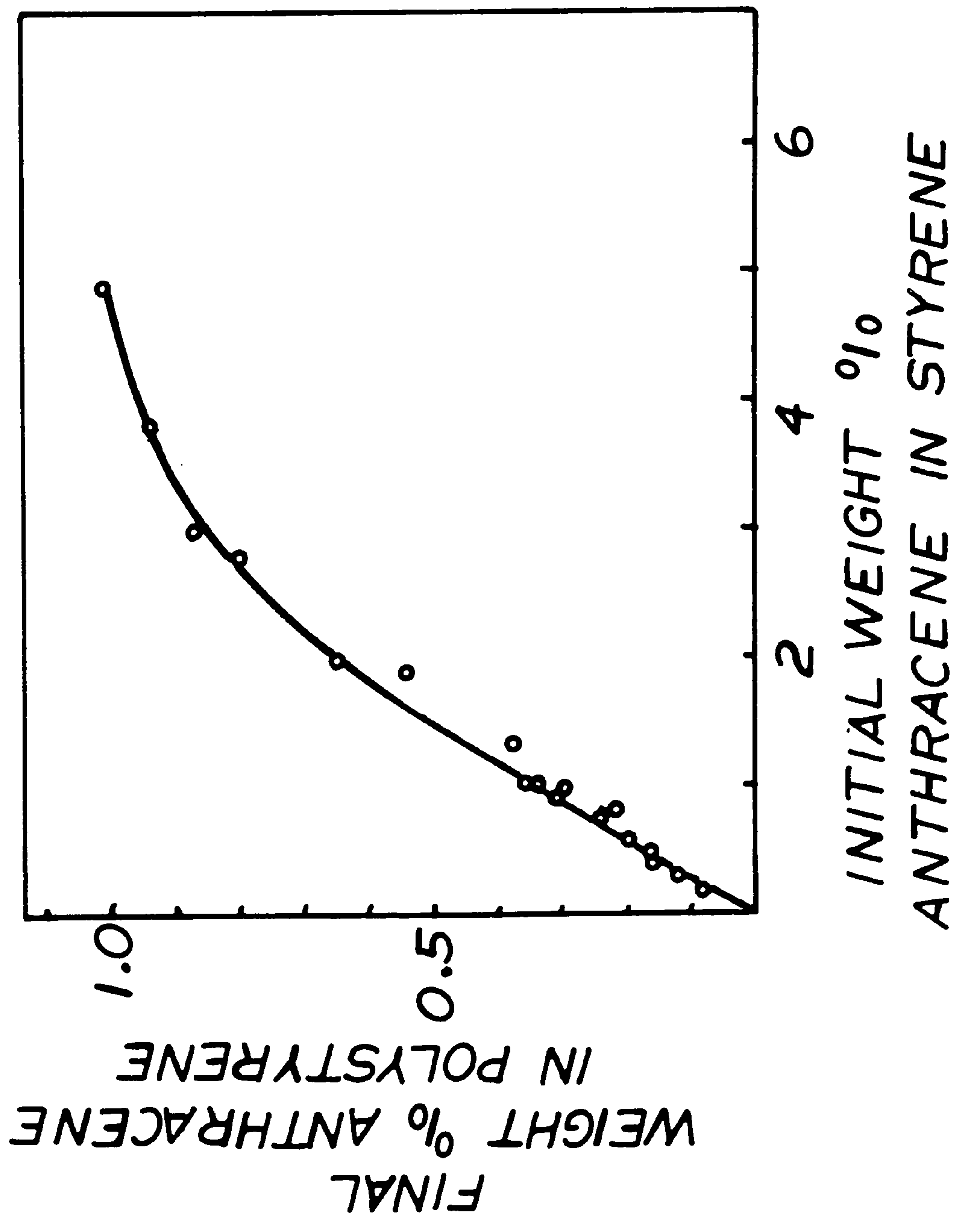

FINAL WEIGHT % ANTHRACENE IN POLYSTYRENE
1.0
0.5
INITIAL WEIGHT % ANTHRACENE IN STYRENE
2
4
6

FIGURE III-4

Intrinsic Viscosity of Polystyrene-Anthracene Samples
Versus Weight Percent of Initial Anthracene Concentration

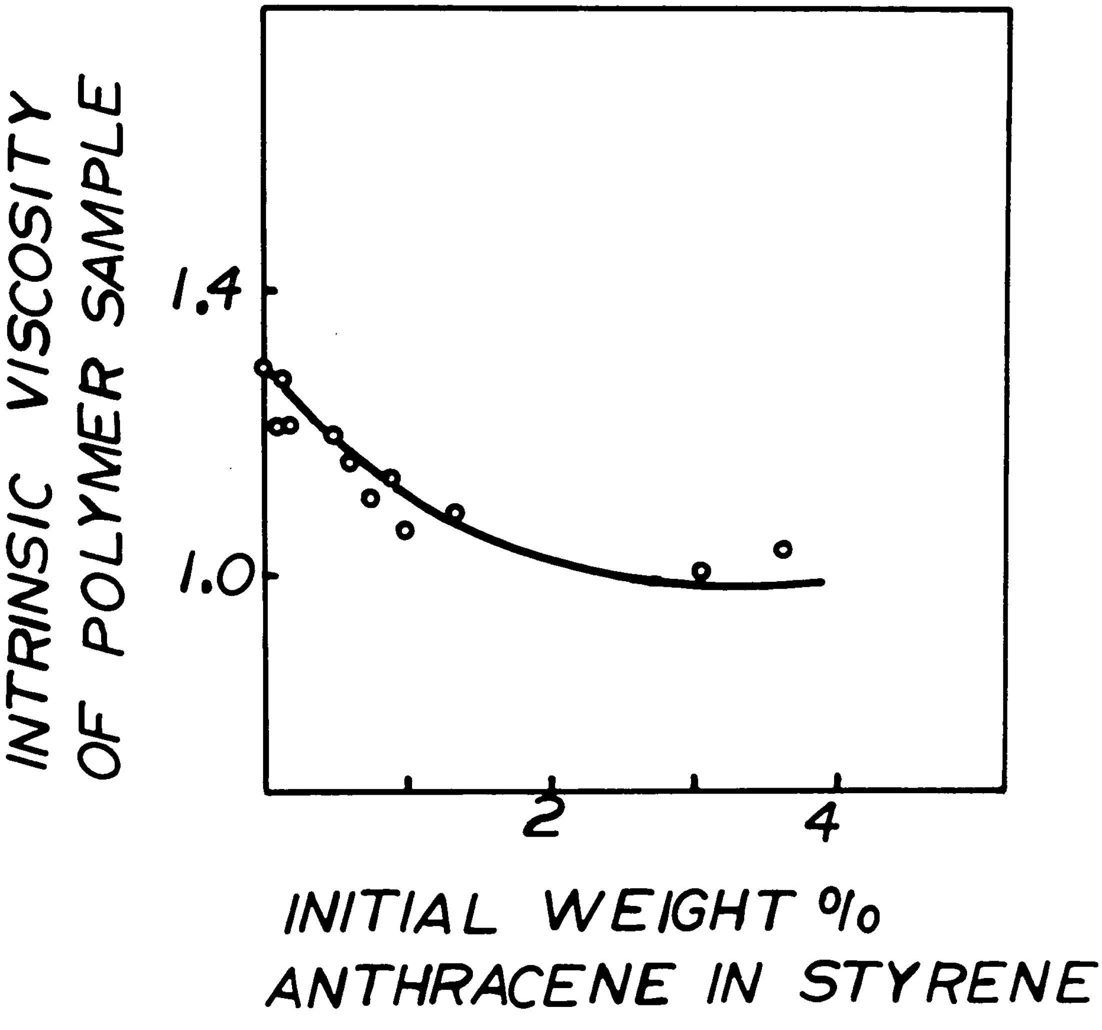
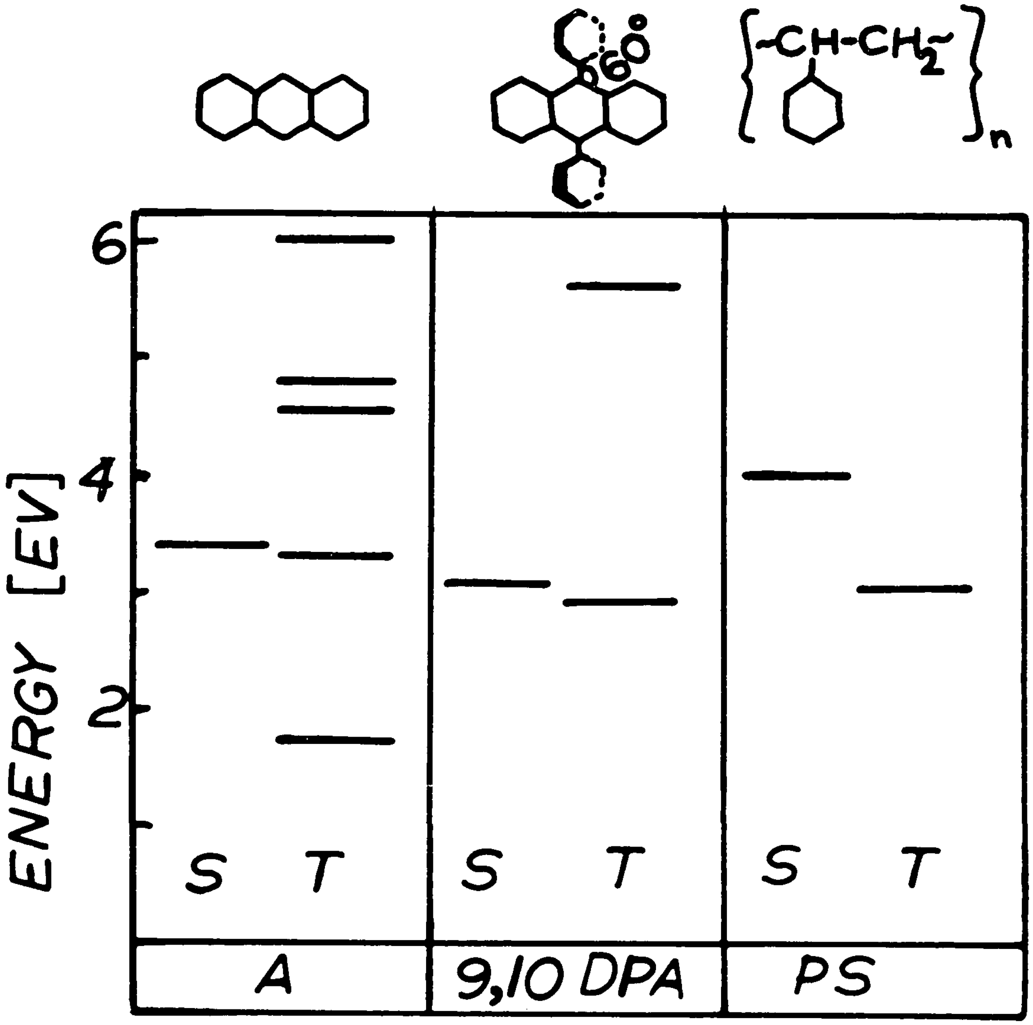

INTRINSIC VISCOSITY OF POLYMER SAMPLE
1.4
1.0
2
4
INITIAL WEIGHT %
ANTHRACENE IN STYRENE

FIGURE III-5

Illustration of the Energy Levels of Anthracene (A),
9,10-Diphenylanthracene (DPA), and Polystyrene (PS)
Relative to the Ground State

The data for the anthracenes is taken from Ref. (59).



S = SINGLET STATES

T = TRIPLET STATES

After polystyrene has transferred its energy to anthracene, about 25% of the anthracene molecules in the excited singlet state emit their energy as fluorescence, the remaining singlet states undergo intersystem crossing to T_2, the second triplet state of anthracene which lies just beneath the first singlet state. This is followed by internal conversion to the first excited triplet state.

9,10-diphenylanthracene has only one triplet state beneath its first singlet level, as is the usual for most compounds. Moreover 9,10-diphenylanthracene has a fluorescence efficiency of one.(41) This means that in effect all of its molecules in the excited state emit energy as fluorescence. Thus 9,10-diphenylanthracene would be expected to be much more stable chemically than anthracene. This was found to be so experimentally.

III-3 EXPERIMENTAL PROOF OF ENERGY TRANSFER

III-3.1 Decrease in the Intensity of Polystyrene Fluorescence

It has been shown that polystyrene and anthracene fulfill all the requirements for singlet-singlet energy transfer. Thus when the polystyrene molecules are excited they have four courses of action open to them:

1) resonance energy transfer
2) deactivation to the ground state by either internal conversion or intersystem crossing.

3) fluorescence

4) chemical reaction

These have been listed in order of increasing time normally required for the event to occur. Resonance energy transfer, if it is to occur, must take place before the molecule fluoresces. This means that we should see a decrease in polystyrene fluorescence with increasing anthracene concentration, since with greater amounts of energy transfer taking place, more and more polystyrene molecules do not reach the stage for fluorescence.

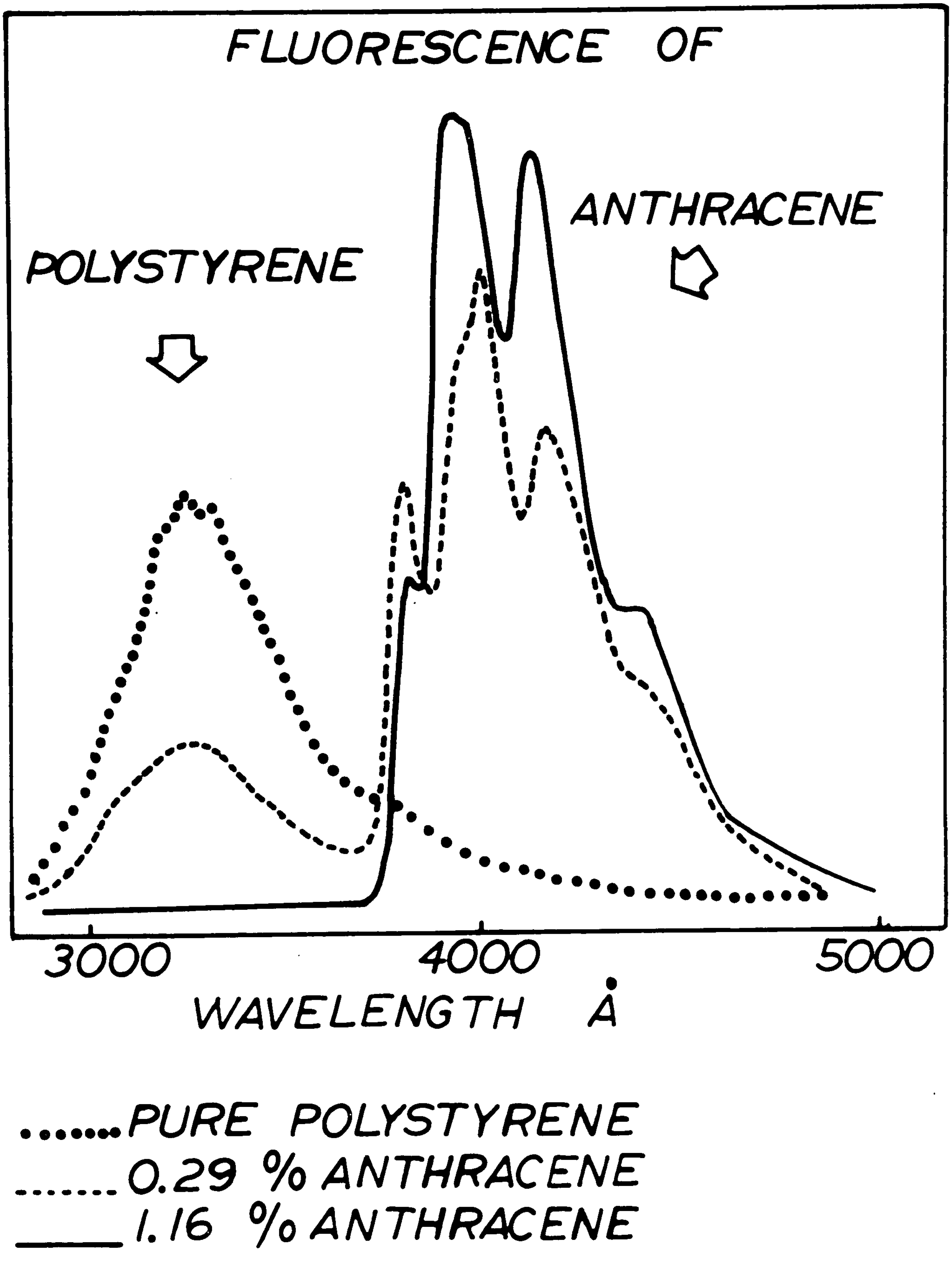
Figure III-6 shows the fluorescence spectra for some samples from 2900-5000 Å. The polystyrene fluorescence from 2900-4000 Å diminishes as we move from zero concentration of anthracene to 0.29% and finally to 1.16% anthracene where it is no longer detected. At the same time the intensity of anthracene fluorescence from 4000-5000 Å continues to increase as a result of increasing resonance energy transfer.

The fluorescence spectra in Figure III-6 are of the front-surface excitation type where fluorescence is observed from the same side upon which the excitation light impinged. Thus the fluorescence observed is the fluorescence from the surface of the sample. Any decrease in polymer fluorescence by anthracene absorption is negligible for this type of arrangement. Figure III-6 indicates then that the polystyrene is transferring from its singlet state, since a decrease in polystyrene fluorescence is an indication of a

FIGURE III-6

Fluorescence Spectra of Polystyrene-Anthracene Samples

From 2900-5000 Å


FLUORESCENCE OF
POLYSTYRENE
ANTHRACENE
3000
4000
5000
WAVELENGTH Å
••••••PURE POLYSTYRENE
......0.29 % ANTHRACENE
____1.16 % ANTHRACENE

diminution of excited singlet states. If it had been transferring from the triplet state, we would not see a decrease in fluorescence. Moreover the fact that the fluorescence of anthracene is increasing indicates that the anthracene is excited to its first singlet level by the polymer. The fluorescence spectra were obtained with excitation wavelength 2700 Å, a wavelength not absorbed by the anthracene.

The spectra do not rule out the possibility of triplet(polystyrene) - triplet(anthracene) transfer. Polystyrene has a phosphorescence spectrum from 4000-4500 Å indicating a triplet level above that of anthracene. However because of the proximity of components required for such transfer, (see Section I-4.2) it is an inefficient process at low concentrations of anthracene. At higher concentrations, most of the excited polystyrene singlets will have been quenched by resonance energy transfer so that there now remain few triplet states(obtained by intersystem crossing from the remaining excited singlet states) to transfer to anthracene. Hence the triplet-triplet transfer process can be considered to be of minor importance in the system.

III-3.2 Measurement of Decay Time of Fluorescence From the System

When N_o molecules are excited to their first electronic state by a pulse of radiation, they emit this excitation energy in a random fashion. If the number of molecules losing their excitation energy per unit time (to which the intensity of fluorescence radiation is proportional), dN/dt, is proportional to N, the number of remaining excited molecules, then

$$dN/dt = -yN \qquad (III-1)$$

$$N = N_0 e^{-yt} \qquad (III-2)$$

where y is a proportionality constant. The minus sign indicates the molecules to be losing their excitation energy. When t has a value such that $yt = 1$, then $N = N_0/e$ and

$$dN/dt = -(1/e)(yN_0) \qquad (III-3)$$

The fluorescence decay time then, means the interval of time during which the intensity of fluorescence has fallen to a value of 1/e of its initial (maximum) value.

When resonance energy transfer occurs, the lifetime of the donor fluorescence becomes smaller with increasing amounts of solute. An expression for the lowering of the fluorescence decay time of the sensitizer with increasing amount of acceptor has been derived by Galanin(60) for dipole-dipole coupling.

Basile and Weinreb(55) studied the system polystyrene-anthracene with particular emphasis on lifetime studies of the fluorescence of molecules excited by ultraviolet radiation or by electron bombardment. Table III-1 gives some of their data which can be interpreted in the following way.

The decay time of fluorescence for pure

TABLE III-1

DECAY TIME OF FLUORESCENCE FOR POLYSTYRENE + SOLUTE*

Weight %	Decay Time(sec.)	
Solute	Anthracene	9,10-Diphenylanthracene
0	13.5×10^{-9}	13.5×10^{-9}
0.01	17.8×10^{-9}	18.7×10^{-9}
0.05	19.2×10^{-9}	19.9×10^{-9}
0.07	19.5×10^{-9}	20.0×10^{-9}
6.0	12.6×10^{-9}	14.9×10^{-9}
7.0	12.8×10^{-9}	14.8×10^{-9}

*Basile and Weinreb's values(55) for the various amounts of anthracene are the initial amounts before polymerization.

polystyrene was measured as 13.5×10^{-9} sec. At low concentrations of anthracene where resonance energy transfer is small, the anthracene is excited mainly by polystyrene fluorescence. Thus the decay time for the fluorescence from the entire system becomes longer than that for pure polystyrene because the observed fluorescence requires two steps, fluorescence of polystyrene followed by absorption by anthracene. As the amount of anthracene increases, the nonradiative energy transfer process becomes predominant. The polystyrene now transfers its energy directly (nonradiatively) to the anthracene and the higher the concentration the faster the rate of transfer. Thus the fluorescence decay time of the system now decreases from the maximum value (the two step process of fluorescence followed by reabsorption). Eventually at high enough concentrations the transfer time becomes so short that the measured decay time is effectively the fluorescent decay time of the accepting solute, anthracene.

The same argument holds for the 9,10-diphenylanthracene system.

III-3.3 Measurement of the Energy Transfer Efficiency of the System

If one uses ultraviolet energy as the excitation energy, then one can, by choosing an appropriate wavelength, selectively excite only one compound in a mixture of compounds. For example anthracene has a very low extinction coefficient from 2650-2900 Å whereas polystyrene has a maximum at 2700 Å. When a system possesses properties such as these,it is possible to show that resonance energy transfer occurs by comparing the fluorescence intensities obtained by direct and indirect excitation.

In direct excitation the solute is excited by a wavelength of light to which the polymer is transparent and the fluorescence intensity (F_0) is measured. In indirect excitation the polymer is excited by a wavelength to which the solute is transparent and the fluorescence intensity (F) is measured. The ratio of the fluorescence intensities $(F)/(F_0)$

of the solute normalized to equal intensity of excitation for the two different wavelengths gives the efficiency of energy transfer. The method is schematically outlined on page 69. The % efficiency of energy transfer is plotted in Figure III-7 for the polystyrene-anthracene system, and in Figure III-8 for 9,10-diphenylanthracene. As can be seen the efficiency of energy transfer at a given concentration for 9,10-diphenylanthracene is lower than that for anthracene. The reason for this behavior will be discussed in detail later.

III-3.4 Fluorescence Spectra Obtained by Direct Excitation of Anthracene in the Polystyrene Matrix

Figure III-9 shows the direct excitation fluorescence spectra for various concentrations of anthracene. The exciting wavelength is 3340 Å. The samples were 12 mm. thick. The excitation occurs on one side of the sample and the detected emitted light must travel a distance of 12 mm. or less depending upon the depth of penetration of the excitation light. The samples are thick enough to absorb all of the light.

As the concentration of anthracene increases, one can see from Figure III-9, that there is a shifting of the spectrum to longer and longer wavelenghts. This is the effect of reabsorption of its own fluorescence by the solute. This occurs when the absorption spectrum overlaps the fluorescence

DETERMINATION OF EFFICIENCY OF ENERGY TRANSFER

DIRECT EXCITATION λ = 3340 Å

100 quanta ⟶ anthracene

↓ fluorescence efficiency 0.26

26 quanta (detected experimenatally)

INDIRECT EXCITATION λ = 2700 Å

100 quanta ⟶ polystyrene

↓ 50 quanta transferred (radiationless process)

anthracene

↓ fluorescence efficiency 0.26

13 quanta (detected experimentally)

Theoretical efficiency of energy transfer:

$$\frac{50 \text{ quanta}}{100 \text{ quanta}} \times 100 = 50\%$$

Experimental Efficiency of Energy Transfer:

$$\frac{13 \text{ quanta}}{26 \text{ quanta}} \times 100 = 50\%$$

FIGURE III-7

Percent Efficiency of Energy Transfer Versus Weight
Percent of Anthracene in Polystyrene
(Solute was added to the monomer before polymerization.)

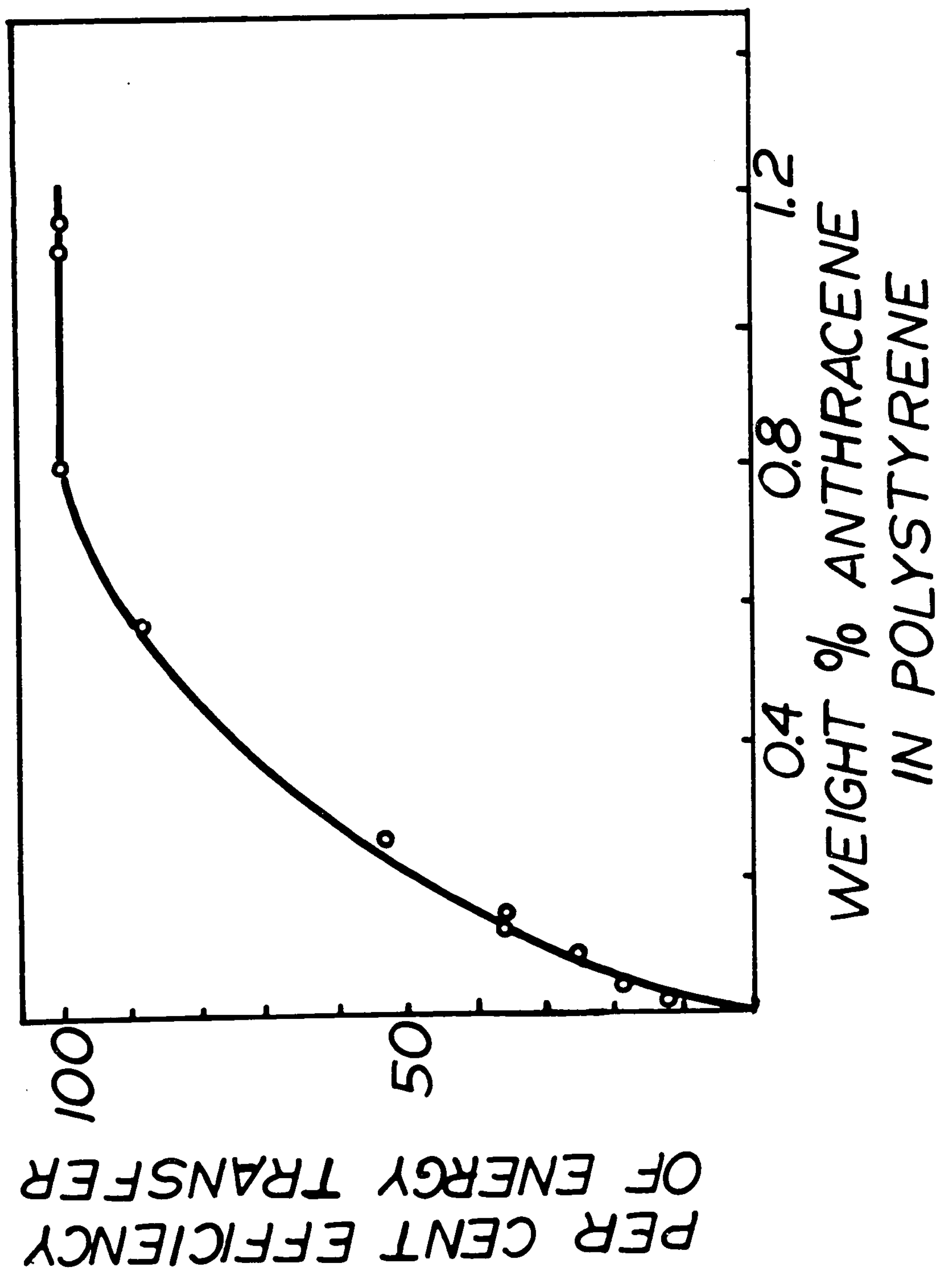

100
50
0.4
0.8
1.2
WEIGHT % ANTHRACENE
IN POLYSTYRENE
PER CENT EFFICIENCY
OF ENERGY TRANSFER

FIGURE III-8

Percent Efficiency of Energy Transfer Versus Weight Percent of 9,10-Diphenylanthracene in Polystyrene

(Solute was added to the monomer before polymerization)

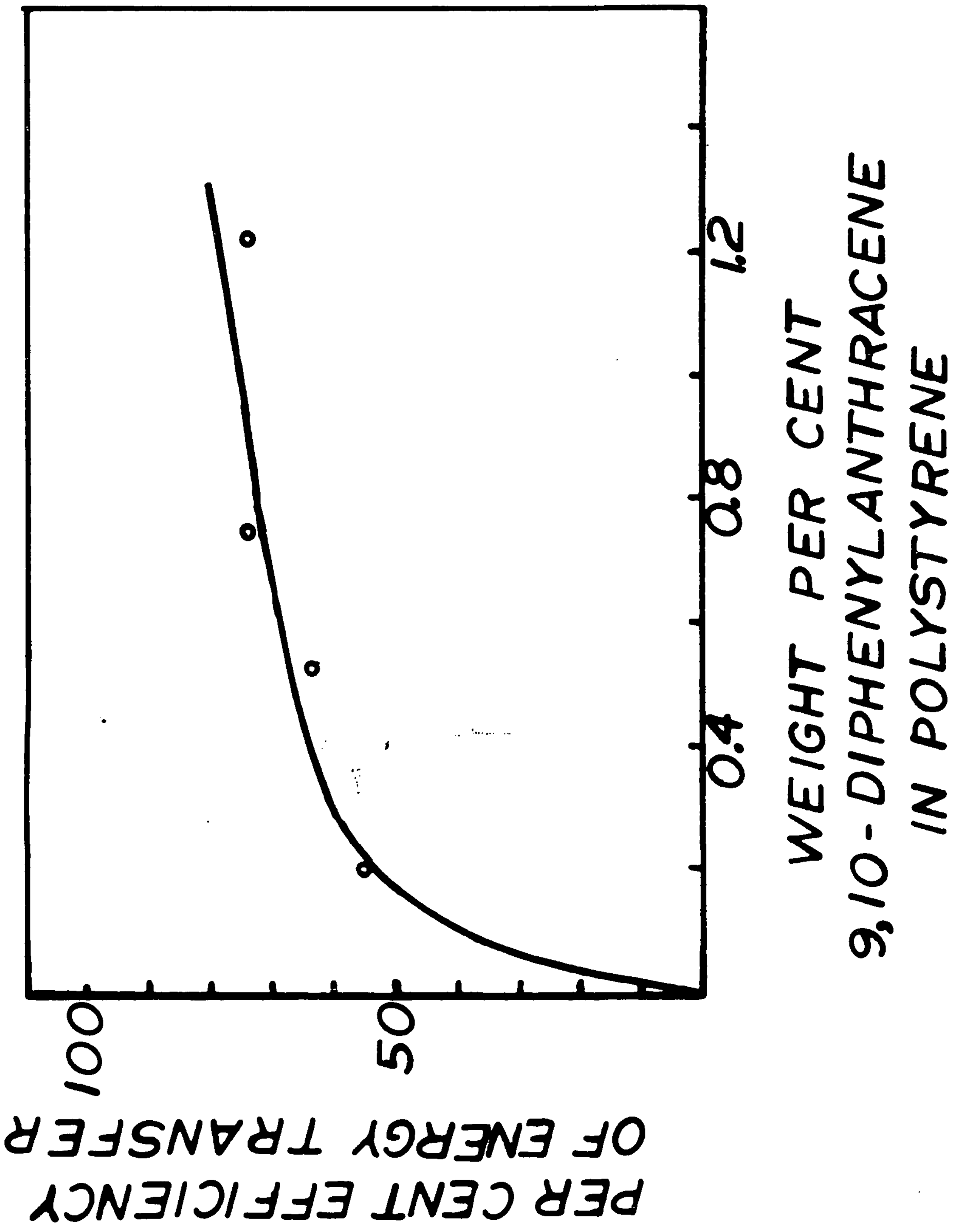
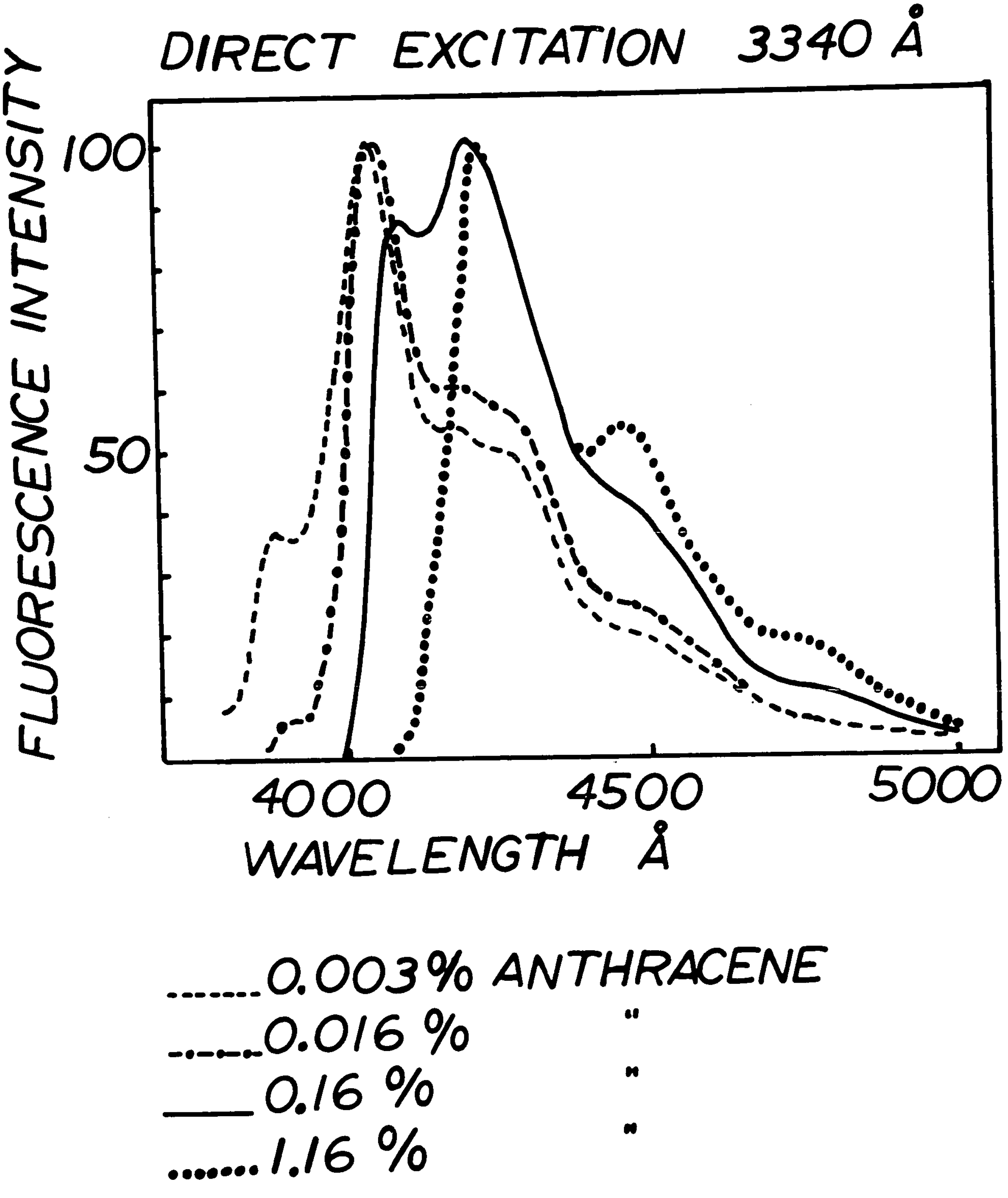

100
50
PER CENT EFFICIENCY
OF ENERGY TRANSFER
0.4
0.8
1.2
WEIGHT PER CENT
9,10-DIPHENYLANTHRACENE
IN POLYSTYRENE

FIGURE III-9

Fluorescence Spectra of Anthracene in Polystyrene Obtained by Direct Excitation (λ = 3340 Å)


DIRECT EXCITATION 3340 Å
FLUORESCENCE INTENSITY
100
50
4000
4500
5000
WAVELENGTH Å
0.003% ANTHRACENE
0.016 % "
0.16 % "
1.16 % "

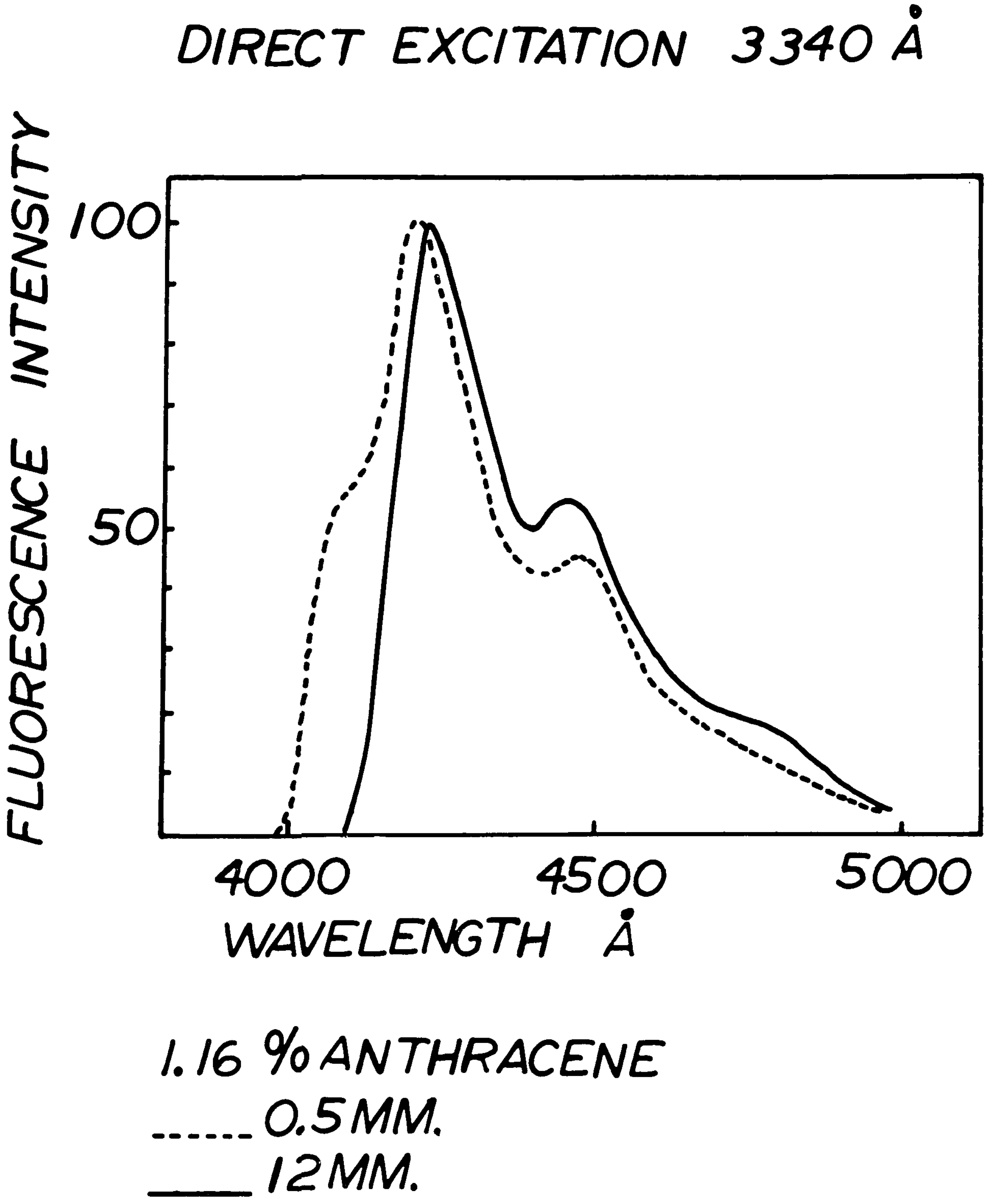
spectrum as is the case with anthracene. The absorption spectrum of anthracene extends down to about 3900 Å and the fluorescence spectrum begins from 3800 Å. Thus the effect of reabsorption of its own fluorescence is to shift the fluorescence spectrum to longer and longer wavelengths. The shorter wavelengths are reabsorbed first. We see the gradual disappearance of the peak at 3900 Å and the reemission of these quanta ocurring at 4100-4300 Å.

In this thesis only a few spectra have been shown of the many spectra that were taken for all the samples prepared. The changes that occur in the spectra with increasing concentration of solute are quite gradual so that if one looks at all of the spectra in order of increasing (or decreasing) solute concentration, one by one, the change is hardly noticeable. However, if one skips over several spectra and then compares it with the first one, one sees the changes illustrated in Figure III-9.

The gradual shift of the fluorescence spectrum of anthracene to the red is a function of anthracene concentration, and hence on the path length through which the emitted light must travel. That the changes seen in the spectra are due only to a physical effect can be proven by taking the fluorescence spectra of the same sample at two different thicknesses. Figure III-10 shows the spectra obtained for a sample containing 1.16% anthracene by weight. One sample is 0.5 mm. thick and the other is 12 mm. thick.

FIGURE III-10

Fluorescence Intensity of Anthracene in Polystyrene Obtained by Direct Excitation for Two Different Thicknesses of the Same Sample


DIRECT EXCITATION 3340 Å
FLUORESCENCE INTENSITY
100
50
4000
4500
5000
WAVELENGTH Å
1.16 % ANTHRACENE
------ 0.5 MM.
_____ 12 MM.

Although both samples contain the same amount of solute, their spectra do not coincide. The thin sample emits at shorter wavelengths. This is because the emitted light has to travel only 0.5 mm. through the sample and in this short distance not all of the short wavelength fluorescence is absorbed. For the 12 mm. sample the optical density is large enough so that all of the fluorescence in the region of overlap with the absorption spectrum is absorbed. Obviously the emitted light when it finally emerges from the thick samples will consist mainly of the long wavelength portion of the fluorescence spectrum.

It has been shown previously (Section III-2.2) that the samples contain a variety of substituted anthracenes due to the different reactions of styrene with anthracene during polymerization. The monosubstituted anthracenes have a fluorescence spectrum which is displaced to longer wavelengths relative to unsubstituted anthracene. Thus a sample containing an initially high concentration of anthracene (5%) before polymerization was deliberately chosen in which to examine the fluorescence spectra at two different thicknesses. This sample should contain the highest amount of monosubstituted anthracenes. Thus although the fluorescence spectrum is no doubt a composite spectrum of the substituted and unsubstituted anthracenes (See Figure V-1), the shifting of the fluorescence spectrum with increasing concentration is largely due to path length as seen in Figure III-10.

III-3.5 Fluorescence Spectra Obtained by Indirect Excitation of Anthracene in the Polystyrene Matrix

The fluorescence spectra were obtained by directly exciting the polymer with light of wavelength 2700 Å. As can be seen from Figure III-11 the spectra are like those obtained from direct excitation with increasing anthracene concentration.

Figure III-12 is a reference curve to convert weight % anthracene to moles/litre of polystyrene which is convenient to have in the discussions to follow.

Figure III-13 shows a plot of the relative total intensity of fluoresecence of anthracene in polystyrene (indirect excitation). From $2x10^{-4}$ to 10^{-3} the increase in intensity is very slight. This is the region where the trivial mechanism is in operation, i.e. the polystyrene fluorescence is absorbed by the anthracene which then emits. The fluorescence intensity starts to rise sharply at $2x10^{-3}$ moles/litre indicating that another more efficient mode of energy transfer has begun. A concentration of $2x10^{-3}$ moles/litre represents a transfer distance of 58.3 Å. The transfer distance is visualized as the radius of a sphere which is occupied in the center by one solute (anthracene) molecule. This value was calculated in the following way:

FIGURE III-11

Fluorescence Spectra of Anthracene in Polystyrene Obtained by Indirect Excitation (λ = 2700 Å)

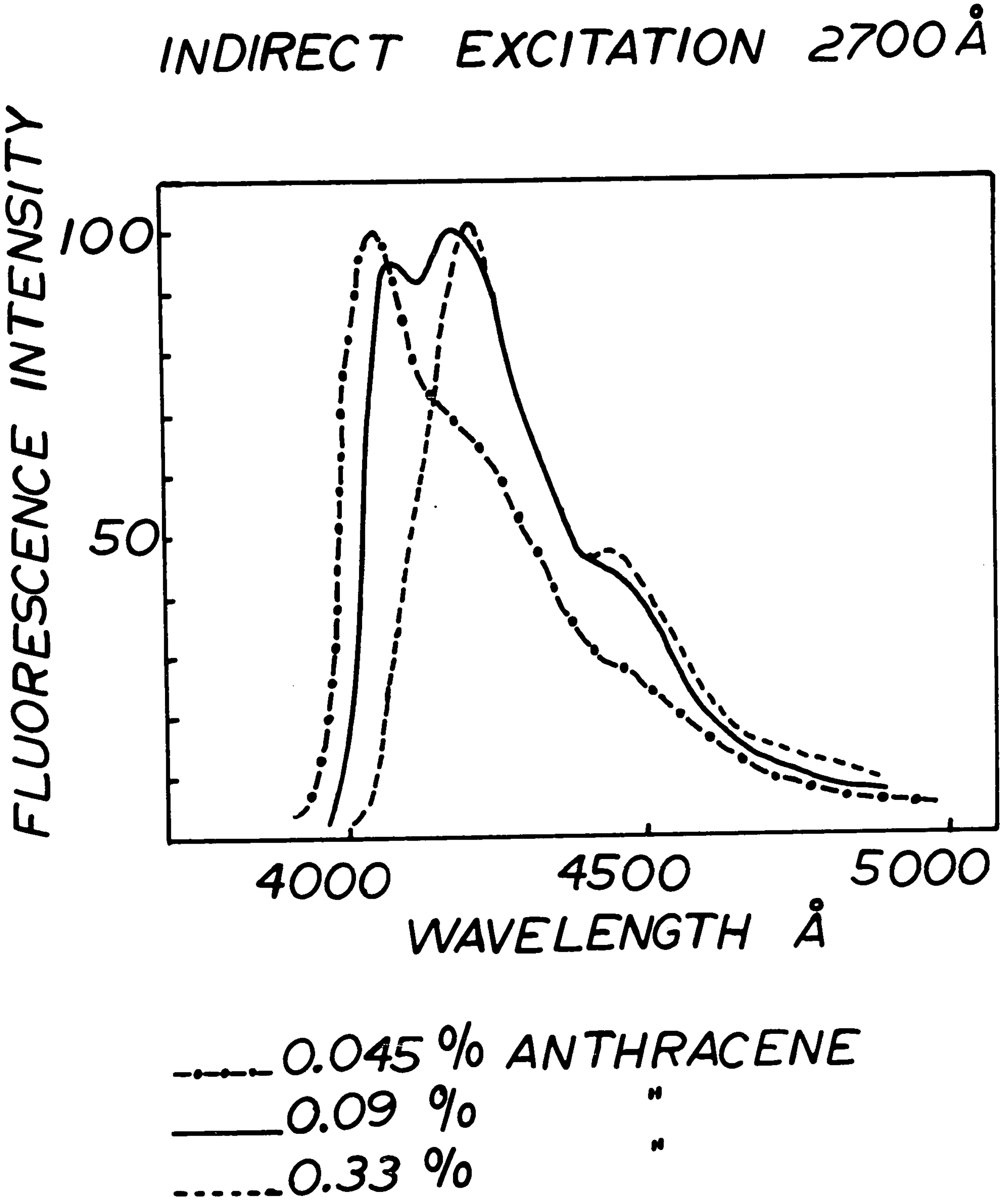

INDIRECT EXCITATION 2700 Å
FLUORESCENCE INTENSITY
100
50
4000
4500
5000
WAVELENGTH Å
-·-·-·- 0.045 % ANTHRACENE
——— 0.09 % "
- - - - - 0.33 % "

FIGURE III-12

Weight % Anthracene in Polystyrene Versus Moles of Anthracene Per Litre of Polystyrene

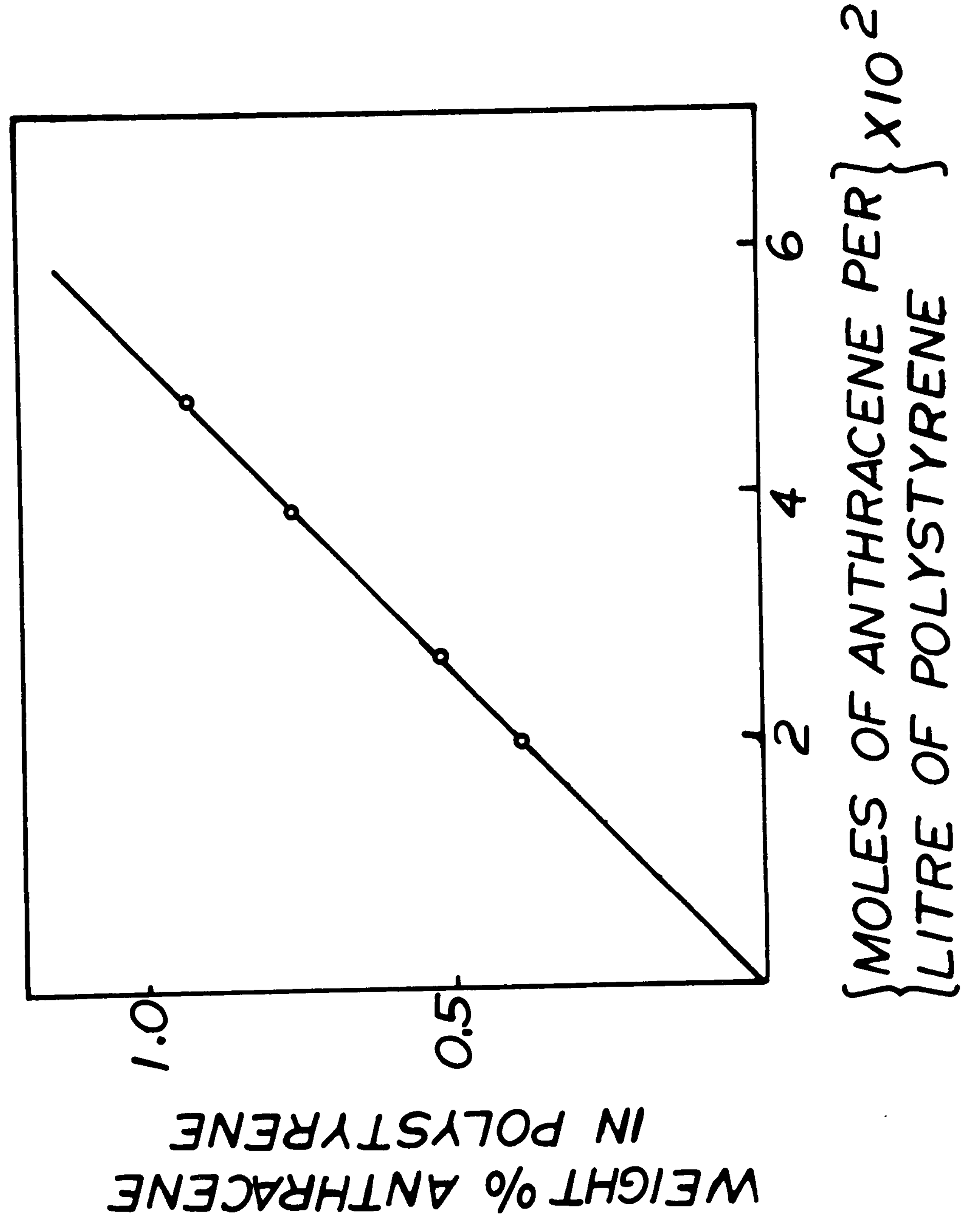
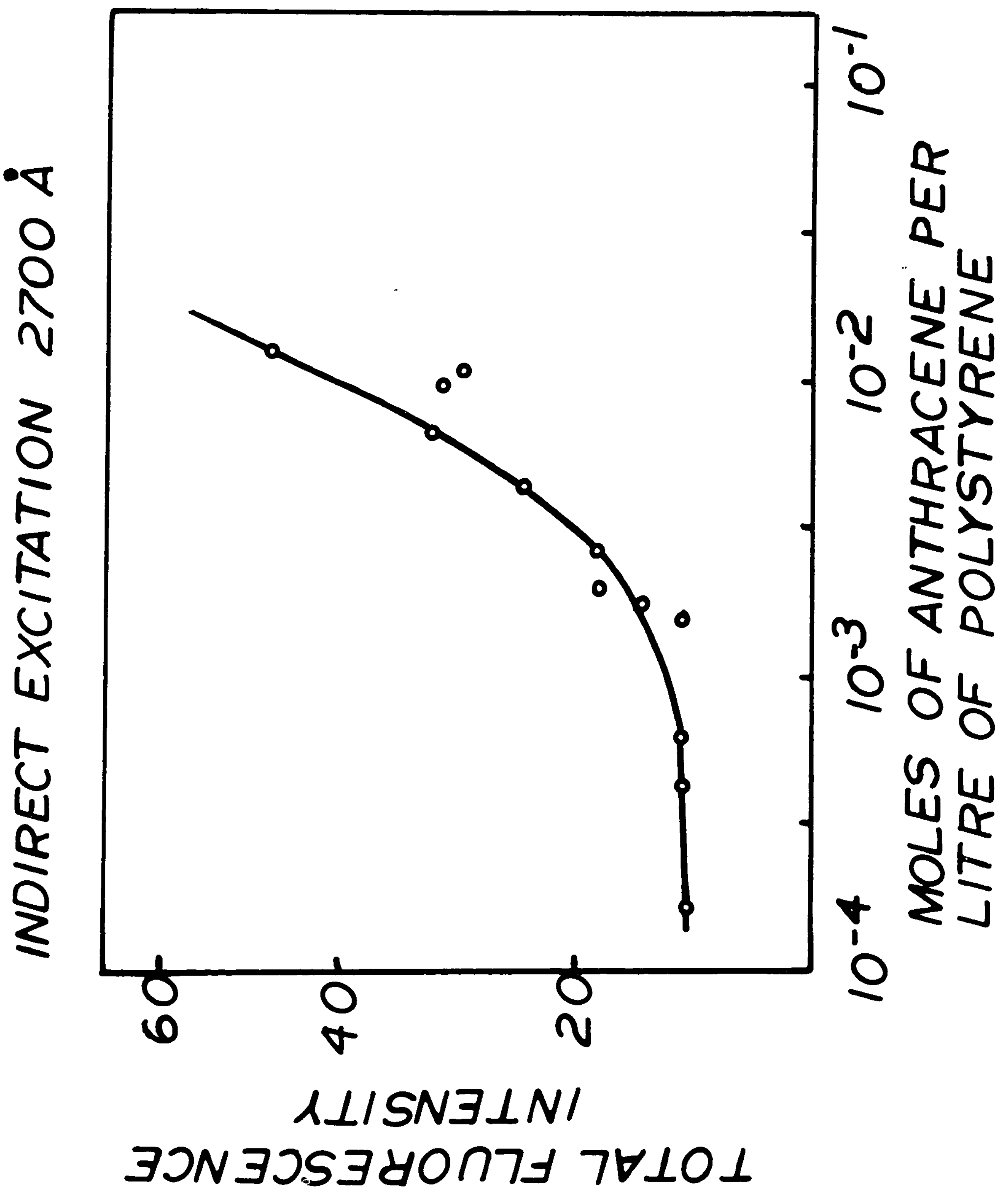

WEIGHT % ANTHRACENE IN POLYSTYRENE
1.0
0.5
2
4
6
{MOLES OF ANTHRACENE PER LITRE OF POLYSTYRENE} X10^2

FIGURE III-13

Relative Total Fluorescence Intensity Versus Moles of Anthracene Per Litre of Polystyrene (Indirect Excitation)


INDIRECT EXCITATION 2700 Å
TOTAL FLUORESCENCE INTENSITY
60
40
20
MOLES OF ANTHRACENE PER LITRE OF POLYSTYRENE
10^{-4}
10^{-3}
10^{-2}
10^{-1}

One anthracene molecule occupies $\dfrac{1000}{2\text{x}10^{-3} \text{ x } 6.023\text{x}10^{23}}$ c.c.

$= 83.02 \text{ x } 10^{-20}$ c.c.

Now 1 cm. = 10^{8} Å, therefore 1 c.c. = 10^{24} Å^{3}

Thus $83.02\text{x}1\text{o}^{-20}$ c.c. can be rewritten as $83.02\text{x}10^{4}$ Å^{3}.

$$\text{Volume of a sphere} = \frac{4\pi r^{3}}{3}$$

$$= 83.02\text{x}10^{4} \text{ Å}^{3}$$

Therefore r = 58.3 Å

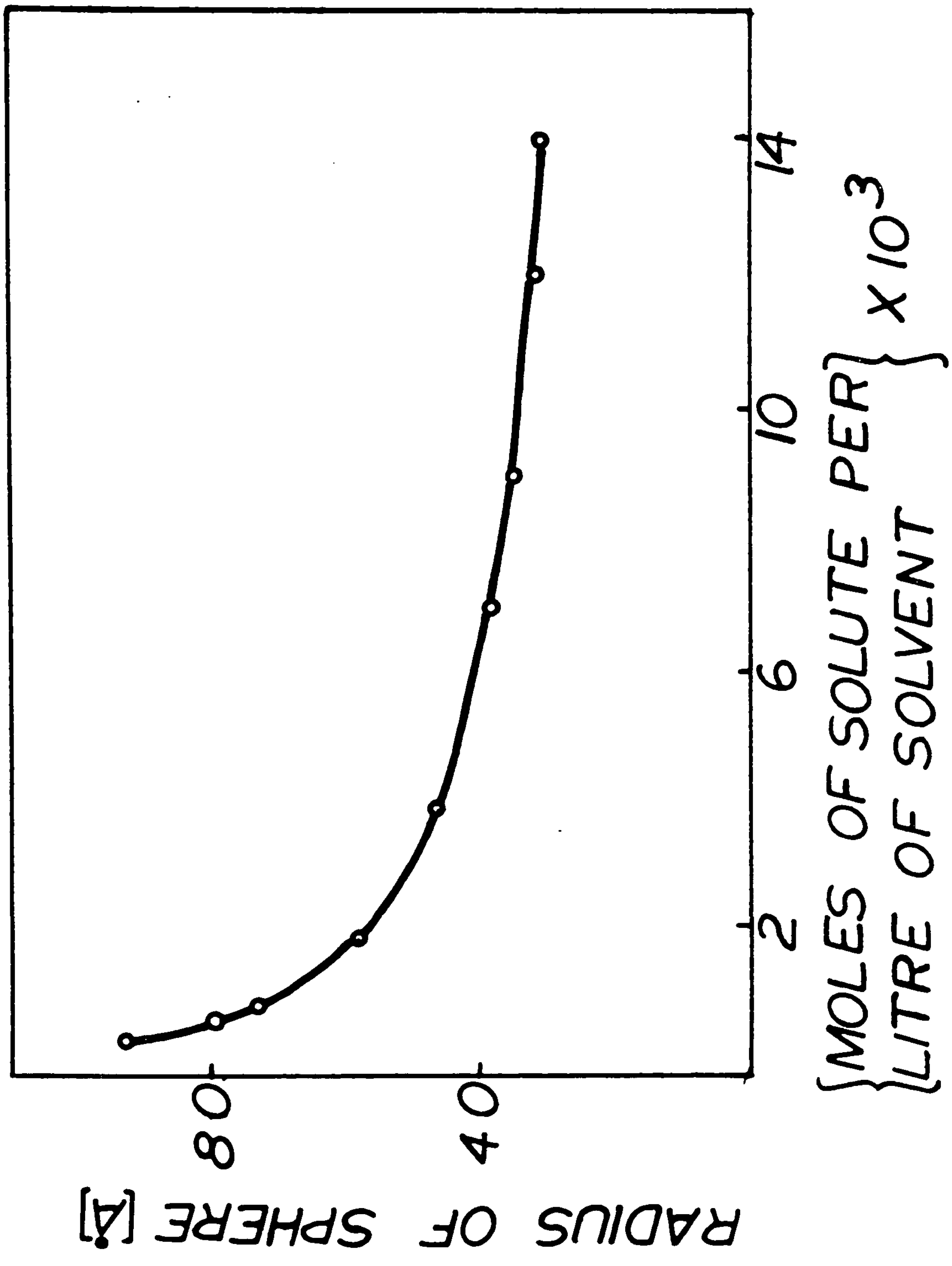
The anthracene molecule is pictured as occupying a sphere of polystyrene with a radius of 53.8 Å such that if an excited polymer segment occurs at a distance less than 58.3 Å then energy transfer has a high probability of occurring, and if the excited segment occurs at a distance greater than 58.3 Å then little or no energy transfer occurs by the radiationless process. Values of r corresponding to various concentrations of solute completely dispersed (no clusters) throughout the polymer matrix are plotted in Figure III-14. Each solvent-solute system however, has its own unique value for r at which energy transfer begins to occur.

III-3.6 Comparison of Fluorescence Intensities Obtained by Direct and Indirect Excitation of the Solute

For very low concentrations of anthracene where nonradiative energy transfer is absent or of minor importance,

FIGURE III-14

Radius of Sphere of Solvent Occupied by One Solute Molecule Versus Moles of Solute Per Litre of Solvent

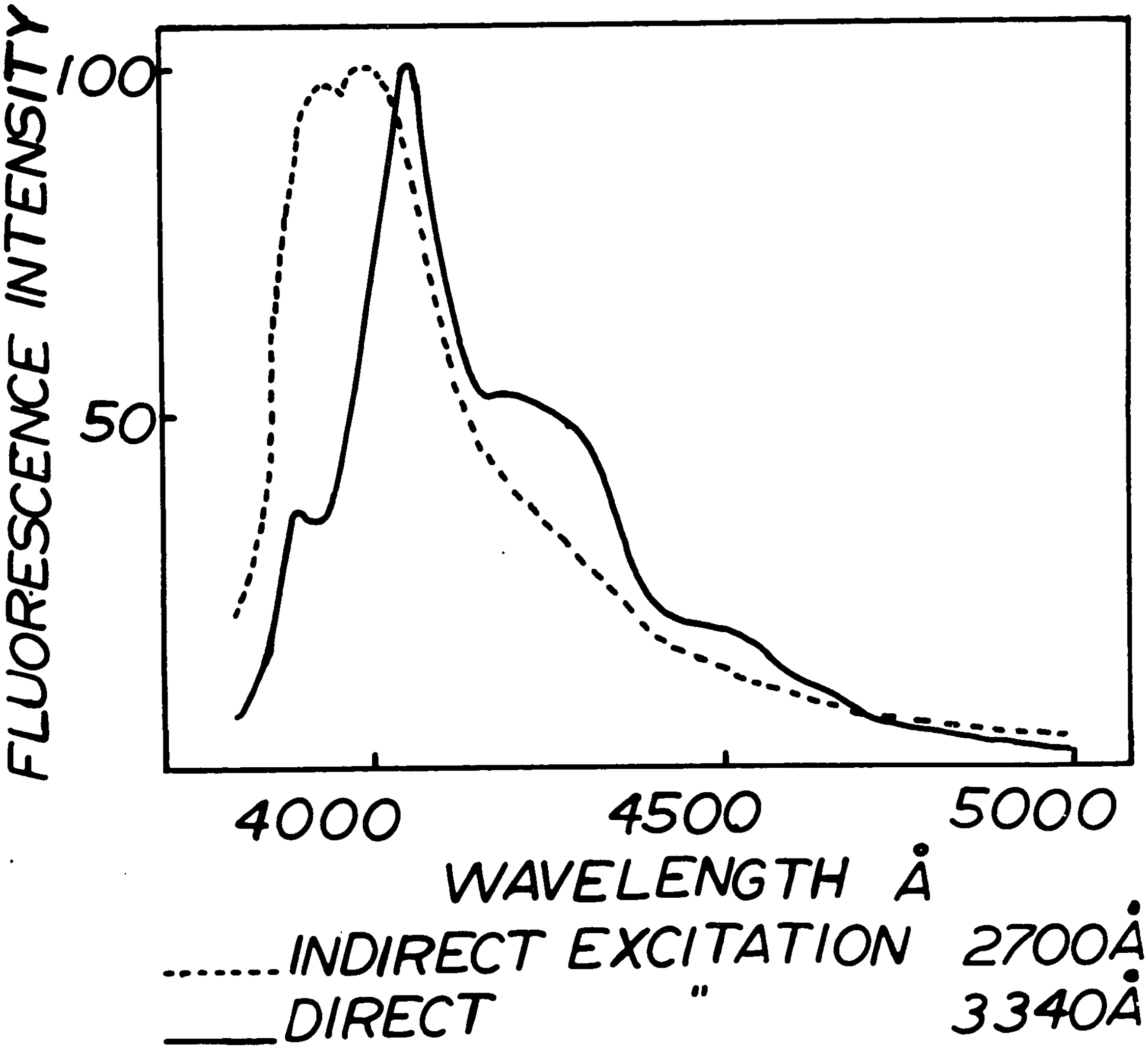

RADIUS OF SPHERE [Å]
80
40
2
6
10
14
{MOLES OF SOLUTE PER / LITRE OF SOLVENT} X 10^3

there is a difference in the spectra obtained by direct and indirect excitation. Examples for two samples are shown in Figure III-15 and in Figure III-16. For the 0.0032% sample (Fig. III-15), part of this difference can be explained by the fact that for indirect excitation the slits were open to 7 mm. on the Beckman unit, a slit width too large to obtain much structural detail. However this does not explain why the maximum for indirect excitation is more in the ultraviolet region than for direct excitation. The emission for indirect excitation occurs at much shorter wavelengths. Also note the absence of the shoulder at 4200-4400 Å in the indirect fluorescence spectrum. 4200-4400 Å is the region where reabsorbed fluorescence quanta are reemitted as discussed in Section III-3.4.

The excitation light at 2700 Å is completely absorbed in the first 0.012 mm. layer of polystyrene. The resultant fluorescence from the polymer is not monochromatic but has a distribution of light from 3000-4000 Å. The extinction coefficient for anthracene in the regions 3000-3200 and 3900-4000 Å (corresponding to about 20% of the total polystyrene emission) is much samller than at 3340 Å. This means that about one fifth of the polystyrene fluorescence can travel a considerable distance into the sample (a larger distance than the excitation light 3340 Å), so that the anthracene excited by this polystyrene fluorescence lies

FIGURE III-15

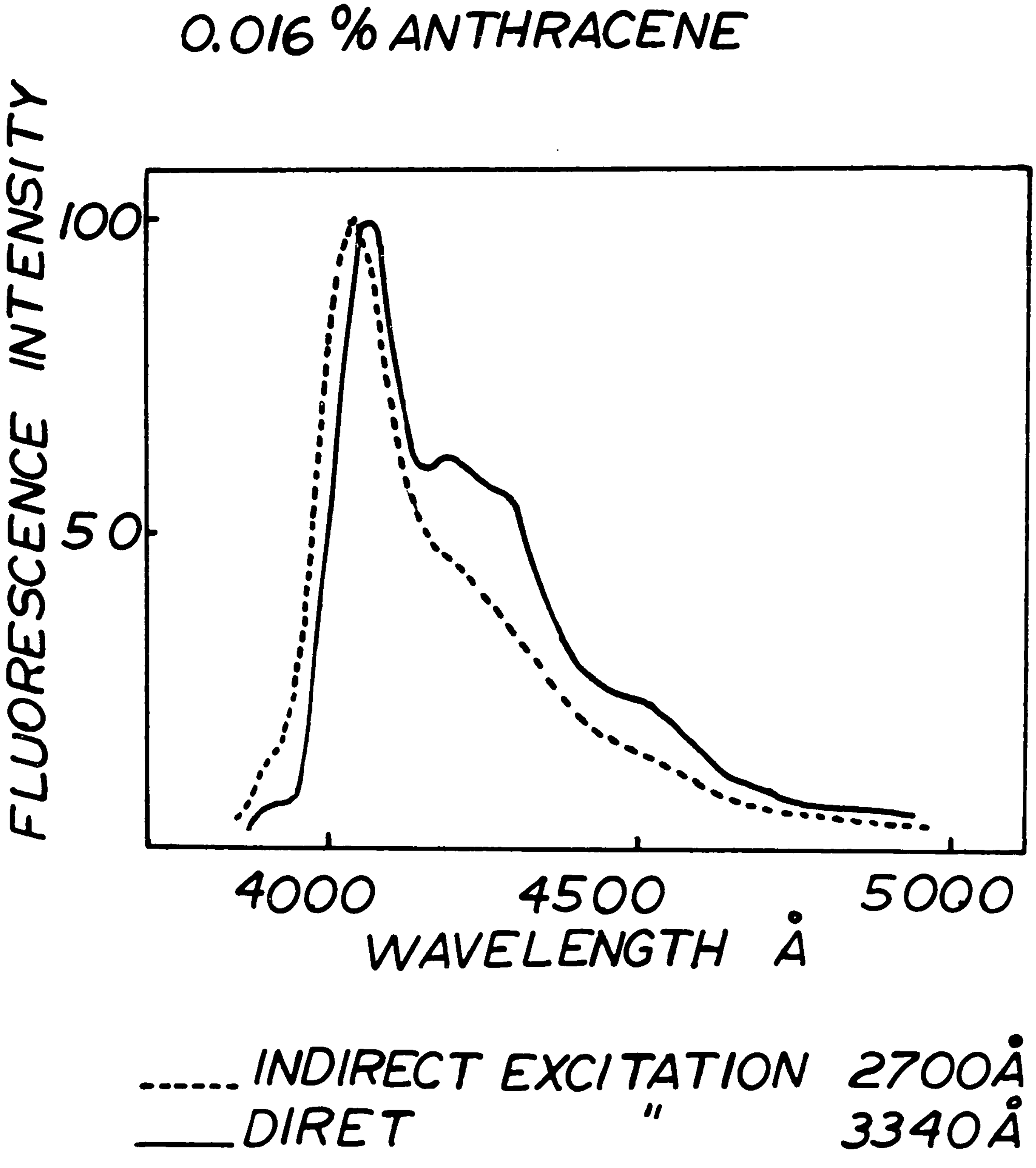
Fluorescence Spectra of 0.0032% Anthracene (by Weight) in Polystyrene Obtained by Direct and Indirect Excitation of of the Solute



0.0032 % ANTHRACENE

FIGURE III-16

Fluorescence Spectra of 0.016% Anthracene(by Weight) in Polystyrene Obtained by Direct and Indirect Excitation of the Solute


0.016 % ANTHRACENE
FLUORESCENCE INTENSITY
100
50
4000
4500
5000
WAVELENGTH Å
------ INDIRECT EXCITATION 2700Å
—— DIRET " 3340Å

deep within the sample. The resultant emission from the anthracene then has little distance left over which to travel and hence will not undergo much reabsorption. This causes the fluorescence spectrum to occur at shorter wavelengths.

In the 0.0032% sample 20% of the 3340 Å excitation light is transmitted. This in effect means that in indirect excitation for this sample, the fluorescence spectrum will also show some polystyrene fluorescence since at this concentration it will not be all reabsorbed.

The effects discussed in the latter paragraph and the one previous to it causes the fluorescence spectrum obtained by indirect excitation to occur at shorter wavelengths than the fluorescence spectrum obtained by direct excitation for the samples in Figure III-15 and Figure III-16.

For the 0.016% anthracene sample (Fig. III-16) the 12 mm. path length is sufficient to absorb all of the 3340 Å excitation light. This means that all of the polystyrene emission is reabsorbed in the 12 mm. path length. Thus the polystyrene fluorescence cannot travel as far as it did in the 0.0032% sample and thus the spectrum is at longer wavelengths, and closely approaches that for direct excitation.

At higher concentrations of anthracene the spectra obtained by direct and indirect excitation are identical. This is because polystyrene fluorescence is not important in the excitation of the anthracene molecules.

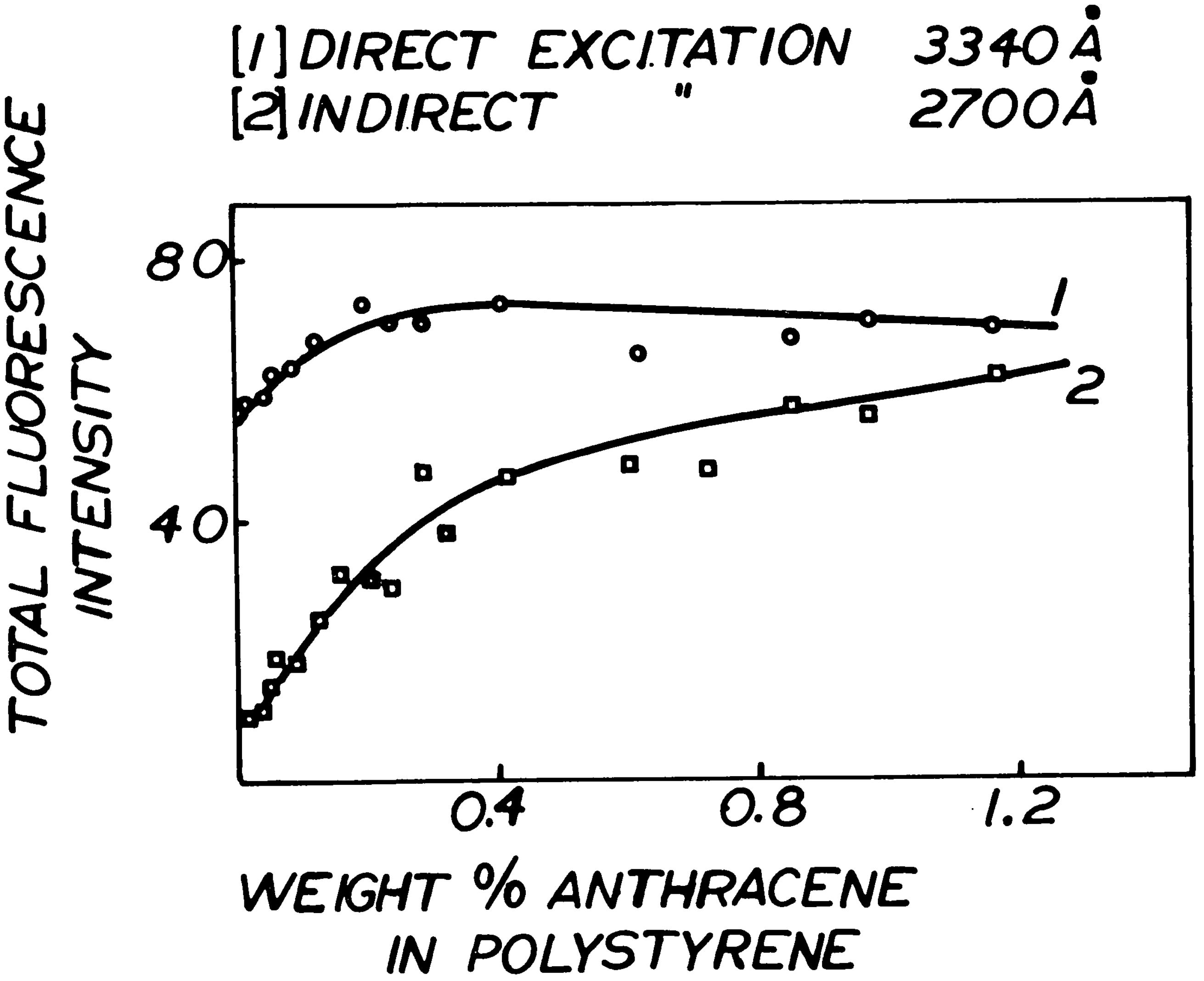
Figure III-17 shows the relative total fluorescence intensities obtained by direct and indirect excitation. For direct excitation, the intensity increases, reaches a plateau and then decreases somewhat. The reason for this is thought to be associated with the ability of anthracene to form dimers. Excimers(61) occur as intermediates in photochemical dimerizations in which an excited molecule and unexcited molecule form a stable dimer whose components are linked by principle valences. The photchemical reaction is the reason for the concentration quenching of fluorescence at room temperature; instead of emitting the excimer undergoes transformation to a stable dimer. This has been found to occur in solutions of anthracene,(49) the dimer precipitating out of solution.

The fluorescence for indirect excitation rises sharply at first and then begins to level off. This leveling off indicates that the efficiency of energy transfer has nearly reached its maximum efficiency and that any further addition of solute does not greatly enhance the amount of energy transfer. The sharp rise of the indirect excitation curve is due to the nature of the energy transfer process, that is the efficiency of transfer is a function of the distance between donor and acceptor to the sixth power (Eq. I-8).

FIGURE III-17

Relative Total Fluorescence Intensities of Anthracene

Obtained by Direct and Indirect Excitation


[1] DIRECT EXCITATION 3340 Å
[2] INDIRECT " 2700 Å
TOTAL FLUORESCENCE INTENSITY
80
40
0.4
0.8
1.2
1
2
WEIGHT % ANTHRACENE IN POLYSTYRENE

III-4 EXCIMER FORMATION IN POLYSTYRENE

The spectrum of polystyrene in solution consists of two bands, one centered at 2800 Å and the other at 3300 Å, which are labelled the S and D band respectively. The D band is attributed to emission from an excimer (a transient dimer formed by the association of excited and unexcited phenyl groups),and the S band to the emission from an unassociated segment. The relative intensities of the S and D band are found to be independent of the polystyrene concentration for very dilute solutions(62) indicating that the excimers are formed intramolecularly.

The fluorescence spectrum of a film of pure polystyrene consists of the D band only indicating that excimer formation in solid polystyrene occurs with practically 100% efficiency. To explain this high efficiency one can consider the following two extremes:

(1) An originally excited segment can form an excimer with the closest segment with 100% efficiency, regardless of whether they belong to the same or different chains.

(2) The probability of an originally excited segment to form an excimer is, on the average, relatively small. However, the energy of the excited segment migrates through the polystyrene medium with high efficiency until energy transfer can take place through either of two paths:

I : direct transfer from the excited segment before excimer formation occurs

II : transfer from the excimer itself.

The data of Hirayama and Basile$^{(63)}$ favor Type I transfer, i.e. direct transfer from the excited segment to the fluorescent solute is much more efficient than the process of excimer formation. This in effect means that excimer formation by method (1) is not probable but that it occurs by method (2) and that energy transfer occurs during migration from segment to segment.

E.S.R. measurements have also been used to show that long-range energy migration and trapping is involved in the production and destruction of polystyrene radicals. When the polymer chain is short, compared with the mean migration lengths, radicals at the end groups are the result. A sample of polystyrene with a number-average molecular weight of 2080, about 20 monomer units in length was irradiated with gamma radiation to about 10 megarads. None of the species observed in the high molecular weight polymer was observed. Instead the spectrum can be attributed to terminal formyl radicals exclusively. Since oxygen was excluded from these samples, Hurrah$^{(64)}$ concluded that these radicals arise from decomposition of end groups containing polymerization catalyst.

The conclusion that energy migrates throughout the polystyrene matrix allows us to derive rate constants for the photophysical processes occurring in the polystyrene-anthracene system by making use of the experimental data.

III-5 CALCULATION OF RATE CONSTANTS

The efficiency of fluorescence from pure polystyrene is:

$$Q_0 = \frac{k_f}{k_f + k_s} \qquad \text{(III-4)}$$

where k_f is the rate constant for the probability of fluorescence, k_s is the total rate constant for the probability of intersystem crossing and nonradiative transition from $S_1 \rightarrow S_0$ (internal conversion).

Windsor and Dawson(65) determined the quantum yields for fluorescence, triplet state formation, and for the nonradiative transtion $S_1 \rightarrow S_0$ for several aromatic hydrocarbons. Some of these values are listed in Table III-2. No such information is available for polystyrene. Basile(66) in writing equation III-4 wrote k_s as k_i representing only the rate of intersystem crossing. He made the assumption that photochemists have been making until about five years ago. This assumption is that all molecules that do not fluoresce are deactivated in the triplet state by some appropriate process. In view of the new data that has been recently published and as seen from Table III-2 it is no longer correct to make this assumption. Thus we shall write

TABLE III-2

QUANTUM YIELDS OF SOME PHOTOPHYSICAL PROCESSES

Compound	$\phi_{S_1 \rightarrow S_0}$	ϕ_f	ϕ_T
Benzene	0.705	0.055	0.24
Naphthalene	0.41	0.19	0.40
1,2-Benzanthracene	0.25	0.20	0.55
Phenanthrene	0.09	0.15	0.76
Fluorene	0.01	0.70	0.31

k_s as the sum of all processes that deactivate the singlet state nonradiatively, i.e. intersystem crossing and internal conversion.

When anthracene is added to polystyrene, then the efficiency of radiative deexcitation, Q_R, of polystyrene is:

$$Q_R = \frac{k_f}{k_f + k_s + k_t c} \qquad \text{(III-5)}$$

where $k_t c$ is the rate parameter for nonradiative transfer to anthracene.

The efficiency of nonradiative transfer to anthracene is given by:

$$Q_{NR} = \frac{k_t c}{k_f + k_s + k_t c} \qquad \text{(III-6)}$$

The correctness of the assumption that k_t is a constant, the same for all molecules, depends on the exact nature of the transfer process. If the excitation remains fixed in a particular solvent molecule until one of the three processes occur, then k_t will indeed not be constant for all molecules but will depend upon the distance from the excited molecule to the nearest solute molecule. However, it has been shown in polystyrene that excitation energy does not remain in a particular solvent molecule but is rapidly transferred from one solvent molecule to another until such time as one of the three processes occur. (Energy transfer, fluorescence, internal conversion or intersystem crossing are the three processes.) Under these conditions equation (III-6) is valid.

From equations (III-5) and (III-6) the total quantum efficiency of energy transfer, F, can be written as:

$$F = Q_R + Q_{NR} = \frac{aQ_0 + Bc}{1 + Bc} \qquad \text{(III-7)}$$

where

$$B = \frac{k_t}{k_f + k_s} \qquad \text{(III-8)}$$

Equation (III-7) may be rewritten as :

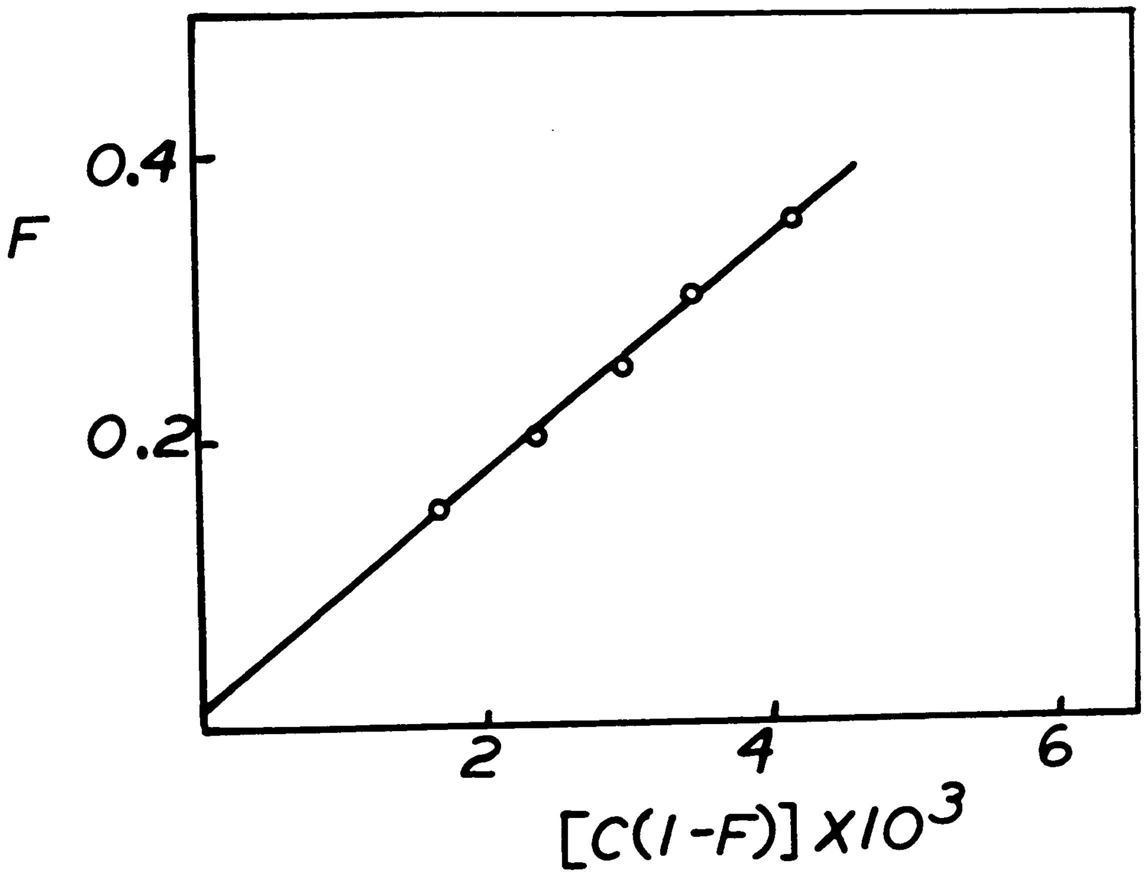
$$F = Q_0 + Bc(1 - F) \qquad \text{(III-9)}$$

For anthracene concentrations greater than 8×10^{-4} mole/litre $a = 1$. A plot of the transfer efficiency versus $c(1 - F)$ in Figure III-18 is linear, the slope of the line giving a value for B and the intercept, Q_0. We obtain a value of 0.015 for the intercept and 80 for the slope of the line.

FIGURE III-18

Efficiency of Energy Transfer (F) versus c(1-F)

Plot is for equation (III-9)


F
0.4
0.2
2
4
6
[C(1-F)] X10^3

Basile(66) made the same sort of plot for his samples of polystyrene-1,1,4,4-tetraphenylbutadiene. For one set of samples for which he removed residual monomeric styrene his value for Q_0 is 0.038. For the samples containing residual styrene his value is 0.092. Since our value is 0.015 it suggests that there is very little residual monomeric styrene present. This is thought to be due to the fact that anthracene reacts efficiently with styrene during polymerization. Moreover, Hirayama and Basile(63) found the fluorescence quantum yield of the excimer of polystyrene in cyclohexane to be 0.02, in close agreement with our value.

Pure polystyrene has a much lower molecular fluorescence quantum yield than does polystyrene + styrene. This is because monomeric styrene in solution has a higher fluorescence yield than the polymer. The monomeric styrene acts as an acceptor of energy from polystyrene. Basile(66) found the fluorescence decay time of polystyrene without monomer to be long, about 19×10^{-9} sec. The decay time of fluorescence for polystyrene containing residual styrene monomer at zero solute concentration (no anthracene) is lower, of the order of 14×10^{-9}sec. which agrees closely with Basile and Weinreb's value(55) of 13.5×10^{-9} sec. The sharp decrease in decay time has been interpreted to mean that polystyrene transfers energy to the residual styrene monomer which in turn may then emit. In other words the residual monomer plays the dual role of both an acceptor and donor molecule.

Pure polystyrene which was polymerized for a period of ten days in our case was found to contain only 0.5% styrene monomer. The samples containing anthracene probably have less as discussed previously. We consider polystyrene + styrene as one component since regardless of whether the excitation energy resides on a polymer segment or on a styrene molecule, it will eventually be transferred to anthracene with an efficiency as already determined experimentally and shown in Figure III-7.

The decay time for the fluorescence of pure polystyrene is defined as(4):

$$T = \frac{1}{k_f + k_s} \qquad \text{(III-10)}$$

From equation (III-4) $k_f = Q_o/T$ (III-11)

Since our value for Q_o is 0.015 indicating little residual styrene, we shall take $T = 19\text{x}10^{-9}$ sec.(66) Thus

$$k_f = 7.9\text{x}10^5 \text{ sec.}^{-1}$$

Substituting for k_f in equation (III-10) we obtain a total rate constant for intersystem crossing and internal conversion of $k_s = 5.2\text{x}10^7$ sec.$^{-1}$

Finally using the value of 80 for B (obtained from the slope of the line in Figure III-18) and substituting for k_f and k_s in equation (III-8) we obtain

$$k_t = 4.2\text{x}10^9 \text{ sec.}^{-1}\text{litre mole}^{-1}$$

It is seen that the order of the three processes is that which was stated earlier in the thesis. The rate of energy transfer $k_t c$ is fastest at high solute concentrations and the rate of intersystem crossing + internal conversion is higher than the rate of fluorescence. This means that polystyrene is more likely to form a triplet state or revert radiationlessly to the ground state rather than fluoresce from the singlet state. It also means that energy transfer must occur before intersystem crossing and before fluorescence.

The fact the the rate for quenching of the singlet state is higher than the rate constant for fluorescence does not mean that chemical reaction must therefore occur in a shorter time than fluorescence. Thus if two excited molecules choose alternative paths at the same time, one fluorescing and the other undergoing intersystem crossing, the latter molecule will still be in existence long after the first molecule has fluoresced. Thus the order of the four processes (p.61) is still correct, that is, energy transfer can occur first, if it does not, then the molecule reverts radiationlessly to the ground state or fluoresces, and it that does not occur, then a chemical reaction will probably occur.

III-6 CALCULATIONS USING FORSTER'S EQUATIONS

The overlap integral in Forster's equations (I-8) and (I-11) is written in terms of frequency γ. Since our spectra were recorded in wavelength λ it is more convenient to rewrite the overlap integral Θ as follows:

$$\Theta = \int_0^\infty \frac{\lambda^4 \, f_B(\lambda) \, \varepsilon_C(\lambda) \, d\lambda}{\int_0^\infty f_B(\lambda) \, d\lambda} \qquad \text{(III-12)}$$

The denominator normalizes the overlap integral to correct for the fact that the emission spectra are recorded in arbitrary units.(67) ε_C has the units litre/mole-cm. and λ is in cm.

The overlap integral for polystyrene-anthracene was calculated to be 3225×10^{-18} and for polystyrene-9,10-diphenylanthracene to be 4225×10^{-18}. Hirayama and Basile(63) calculated a value of 4530×10^{-18} for the latter system. Substituing for the well-known constants in equation (I-11) we obtain

$$R_o^6 = \frac{9000 \times (0.69)^2 \times 2.3}{128 \times (3.14)^5 \times 6.023 \times 10^{23}} \, \phi_f \, n^{-4} \, \Theta \qquad \text{(III-13)}$$

The refractive index for polystyrene was taken to be n=1.55.(68)

R_o for polystyrene-anthracene was calculated to be 12.3 Å and 12.9 Å for 9,10-diphenylanthracene in polystyrene. These values were calculated using the value of 0.015 for ϕ_f. However we have shown that energy transfer occurs from the polymer segment rather than from the polymer excimer. The polymer segment can be approximated by ethylbenzene whose fluorescence value in cyclohexane is 0.18. If we use this value in doing the calculations we obtain R_0 = 18.6 Å for polystyrene-anthracene and 19.5 Å for polystyrene-9,10-diphenylanthracene. The maximum value that can be predicted with Förster's theory by this method is about 20 Å.

Now it was seen in Figure III-13 that energy transfer begins to occur at 58 Å and that R_0 (the transfer distance at which energy transfer or emission can occur with equal probability) which corresponds to 50% efficiency of energy transfer in Figure III-7 is 36 Å. Thus the experimental data point to a much more efficient system than that predicted by Forster's equation. The reason for this is that Forster's equation predicts transfer distances for accepting and donating molecules that keep the excitation energy localized at fixed points. Since energy migrates in polystyrene, the probability of an excited polymer segment occurring at a distance favorable to energy transfer is greatly enhanced. Therefore we should see greater transfer distances than those predicted by Forster's equation.

Forster's equation also predicts that the efficiency of energy transfer is a little higher for polystyrene containing 9,10-diphenylanthracene than for anthracene. The opposite is true experimentally. The reason for this is that in thermally polymerizing styrene in the presence of anthracene, some of the solute becomes attached to the polymer chain.(48)

Thus in this case there is intramolecular energy transfer as well as intermolecular energy transfer from polystyrene to anthracene. This probably gives it an edge in efficiency of energy transfer over the 9,10-diphenylanthracene system where the solute is not attached to the polymer.

Calculation of the rate of energy transfer from equation (I-8) yields the value 6.9×10^{6} $sec.^{-1}$ for a concentration of 2×10^{-3}moles/litre of polystyrene. The rate constant k_t as calcualted from the experimental data on page 95 is 4.2×10^{9} $sec.^{-1}$ litre $mole^{-1}$, so the rate of transfer $k_t c$ is $(4.2\times10^{9})(2\times10^{-3}) = 8.4\times10^{6}$ which agrees satisfactorily with Forster's value. Our rate of transfer is, of course, higher in value as was expected.

III-7 SUMMARY AND CONCLUSIONS

It has been shown that energy transfer from polystyrene to anthracene occurs with high efficiency, much higher than that predicted by Forster.(11-5) This greater efficiency is attributed to the fact that energy migration in polystyrene enhances the probability of the optimum conditions for energy transfer.

The efficiency of energy transfer was determined by direct and indirect excitation of the solute in the polymer matrix and the resultant fluorescence intensities compared. This was possible since it was shown that for the samples where energy transfer occurs, the fluorescence spectra obtained by the two different excitation methods are identical. Energy transfer in polystyrene approaches 100% efficiency at 0.8% of anthracene by weight.

The extent of formation of the Diels-Alder adduct between styrene and anthracene during polymerization of the monomer has been determined experimentally and the solute concentrations corrected to their true value in the final product. All investigators previous to this work neglected to do this so that a significant error exists in their data for this system.

Having now studied the photophysical properties of the polystyrene-anthracene system, we would now like to study the effects of these photophysical processes on the chemical degradation of polystyrene.

CHAPTER IV

DEGRADATION OF POLYSTYRENE

CHAPTER IV

DEGRADATION OF POLYSTYRENE

IV-1 INTRODUCTION

The degradation of pure polystyrene has been studied in air, in vacuum, in pure oxygen and in inert atmospheres such as nitrogen.(28,69-72) Gamma rays and ultraviolet rays have been used to initiate the degradation.

The effect of a number of additives on the degradation of polymers has been studied and the conclusion reached that energy transfer was responsible for some radiation protection by these additives. Gardner and Harper(73) found that polyethylene can be made more stable to gamma radiation by mixing aromatic compounds into it. They noted that aromatic compounds that have the greatest resonance energy protect the polymer to the greatest extent and they concluded that some form of energy transfer from polymer to additive had occurred. Gardner and Epstein(74) studied the effect of pyrene and p-terphenyl on methylmethacrylate during irradiation by high-energy electrons and by ultraviolet light. They too concluded that energy transfer plays a role in radiation protection.

Pivovarov and Lukovnikov found that the intensity of polystyrene fluorescence diminished with increasing amounts of common light stabilizers for this polymer.(75) Among the stabilizers used were p-tertiarybutylphenylsalicylate and 2-hydroxy-4-methoxybenzophenone. From their calculations they postulated that for the polystyrene stabilizers they investigated, the protective effect is mainly due to energy transfer and not light absorption, i.e. shielding.

Thus far, however, no one has taken a system, polymer + additive, whose energy transfer efficiency is known, and then decomposed the polymer in such a way as to cause the additive to exert only negligible screening protection. Such an experiment would clearly show the correlation between radiation protection and percent efficiency of energy transfer. Polystyrene has a maximum extinction coefficient at 2700 Å where anthracene has a minimum extinction coefficient. This allows us to selectively excite the polymer with ultraviolet radiation so that any resulting protection would have to be due to energy transfer.

IV-2 ULTRAVIOLET RADIATION

A unit of polystyrene contains one tertiary C-H bond, two secondary C-H bonds, and five benzenoid C-H bonds. These bond energies are 71, 76, and 104 kcal/mole respectively. Ultraviolet light of wavelength 2700 Å which has an energy of 106 kcal/mole is thus able to break all of these bonds. For degradation of polystyrene in vacuum the following mechanism can be written:(72)

$$-CH_2CHC_6H_5- \xrightarrow{h\gamma} -CH_2\dot{C}C_6H_5- + H\cdot \qquad (IV\text{-}1)$$

$$-CH_2CHC_6H_5- + H\cdot \rightarrow -CH_2\dot{C}C_6H_5- + H_2 \qquad (IV\text{-}2)$$

$$-CH_2\dot{C}C_6H_5- + H\cdot \rightarrow -CH{=}\dot{C}C_6H_5- + H_2 \qquad (IV\text{-}3)$$

$$2(-CH_2\dot{C}C_6H_5) \rightarrow (-CH_2\dot{C}C_6H_5)_2 \qquad (IV\text{-}4)$$

$$H\cdot + H\cdot \rightarrow H_2 \qquad (IV\text{-}5)$$

Thus the processes that can be followed to determine the extent of degradation in polystyrene are hydrogen gas yields, unsaturation, crosslinking and radical formation. If anthracene can indirectly protect the polymer from radiation damage, then one should see a decrease in the yield for one or all of these processes.

IV-2.1 Gas Yields

Grassie and Weir(72) have stated that in the photolysis of pure polystyrene, the quantum yield (molecules of product obtained/ number of quanta absorbed) is 4.3×10^{-2} for hydrogen gas. In attempting to reproduce this work at 2537 Å using an oil manometer (n-butylphthalate), a much lower value was obtained as seen from Table IV-1. The oil in the manometer was outgassed under high vacuum for 16 hours before use and the pressure readings made with a cathethometer. Fox and Isaacs(76) reported their value to be about 10^{-4}. Thus Grassie and Weir's value is too high and from our results appears to be about ten times too high.

TABLE IV-1

QUANTUM YIELD OF HYDROGEN GAS FOR POLYSTYRENE BY PHOTOLYSIS AT 2537 Å

Pressure Increase mm. Hg/hr.	Moles/sec./cm^2.	ϕ
0.098	3.1×10^{-11}	2.3×10^{-3}
0.083	2.7×10^{-11}	2.0×10^{-3}

The polystyrene sample and manometer were kept at a temperature of 25°C.

The flux obtained from a high pressure mercury lamp at 2700 Å will be much less than that emitted by a 2537 Å resonance lamp whose output is concentrated at this wavelength. Moreover the quantum yield for hydrogen gas from polystyrene is very low. This means that extremely sensitive equipment would be required to determine the relative differences in gas yields for the anthracene-polystyrene samples decomposed by ultraviolet light of wavelength 2700 Å. For this reason it was decided to determine the extent of crosslinking via percent insolubility of the polymer exposed to ultraviolet radiation.

IV-2.2 Percent of Insoluble Material in the Ultraviolet Irradiated Films

A semi-circular sample of pure polystyrene was irradiated alongside a semi-circle of polystyrene + anthracene with ultraviolet light. The filter used consisted of a double layer as described in Section II-10. The upper layer was an aqueous solutions of copper sulphate and the botton layer, acridinium chloride and Cation X. The percent transmission of this filter together with the mercury lines emitted from the high pressure mercury lamp are illustrated in Figure IV-1. The amount of light transmitted from 2600-3000 Å amounts to 4.7 watts whereas the light transmitted from 2300-2500 Å is 0.5 watts. (The data are those of the manufacturer of the u.v. lamp.) The wattage stated here is for the sole purpose of comparing the intensities of the various lines. Thus about 12% of the radiation absorbed by polystyrene comes from the very short u.v. (2300-2500 Å) where anthracene has a high extinction coefficient. It is in this region that anthracene is capable of screening the polymer a little, but the screening will certainly be not as high as 12%. The amount of incident light absorbed by anthracene and by the Diels-Alder adduct of styrene and anthracene at 2700 Å is shown in Table IV-2 for a film thickness of 0.012 mm.

The efficiency of energy transfer is 100% at o.8% anthracene, an amount that has only 14% efficiency

FIGURE IV-1

Illustration of the Mercury Emission Lines From the High Pressure Mercury Lamp and the Percent Transmission of the Filter Used in Conjunction With the Lamp

The filter consists of copper sulphate in the upper layer and of acridinium chloride and Cation X in the lower layer. (See Section II-10 for full details)

FILTER FOR U.V. LAMP

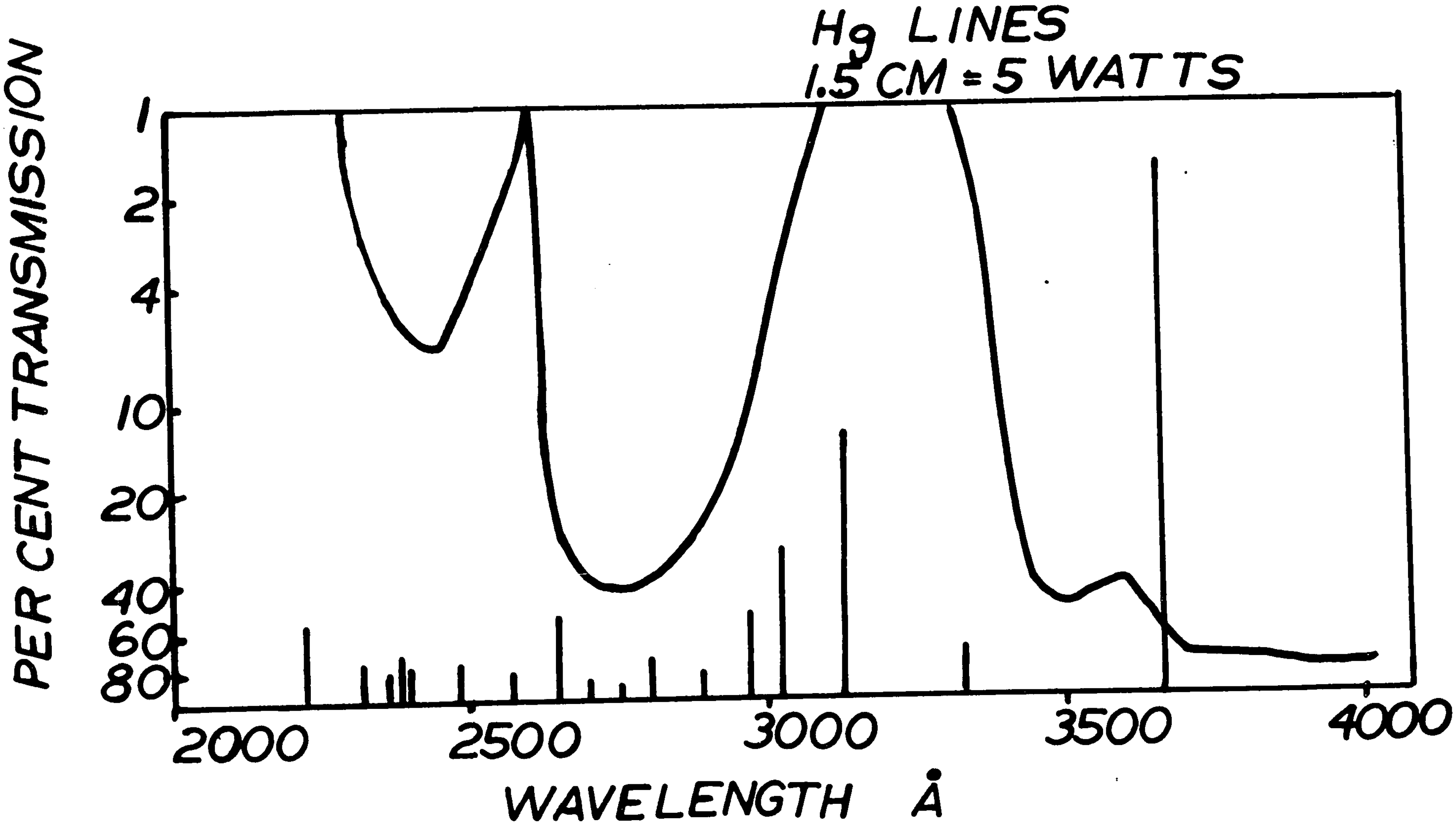


TABLE IV-2

EXTENT OF SCREENING BY ANTHRACENE AND BY THE DIELS-ALDER ADDUCT OF STYRENE-ANTHRACENE

% Solute in Polystyrene	Fraction of Incident Light Absorbed at 2700 Å by Anthracene	Fraction of Incident Light Absorbed at 2700 Å by Diels-Alder Adduct
0.1	0.02	0.007
0.5	0.09	0.03
1.0	0.17	0.07
2.0	0.29	0.12
3.0	0.38	0.18

Polystyrene Film Thickness = 0.012 mm.

in screening. For samples containing up to 2% of the Diels-Alder adduct the screening can be considered to be negligible since this compound has a very low extinction coefficient.

The long wavelength line at 3660 Å, the most intense line in the mercury emission spectrum as seen in Figure IV-1, is not filtered out. If the filter had been such that it filtered this line out, then the number of quanta emitted from 2700 to 3000 Å would have been too low to cause any significant degradation in polystyrene in a reasonable period of time. Since only the anthracene absorbs the 3660 Å line, it is unnecessary to filter it out. A quick calculation, as shown on the next page, indicates that the line is not intense enough to excite all the anthracene molecules.

Let the number of excited singlet states of anthracene be represented by (A^*) and the number of anthracene molecules in the ground state by (A_0). We therefore would like to determine the value $(A^*)/(A_0)$.

Let us assume that with ultraviolet radiation the system has reached steady state conditions so that

$$d(A^*)/dt = 0 \tag{IV-1}$$

$$= \Delta I - \sum_s k_s(A^*) \tag{IV-2}$$

where ΔI is the amount of light absorbed, k_s is the quenching rate constant for the excited singlet states by s different processes.

From Beer-Lambert's law

$$\Delta I = I_0(1 - e^{-dcL}) \tag{IV-3}$$

where I_0 is the incident light, d is the extinction coefficient of the compound, and L is the path length of absortion. The concentration of the compound in the polymer is represented by c. We shall make the assumption that all of the light is absorbed so that dcL is very large in value. Thus e^{-dcL} is approximately equal to zero and

$$\Delta I = I_0 \tag{IV-4}$$

From equation (IV-2)

$$(A^*) = \Delta I/\sum_s k_s = I_0 \times T \tag{IV-5}$$

where T is the fluorescence lifetime of anthracene.

For the caculation let us take a low

concentration sample of anthracene (0.05%):

Number of anthracene molecules in a thin film (weight 0.1 gm.) is

$$\frac{0.0005 \times 0.1}{\text{mol. wt. of anthracene}} \times 6.023\times10^{23}$$

$$= 3.3\times10^{16}$$

From uranyl oxalate actinometry (77-8) the flux is 13×10^{18} quanta/sec. on the entire sample.

From equation (IV-5)

$$(A^*) = 13\times10^{18} \times 10^{-8}$$

$$= 13\times10^{10}$$

The number of molecules in the ground state (A_0) is equal to the total number of anthracene molecules minus those in the excited state i.e.

$$3.3\times10^{16} - 13\times10^{10} \approx 3.3\times10^{16}$$

Therefore

$$(A^*)/(A_0) = 13\times10^{10}/3.3\times10^{16}$$

$$= 4\times10^{-6}$$

Thus even if every single quantum at 3660 Å is absorbed there are more than enough unexcited anthracene molecules to participate in energy transfer from polystyrene.

When polystyrene is irradiated with ultraviolet light at 2700-3000 Å, it forms crosslinks with the result that part of the polymer is insoluble in organic solvents in which it is normally soluble. By dissolving the irradiated samples in tetrahydrofuran the amount of insoluble material can be determined by filtering it out from the solution and weighing it.(See Section II-10.2 for full details of the method.)

The polymer samples containing fluorescent solute yielded less insoluble material than the pure polymer for the same amount of irradiation. (Irradiations were carried out under high vacuum.) The decrease in insoluble material divided by the total amount of insoluble material for pure polystyrene times 100 gave the percent photoprotection for the polymer. The experimental values obtained are shown in Figure IV-2. The efficiency of energy transfer curve from Figure III-7 has been redrawn in Figure IV-2. It is seen that the points fall close to the energy transfer curve. However the values appear to be too high for the 0-0.1% region (solid circles on Figure IV-2). The reason for this is probably that the pure polymer used for comparative purposes had an intrinsic viscosity of 1.5 whereas the value for the anthracene-containing samples was 1.2. Using a value of 0.743 for a and 9.185×10^{-5} for K and substituting into the relation(68)

$$(n) = KM^{a} \qquad \text{(IV-6)}$$

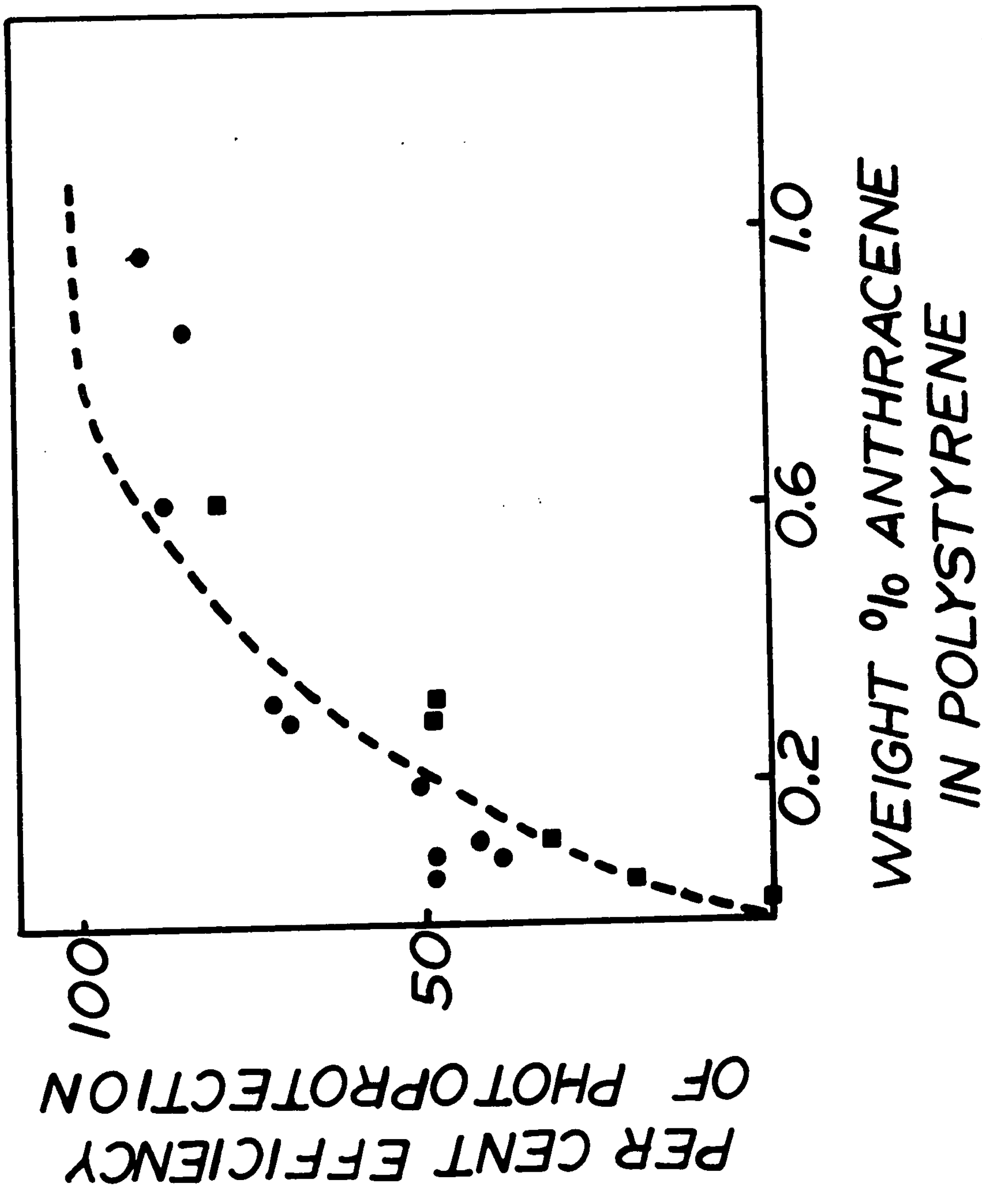
the viscosity molecular weight of 466,800 was found for pure polystyrene and 347,800 for the anthracene-containing samples. The higher molecular-weight polystyrene will form insoluble material more quickly since fewer crosslinks are needed for gel formation giving a psuedo-protection value to the anthracene-polystyrene samples. Kato(69) has shown that the amount of insoluble material increases with increasing molecular weight of polystyrene for the same number of quanta absorbed. In view of this, it is desirable to obtain

FIGURE IV-2

Percent Photoprotection of Polystyrene Verus Percent of Anthracene

The anthracene was added to the monomer before polymerization.

Solid Circles:	Pure Polystyrene of different molecular weight distribution used for comparison.
Solid Squares:	Pure Polystyrene precipitated from corresponding polystyrene-anthracene sample used for comparison.


PER CENT EFFICIENCY
OF PHOTOPROTECTION
100
50
0.2
0.6
1.0
WEIGHT % ANTHRACENE
IN POLYSTYRENE

samples with the same molecular weight distribution. Since anthracene affects the molecular weight distribution, it was decided to obtain pure polystyrene from the anthracene-polystyrene samples by precipitating them in methanol. The anthracene and Diels-Alder adduct are soluble so that the polymer can be filtered out, and washed with cold methanol. This precipitation was done only once so as not to remove too much of the low molecular-weight polymer, thus keeping the molecular weight distribution as close as possible to that of the original sample. A single precipitation was sufficient to remove the anthracene to the level that it could not be detected by ultraviolet spectroscopy for samples originally containing up to 0.6% anthracene.

The experiment was repeated but this time for each anthracene-polystyrene film irradiated, the amount of insoluble material was compared to the amount of insoluble material obtained from the repricipitated polystyrene(as described above) derived from the sample. The results are presented in Figure IV-2 (solid squares). It can be seen that the results agree very nicely with the efficiency of energy transfer.

Although the Diels-Alder adduct absorbs very little of the excitation light, the fact that it does absorb means it could have an undetermined chemical effect on the polymer. Thus it was decided to study polystyrene-anthracene samples with none of the adduct present. The samples were prepared by adding the required amount of anthracene to pure polystyrene in benzene and the solvent evaporated. The other advantage to this is that all of the samples will have the same molecular-weight distribution since the same batch of polymer was used to prepare the various films.

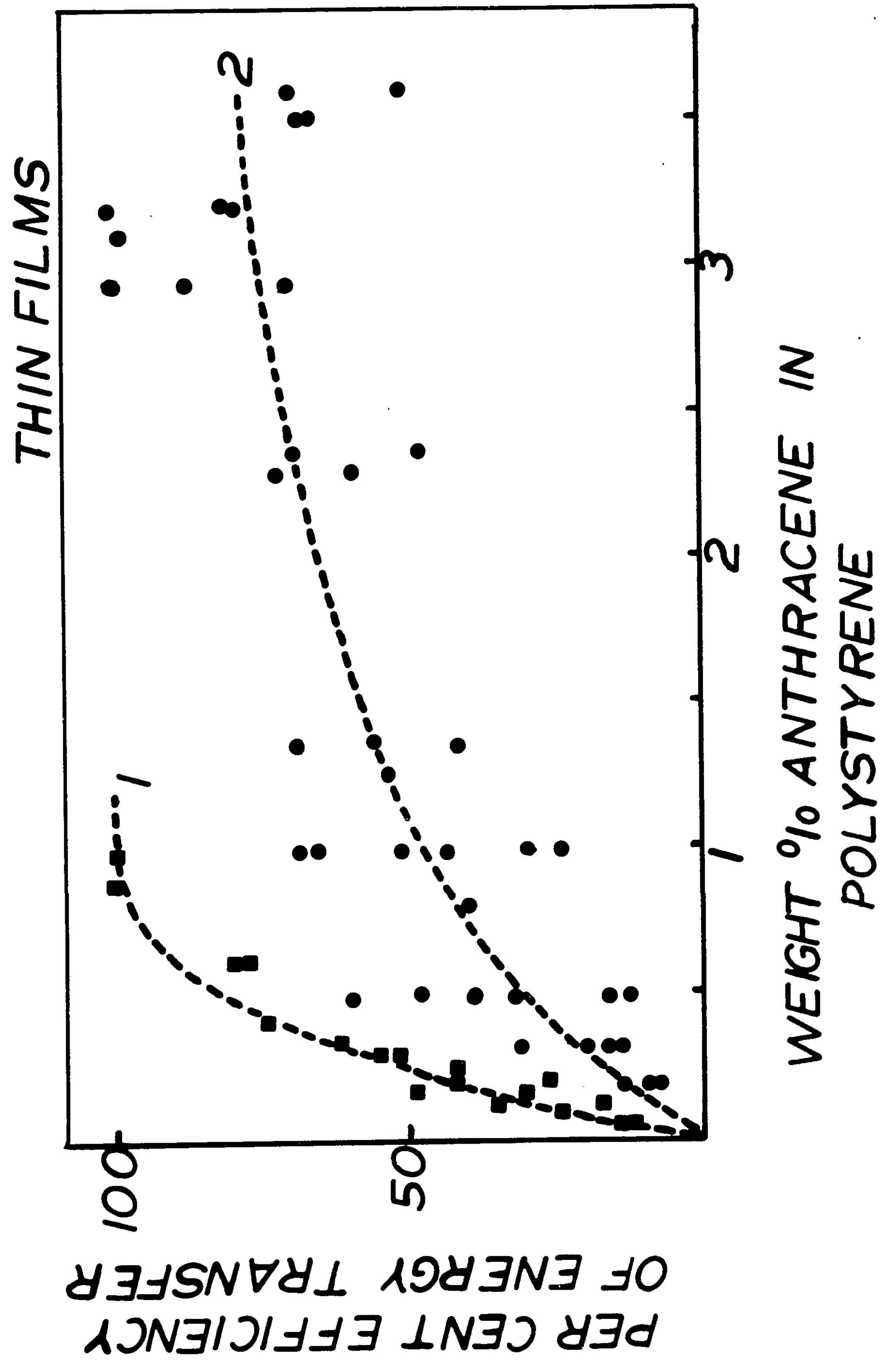
Before degrading the films the percent efficiency of energy transfer was measured to make sure that we had the same efficiency as in the thermally copolymerized system. The transfer efficiencies measured as described in Section II-4 are shown in Figure IV-3. For the thermally copolymerized system the energy transfer curve has been redrawn from the photophysical measurements (Figure III-7). The data for the thin films (solid squares) fall on this line. However the efficiency of energy transfer for the system to which anthracene was added to polystyrene at room temperature falls much below that of the thermally copolymerized system(solid circles). Moreover reproducibility is poor, and the explanation for this is that anthracene being a crystalline material, probably separates into microcrystals as the solvent evaporates from the solution at room temperature. Thus the number of sites to which polystyrene can transfer is much smaller than if the anthracene molecules were completely isolated from one another. Thus poor reproducibility is probably due to the difference in amount of crystallization of the anthracene in the various films. One sees then that it

FIGURE IV-3

Percent Efficiency of Energy Transfer for Thin Polystyrene Films Containing Anthracene

Solid Squares: Anthracene Added to Monomer Before Polymerization

Solid Circles: Anthracene Added to Polymer (After Polymerization)
At Room Temperature


THIN FILMS
1
2
100
50
1
2
3
WEIGHT % ANTHRACENE IN POLYSTYRENE
PER CENT EFFICIENCY OF ENERGY TRANSFER

necessary to add the solute to the monomer before polymerization at high temperatures in order to insure good dispersion throughout the sample.

The efficiency of energy transfer for the films made from the thermally copolymerized system remains the same within experimental error. Reproducibility is good. The reason that no decrease in efficiency of energy transfer occurs is that since 70% of the original amount of anthracene went into the formation of the sytrene-anthracene Diels-Alder adduct, the remaining 30% anthracene is hindered, by this large amount of impurity, in its formation of the critical nuclei for incipient crystallization. No doubt some clusters of anthracene are formed but certainly not to the extent that is possible where only pure anthracene is present in the polymer matrix. Anthracene is soluble in polystyrene up to only 3.5% by weight. At higher concentrations one can see the crystals of anthracene precipitated in the film.

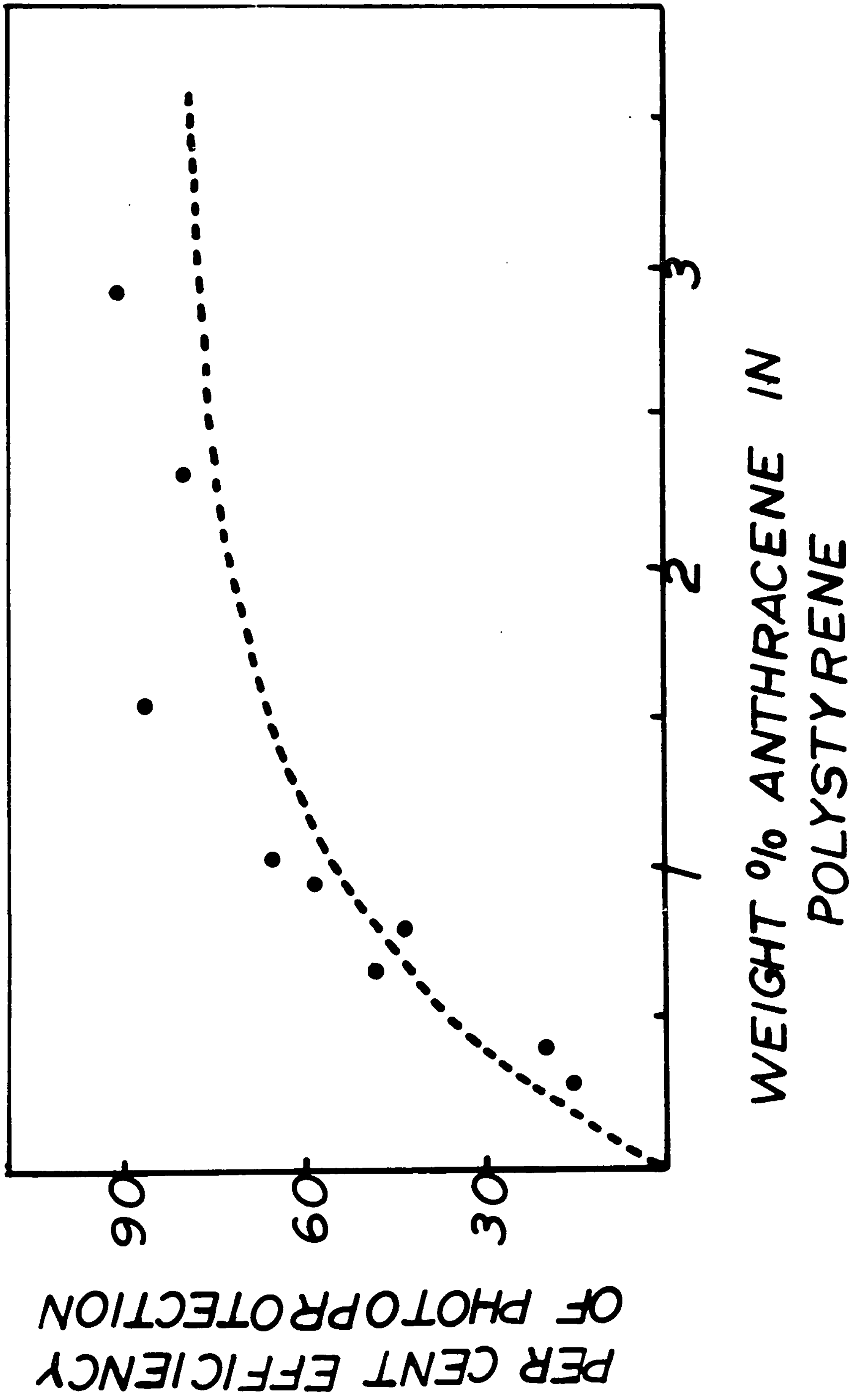
Nevertheless the samples to which anthracene had been added after polymerization of the monomer were irradiated with ultraviolet light and the amount of insoluble material determined. Comparison with the amount for pure polystyrene gave the extent of photoprotection. These values are plotted in Figure IV-4. The energy transfer curve has been redrawn from Figure IV-3.

If one looks at Table IV-2 it is noted that at 2 and 3% anthracene there is screening by the solute

FIGURE IV-4

Percent Photoprotection of Polystyrene Versus Percent of Anthracene

The anthracene was added to the polymer at room temperature.


PER CENT EFFICIENCY
OF PHOTOPROTECTION
90
60
30
1
2
3
WEIGHT % ANTHRACENE IN
POLYSTYRENE

to the extent of 30 and 40%. Thus when anthracene is added to polystyrene at room temperature one obtaines a very inefficient system with respect to energy transfer and hence poor radiation protection.

It should be mentioned here that irradiation of the polymer films to which anthracene had been added after polymerization resulted in a very small but detectable band occurring at 3950 Å, indicating that some monosubstituted anthracene is formed, namely some of the anthracene must combine with a polystyrene radical. The amount is small and can be discounted as an inhibition of the observed crosslinking in the polymer. This observation could not be made on the thermally copolymerized samples because the band at 3950 Å already exists due to the formation of monosubsituted anthracenes during the polymerization process.

Table IV-3 gives the amount of photoprotection for 9,10-diphenylanthracene-anthracene samples. The efficiency of photoprotection for this system is very poor. It was not studied in detail because this solute screens the polymer quite heavily in the region of ultraviolet radiation used.

At low concentrations (0.2%) the solute probably does not form many microcrystals, hence there is protection in excess of that provided by screening. At higher concentrations the solute begins to form microcrystals efficiently so that the transfer efficiency goes down from that measured in the solid cylindrical samples. Moreover

TABLE IV-3

ULTRAVIOLET RADIATION PROTECTION OF POLYSTYRENE BY 9,10-DIPHENYLANTHRACENE

% 9,10-Diphenyl-Anthracene	% of Light at 2700 Å Absorbed by Solute	% Photoprotection	
		(1)	(2)
0.20	20	45	35
0.53	40	27	53
0.75	50	35	43
1.23	60	68	65

these microcrystals do not provide as large a screening effect as in the case where they are isolated from one another in the matrix. Hence the screening values shown in Table IV-3 are probably too high for polystyrene films which have been made by evaporation from a benzene solution.

9,10-diphenylanthracene does not interact chemically with styrene during polymerization. Thus this solute when thermally copolymerized with styrene would probably be much more efficient in resistance to radiation than when it is added to a solution of polymer at room temperature. Prevention of aggregation, that is, the formation of microcrystals is important in maintaining maximum energy transfer efficiency.

Finally one might argue that crosslinking may have an effect on the percent efficiency of energy transfer in the system. Basile(79) found the fluorescent decay time for crosslinked polystyrene to be about 10% higher than for uncrosslinked polymer. He attributes the lengthening of the decay time for crosslinked polystyrene to such effects as more complete removal of the residual styrene. Increasing the concentration of crosslinking agent almost twenty-fold has no measureable effect on the decay time. This means that the cross-linked polymer can participate in energy transfer just as the uncrosslinked polymer. Thus as the polymer decomposes resulting in an increase in crosslinking, there should be no change in the transfer efficiency of energy to the solute.

IV-3 GAMMA RADIATION

Since it was not possible to determine gas yields easily with ultraviolet radiation it was decided to use gamma radiation instead and to use the gas yields so obtained as a measure of the amount of radiation protection.

Gamma rays are electromagnetic waves of the same nature as visible or ultraviolet light but of a much shorter wavelength and are emitted by radioactive isotopes covering a very broad spectrum of energies. The radioactive isotope used in our work was Co^{60} which has a half-life of

5.3 years. It emits two types of photons, a β photon with and energy of 0.306 Mev. and γ photons of two energies 1.17 and 1.33Mev.(80) The absorbed photons are rapidly converted into fast moving electrons which produce most of the observed ionizations and are responsible for nearly all of the chemical changes that take place.

The difference between using ultraviolet light (2700-3000 Å) and gamma radiation is that in the former the highest energy state produced in the molecule is the first singlet state whereas in the latter higher singlet states are formed and ionization occurs as well. However, investigators have found that the efficiency of energy transfer is the same whether investigated with ultraviolet light or ionizing radiation.(81-2) This in effect supports the theory that when molecules are excited to upper singlet states, they very rapidly cascade down to the first singlet level where events resume their normal pace. Thus we should see gamma radiation protection unless the upper singlet states play a role in the degradation of polystyrene.

Gamma radiation follows the principle of non-specificity, that is, since ionizing radiation transfers its energy to molecules via the charged particles liberated in the medium and these in turn interact with the electrons of the molecules lying close in their path, the probability of dissipating energy in a particular part of a molecule is simply proportional o the electron density in that region.

Consequently it can be assumed, a priori, that primary events in a given molecule occur at random. However the site at which a chemical bond is broken is not necessarily the site at which the energy absorption occurred. On pages 122-3 calculations for the electron densities of polystyrene and anthracene are shown. The electron fraction of a sample of polystyrene containing 3% anthracene is 0.97 meaning that anthracene receives only 3% of the gamma radiation, an amount that can be considered to be negligible to the amount absorbed by the polymer.

Dosage in our work is expressed in rads. The rad is the unit of absorbed dose and is equivalent to 100 ergs per gram or $6.25\text{x}10^{13}$ electron volts (e.v.) per gram. The dose rate of the Co^{60} cell varied from 0.35 to 0.32 megarads/hr. for this work.

IV-3.1 Gas Yields

Polystyrene was irradiated for various doses and the total moles of gas determined. Mass spectrometry indicated that the major product was hydrogen with a trace of methane. For the samples irradiated above 20 megarads there was sufficient gas collected to run it through the gas chromatograph. Only a hydrogen peak was detected. The moles of gas per gram of polymer is plotted versus dosage in Figure IV-5 for pure polystyrene and in Figure IV-6 for 1.23% 9,10-diphenylanthracene.

CALCULATION OF ELECTRON DENSITY IN POLYSTYRENE AND SOLUTE

Electron Density of Polystyrene

Polystyrene C_8H_8

Atomic number of carbon is 6	$8 \times 6 = 48$
Atomic number of hydrogen is 1	$8 \times 1 = 8$
Number of electrons per molecule	56

Number of electrons per mole 337×10^{23}

Molecular weight of styrene is 104

Therefore the electron density of polystyrene is

$$\frac{337 \times 10^{23}}{104} = 3.24 \times 10^{23} \text{ electrons/gram}$$

Electron Density of Anthracene

Anthracene $C_{14}H_{10}$

Atomic number of carbon is 6	$14 \times 6 = 84$
Atomic number of hydrogen is 1	$10 \times 1 = 10$
Number of electrons per molecule	94

Number of electrons per mole 566×10^{23}

Molecular weight of anthracene is 178

Therefore the electron density of anthracene is

$$\frac{566 \times 10^{23}}{178} = 3.17 \times 10^{23} \text{ electrons/gram}$$

Electron Fraction of Polystyrene for a Sample Containing 3% Anthracene

Weight of polymer is 0.8 gm.

3% of this weight is anthracene 0.024 gm.

Electron fraction of polystyrene

$$\frac{(0.8 - 0.024) \times 3.24 \times 10^{23}}{(0.8 - 0.024) \times 3.24\times10^{23} + 0.024\times3.17\times10^{23}} = 0.97$$

Workers in radiation chemistry prefer to express their yield of products by gamma rays in terms of a G value. The use of the symbol G for expressing radiation chemical yields was first introduced by Burton(83) who defined the "G" value as the absolute chemical yield expressed as the number of individual chemical events occurring per 100 e.v. of absorbed energy. Tables IV-4 and IV-5 list the $G(H_2)$ values for polystyrene-anthracene and for polystyrene-9,10-diphenylanthracene respectively. As can be seen there is no change in gas yields regardless of the amount of solute. The significance of this will be discussed later. The $G(H_2)$ values agree well with the values reported by others.(46,73,79)

IV-3.2 Gelation Dose

To find the critical conditions for gel formation let us consider a polymer system consisting initially of linear molecules, each of which has a degree

FITURE IV-5

Gas Yields for Pure Polystyrene Versus Dose of Gamma Radiation

GAS YIELD
PURE POLYSTYRENE

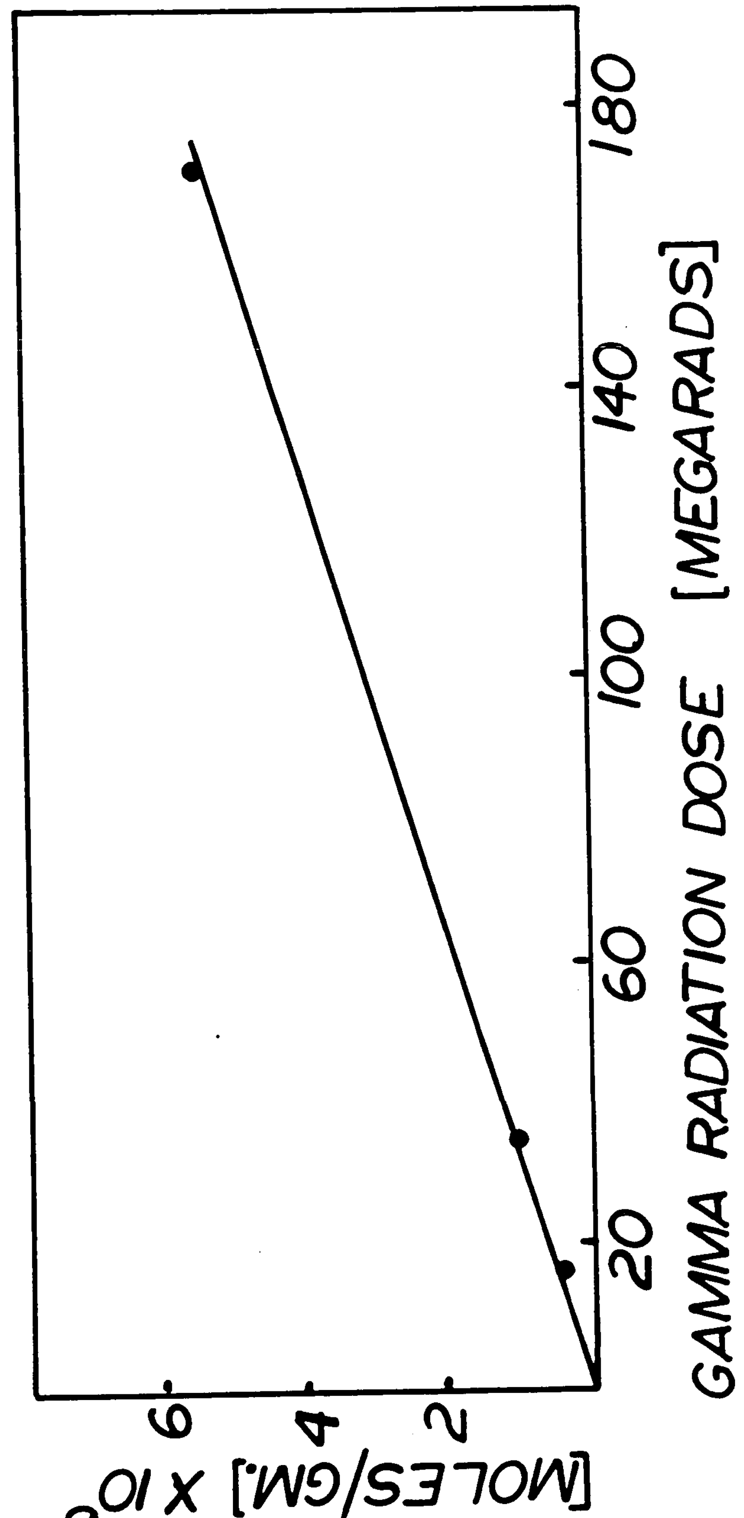


FIGURE IV-6

Gas Yields for 1.23% 9,10-Diphenylanthracene in Polystyrene Versus Dose of Gamma Radiation

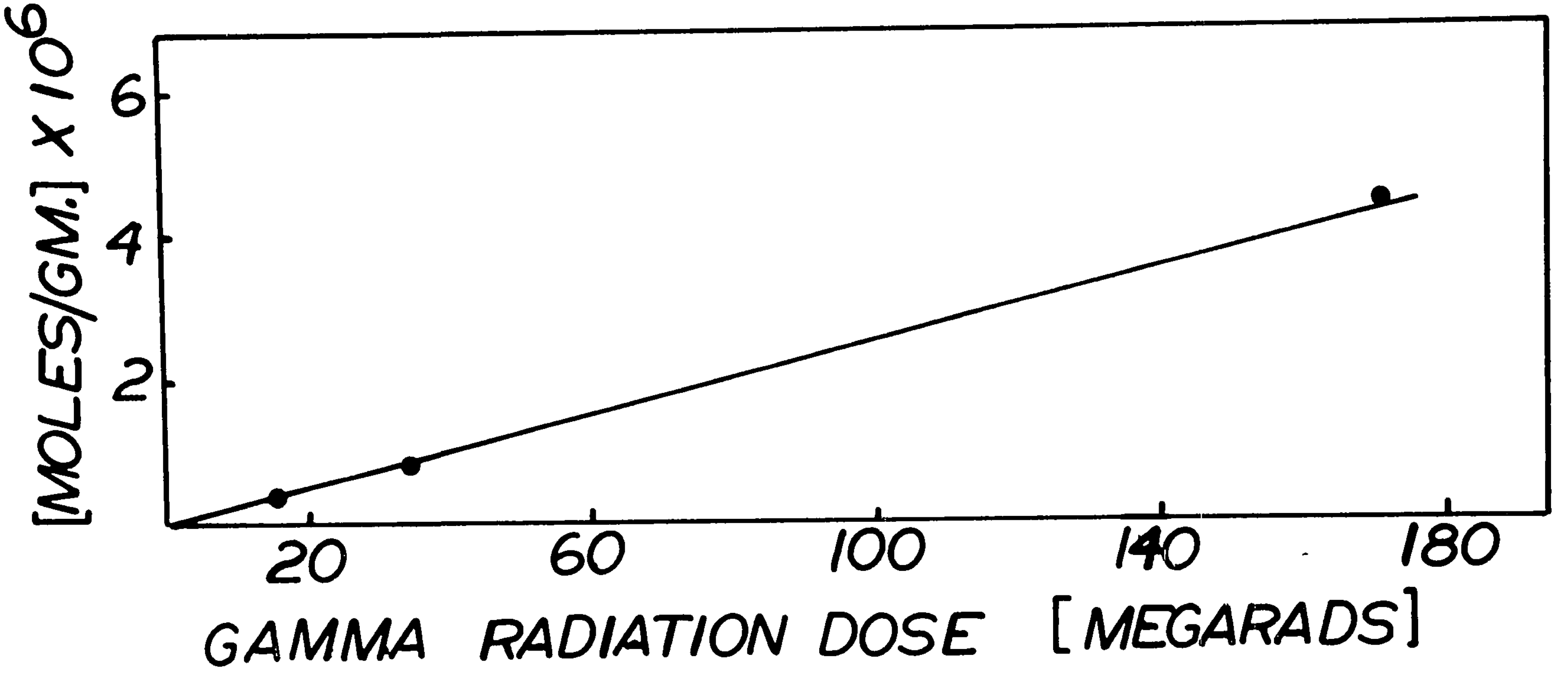

GAS YIELD
1.2% 9,10-DIPHENYLANTHRACENE

TABLE IV-4

GAS YIELDS FOR GAMMA RADIATION OF POLYSTYRENE -ANTHRACENE

Electron Fraction of Anthracene	452.25 Hours of Gamma Radiation $G(H_2)$
0.0030	0.028
0.0064	0.031
0.0084	0.027
0.0103	0.027
0.0266	0.029
0.0480	0.027

Error: ±0.5%

TABLE IV-5

GAS YIELDS FOR GAMMA RADIATION OF POLYSTYRENE-9,10-DIPHENYL-ANTHRACENE

Electron Fraction of 9,10-DPA	Hours of Gamma Radiation $G(H_2)$ 42	90	452.25
0	0.028	0.029	0.034
0.0020	0.024	0.027	0.029
0.0053	0.022		
0.0075	0.024	0.025	
0.0123	0.025	0.026	0.028

Error: ±0.5%

of polymerization P in which crosslinking occurs at random. The critical conditions under which a primary molecule such as B_0 selected at random belongs to an infinite network, can be derived on the basis of the expected number of crosslinked units n in any of the primary molecules B_1, B_2 ... which are linked to B_0. Since crosslinking occurs at random

$$n = W_c(P - 1) \qquad \text{(IV-7)}$$

where W_c is the probability that any one monomer unit of B_0 is crosslinked and (P - 1) represents the remaining monomer units of B_0.

If n is less than 1 the probability that each following molecule from B_0 is linked to another one decreases at each further step in passing from one molecule to the next and hence the molecule under consideration cannot have the structure of an infinite network. On the contrary if n is greater than 1 this probability increases at each step and an infinite network structure arises. Thus for incipient gel formation the condition is n = 1.

$$W_c = 1/P \qquad \text{(IV-8)}$$

It follows that a gel forms when each molecule has at least one crosslink linking it into the network.

The intrinsic viscosity of a polymer solution is traditionally used in polymer chemistry for determining molecular weights of macromolecules. Although this method is not an absolute one, the empirical relationship $(\eta) = KM^a$ has been found to hold over a considerable range of molecular weights for a number of polymers.(80) In this relationship (η) is the intrinsic viscosity, M is the number- or weight-average molecular weight and K and a are constants. By calibrating the intrinsic viscositites versus the absolute molecular weights, measured by osmotic pressure, end group determination, light scattering or other absolute methods, the two constants a and K can be determined and the molecular weights for the corresponding polymer can then be computed from simple viscosity measurements without recourse to more laborious techniques.

It is known that crosslinking exceeds chain scission in the radiolysis of polystyrene, the scission to crosslinking ratio being 0.14.(84) This results in a net increase in molecular weight and hence an increase in the intrinsic viscosity of the polymer. Above the gel point some of the macromolecules form an insoluble three-dimensional network. With increasing dose the gel fraction increases and the soluble fraction decreases. Wall and Brown (85) studied the intrinsic viscosity in the pre-gel range for polystyrene irradiated in vacuum with gamma rays. They found that the intrinsic viscosity increased steadily with dose. As the gel point is approached the viscosity rises sharply and the critical gel dose is thus rather well defined.

Samples of polymer containing anthracene and having an intrinsic viscosity of 1.26-1.36 were chosen for our study. These samples were in the form of polystyrene chips cut from the solid cylinder of the thermally copolymerized system. The intrinsic viscosities were determined after various periods of gamma irradiation in vacuum. The results are shown in Figures IV-7 to IV-9. As can be seen, the increase in concentration of anthracene in the samples causes an increase in the dosage to incipient gelation of the sample. Since the initial intrinsic viscosities of the samples are about the same, it is assumed that the same crosslinking density is required for each sample to reach gelation. Thus the large dosage required for the 0.61% sample does not mean that more crosslinks are formed before the sample becomes a gel, but that the anthracene has dissipated a portion of the absorbed energy harmlessly. On plotting the gelation dose versus percent anthracene as in Figure IV-10,one can see that the gelation dose is not a linear function of anthracene concentration. One should expect a linear relationship if the solute were acting merely as a radical trap. However a plot of the percent efficiency of energy transfer versus dose shows a linear relationship for the system of polystyrene-anthracene (Figure IV-11). This shows that the amount of radiation protection is directly proportional to the efficiency of energy transfer. The intercept on the X-axis (13 megarads) represents the gelation dose for pure polystyrene that would have the same molecular weight distribution as the anthracene-containing samples.

FIGURE IV-7

Intrinsic Viscosities of 0.05% and 0.17% Anthracene in Polystyrene Versus Dose of Gamma Radiation

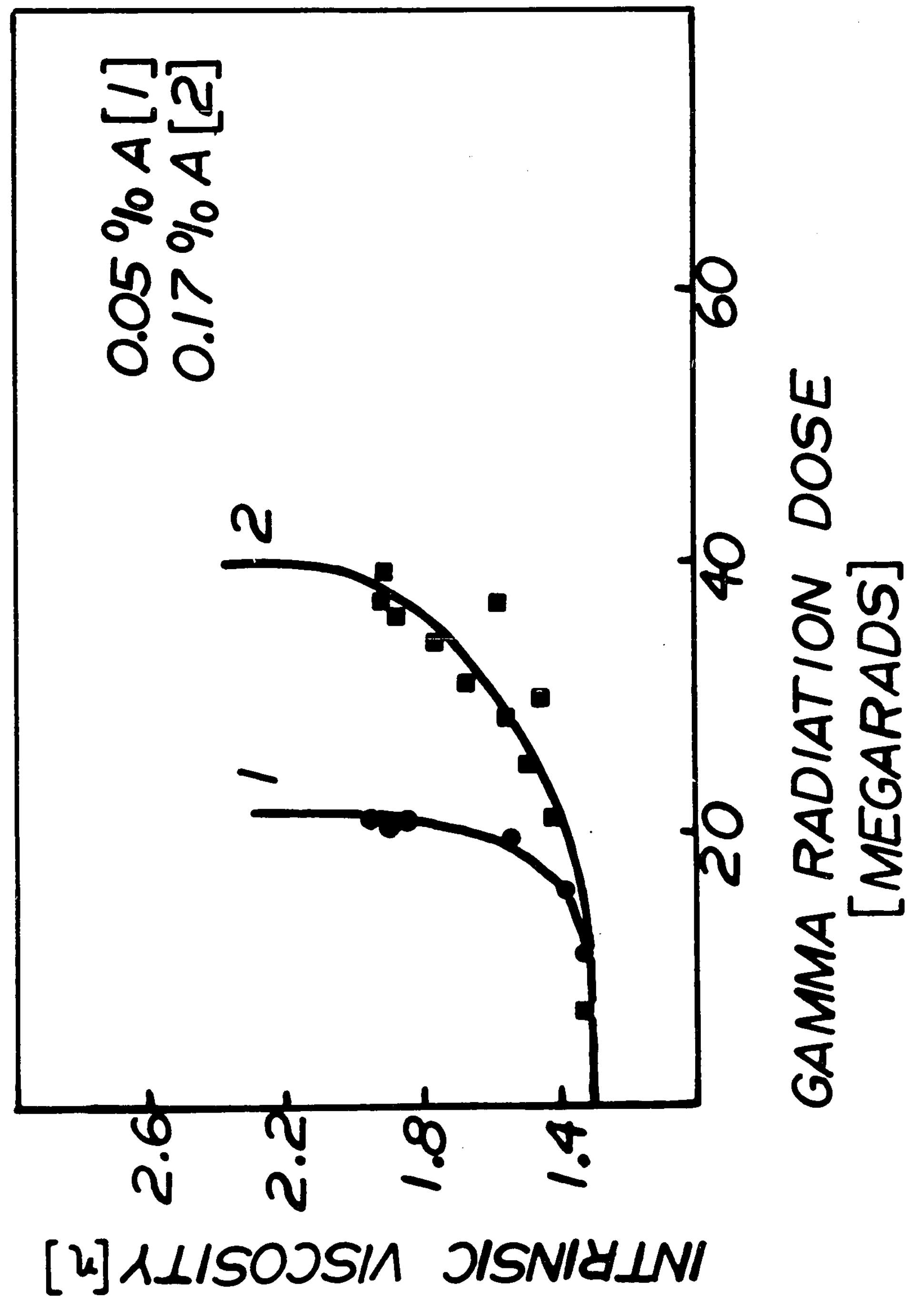

INTRINSIC VISCOSITY [η]
2.6
2.2
1.8
1.4
20
40
60
GAMMA RADIATION DOSE [MEGARADS]
1
2
0.05 % A [1]
0.17 % A [2]

FIGURE IV-8

Intrinsic Viscosities of 0.26% Anthracene in Polystyrene Versus Dose of Gamma Radiation

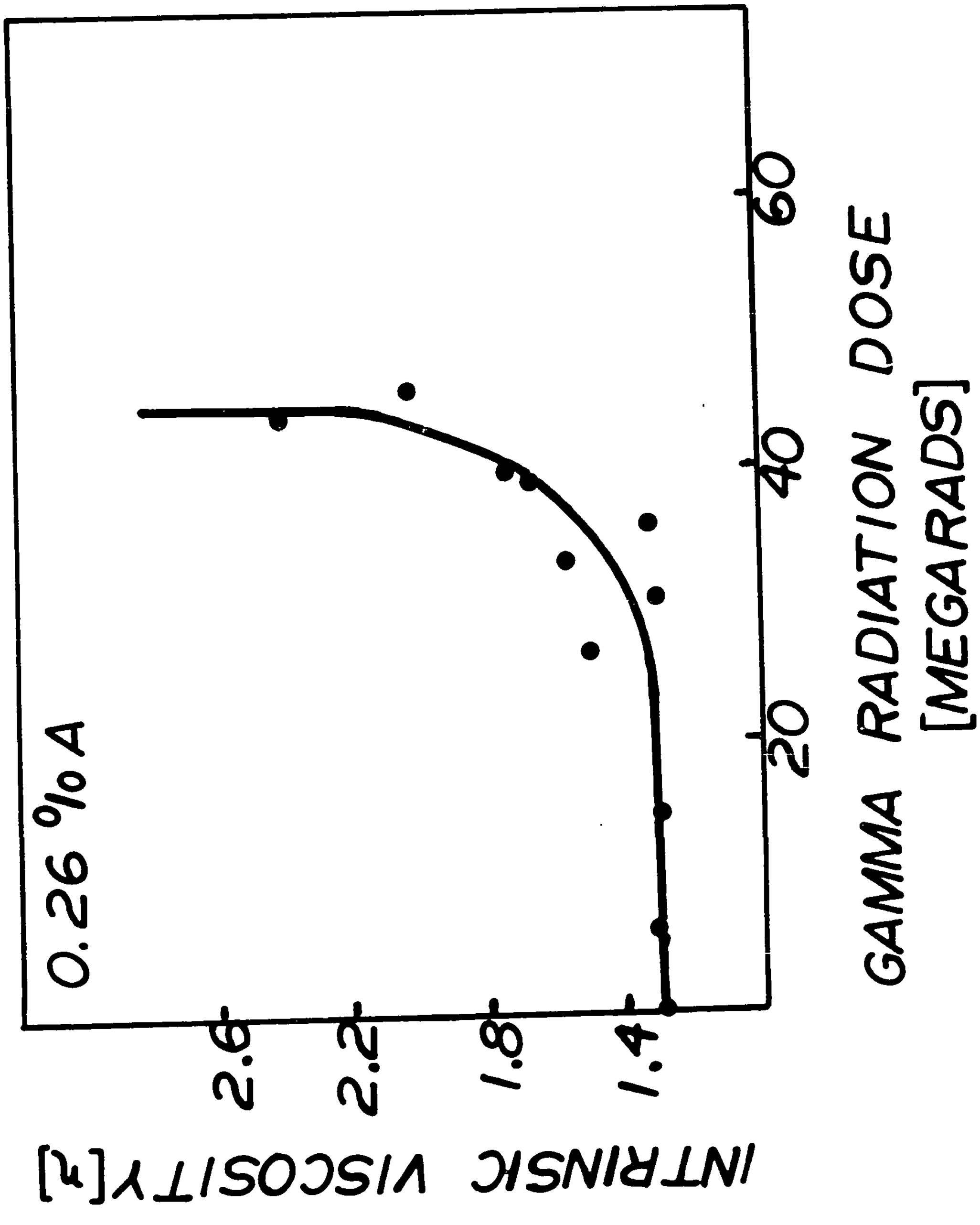

0.26 % A
INTRINSIC VISCOSITY [η]
2.6
2.2
1.8
1.4
20
40
60
GAMMA RADIATION DOSE
[MEGARADS]

FIGURE IV-9

Intrinsic Viscosities of 0.3% and 0.6% of Anthracene in Polystyrene Versus Dose of Gamma Radiation

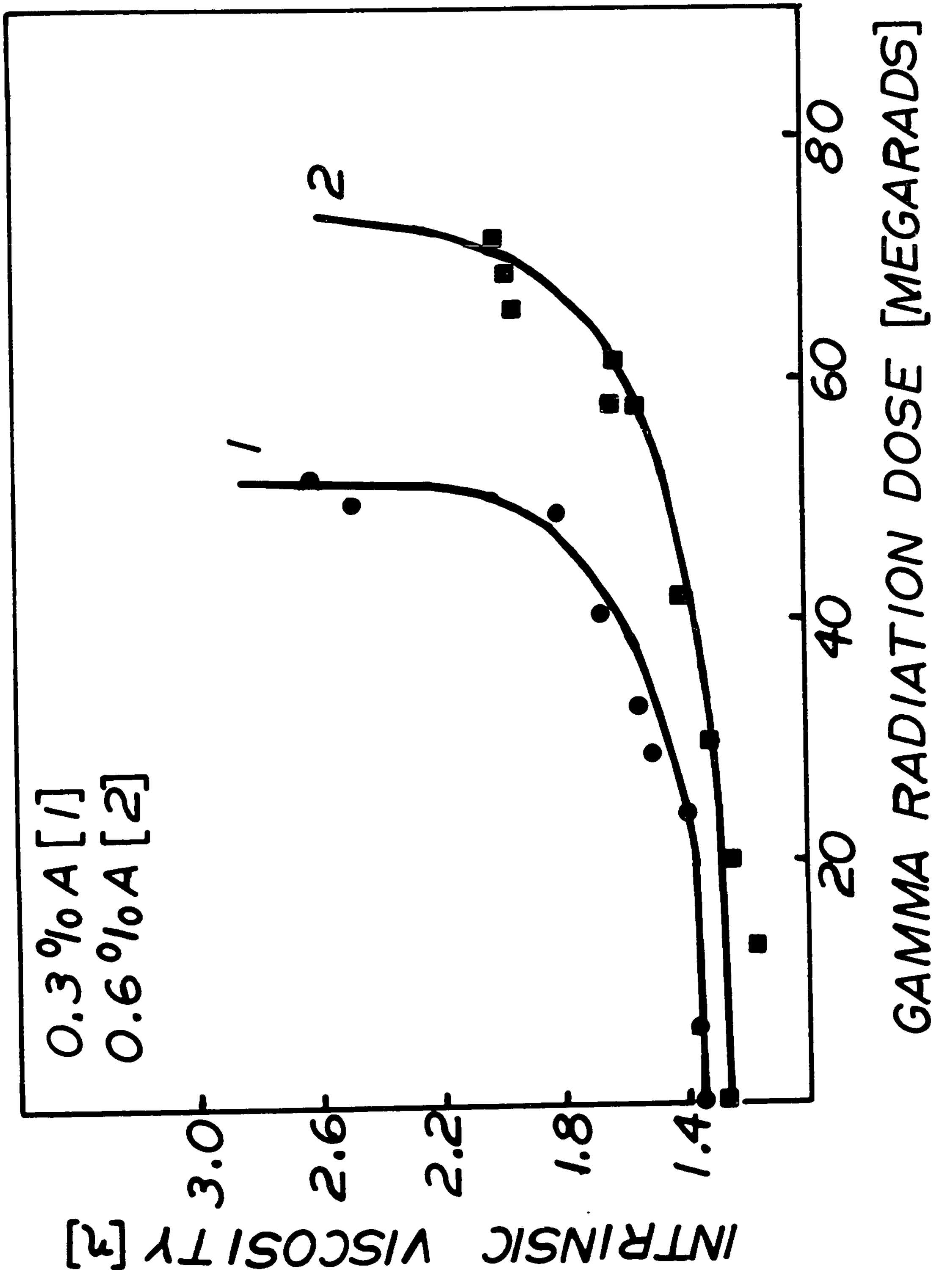

0.3%A [1]
0.6%A [2]
1
2
3.0
2.6
2.2
1.8
1.4
20
40
60
80
GAMMA RADIATION DOSE [MEGARADS]
INTRINSIC VISCOSITY [η]

FIGURE IV-10

Gelation Dose Versus Weight Percent of Anthracene in Polystyrene

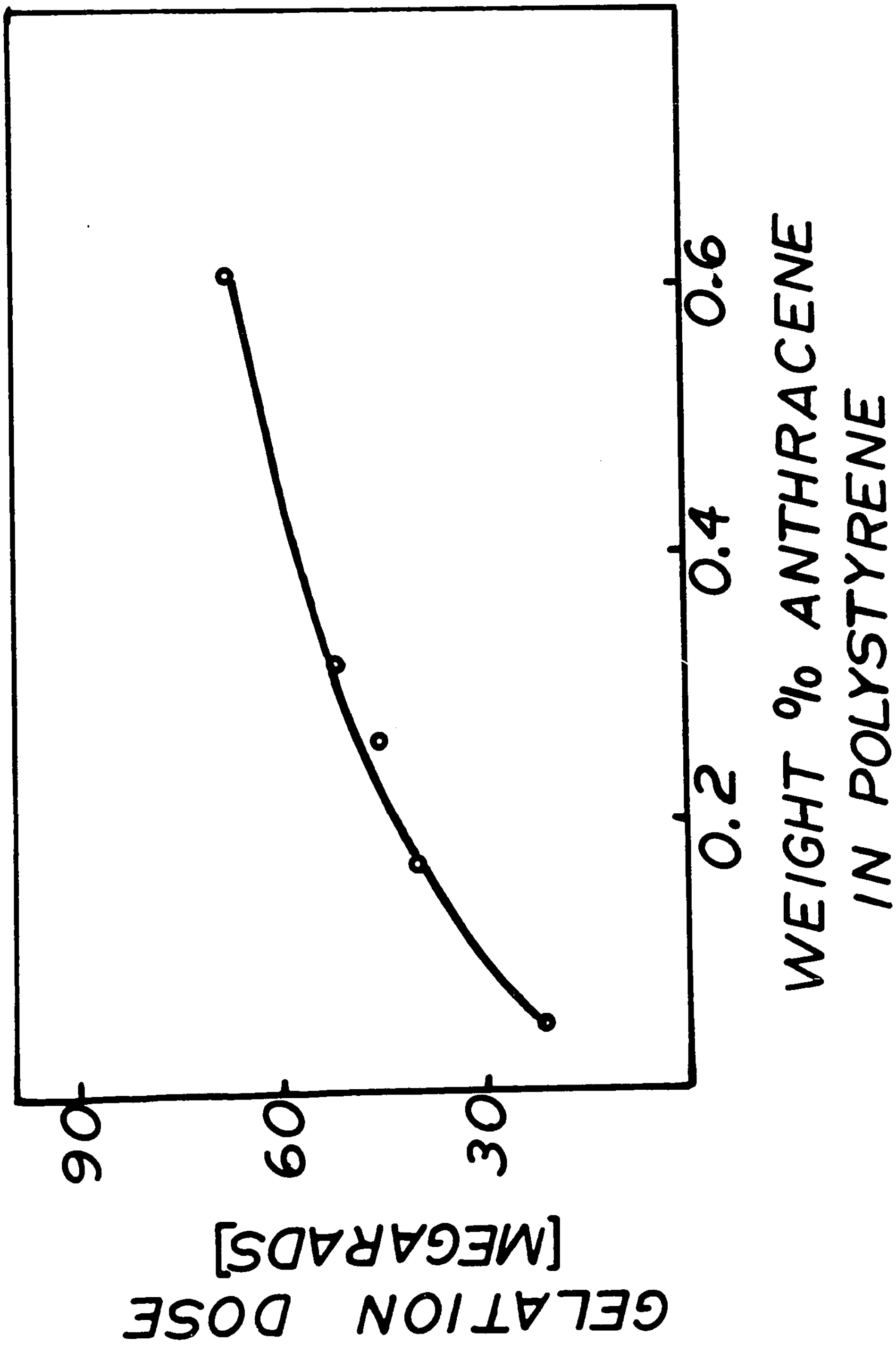
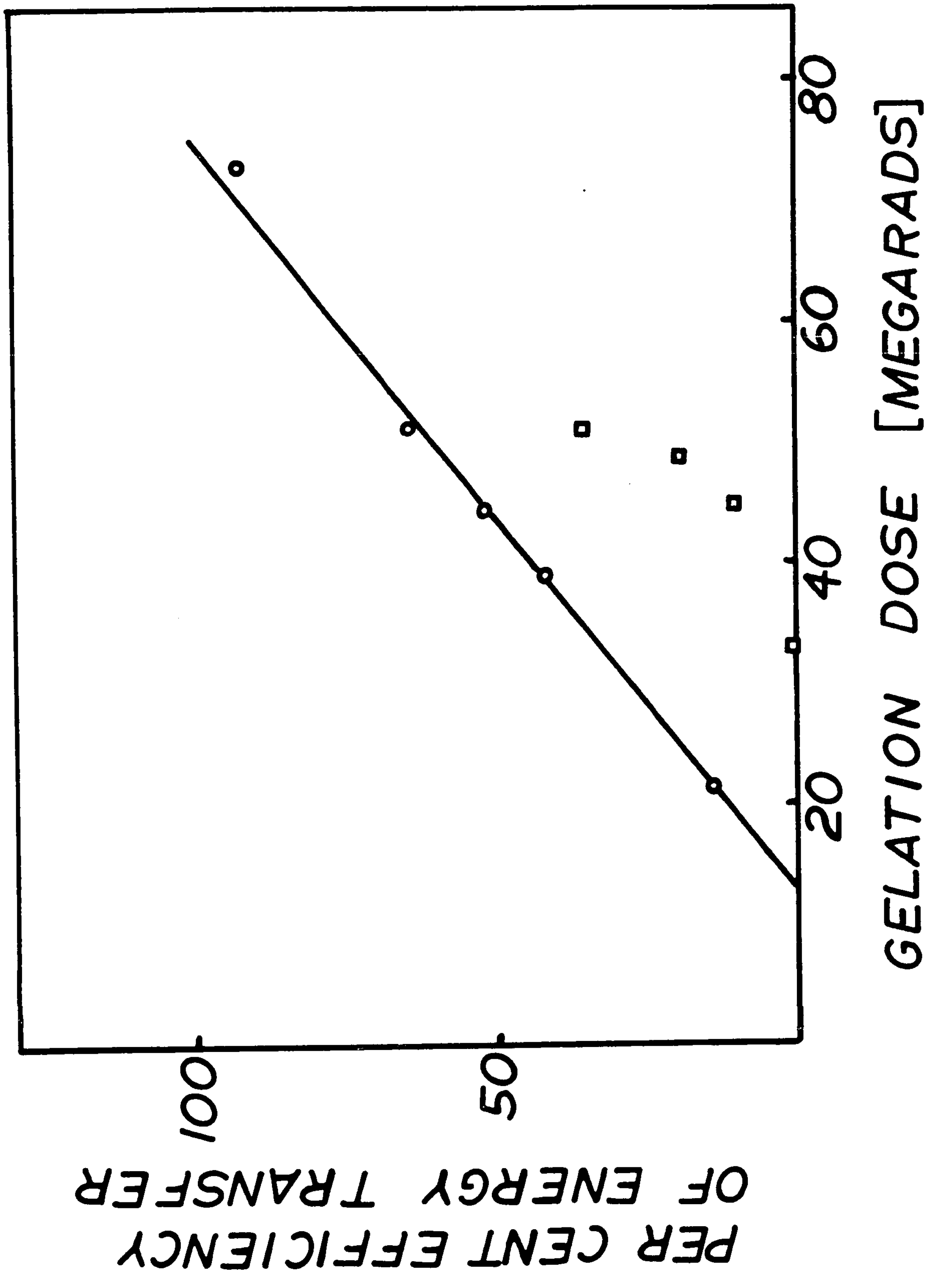

GELATION DOSE [MEGARADS]
90
60
30
0.2
0.4
0.6
WEIGHT % ANTHRACENE IN POLYSTYRENE

FIGURE IV-11

Percent Efficiency of Energy Transfer Versus Gelation Dose For the Corresponding Sample of Anthracene-Polystyrene

Open Circles: Anthracene was added to the monomer before polymerization.

Open Squares: Anthracene was added to the polymer at room temperature.


GELATION DOSE [MEGARADS]
20
40
60
80
PER CENT EFFICIENCY OF ENERGY TRANSFER
50
100

Since the intrinsic viscosity is a measure of the hydrodynamic volume of the molecule being studied, its magnitude is greatly affected by the geometric structure of the molecule and in particular for a given molecular weight, the viscosity is strongly dependent upon the extent of branching in the polymer. It follows that when studying the influence of irradiation on the changes in molecular weight of polymers belonging to the crosslinking type, the viscosity method can be misleading since the increase in molecular weight necessarily proceeds via chain branching. This particular problem was considered by Shultz, Roth, and Rathmann(86) who derived the expected change in viscosity as a function of radiation dose by combining the statistical theory of crosslinking with the theory for branched molecules developed by Zimm and Stockmayer.(87) They expressed their results as a function of the ratio (D/D*) of the actual radiation dose D to the criticial radiation dose D* required for incipient gel formation. The shape of the theoretical curves depends on the magnitude of the exponent a of the viscosity-molecular weight relationship corresponding to the unirradiated polymer.

Now two samples of styrene polymerized at different times but under approximately the same conditions, were irradiated. One sample had an initial intrinsic viscosity of 1.52 whereas the value for the other sample is 1.54. One would expect therefore to have the same gelation dose for both samples. This was not the case. From Figure IV-12 it is obvious that one sample required a dose of only 22.5 megarads whereas the other sample required 33 megarads. For the latter sample it is seen that the viscosity increases much more quickly and to a higher value before gelation sets in. The difference between the two pure samples can only be attributed to a difference in molecular weight distribution resulting in a difference in crosslinking. The data from Figure IV-12 is replotted in Figure IV-13 in the form $(\eta)/(\eta_0)$ versus D/D* where (η) is the intrinsic viscosity of the irradiated polymer, (η_0) is the intrinsic viscosity of the unirradiated polymer, D is the dose of gamma radiation for the polymer and D* is the gelation dose. As can be seen the two curves do not fall on one another, hence their values for a and K are different and the intrinsic viscosity measurements are not sufficient to determine the extent of crosslinking in both samples. At D/D* of 0.8 the difference between the two values of $(\eta)/(\eta_0)$ is 1.485-1.180 = 0.305 which results in about 10 megarads difference between the gelation dose of the two samples.

For the polystyrene-anthracene samples we have plotted the data from Figures IV-7 to IV-9 in Figure IV-14 in a similar fashion. We see that there is no such drastic difference between the curves. The points fall in a span of 1.20 - 1.11 = 0.09 for $(\eta)/(\eta_0)$ at 0.8 for D/D*. The difference is negligible for the 0.048% and 0.26%

FIGURE IV-12

Intrinsic Viscosities of Pure Polystyrene Versus Dose of Gamma Radiation

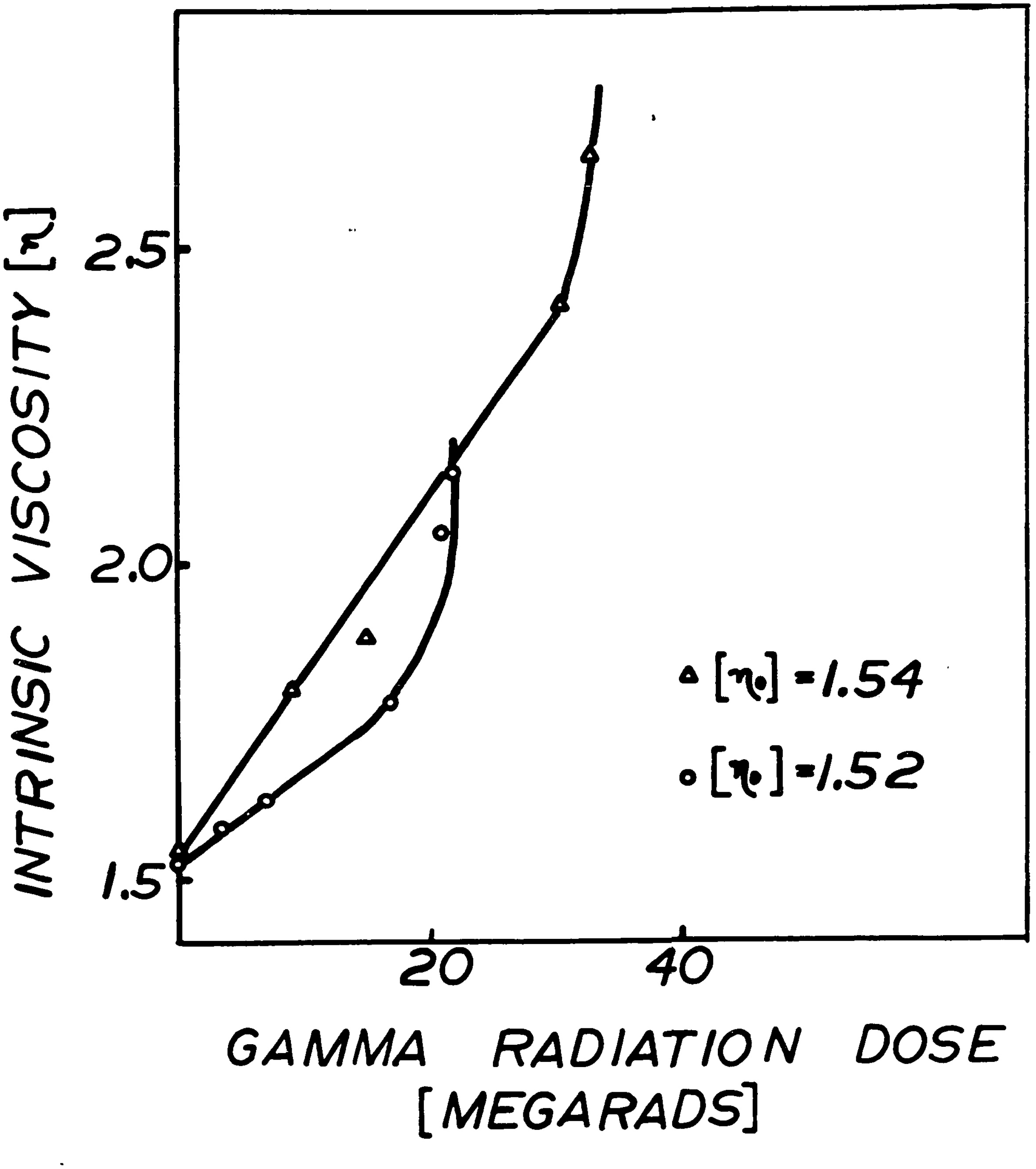
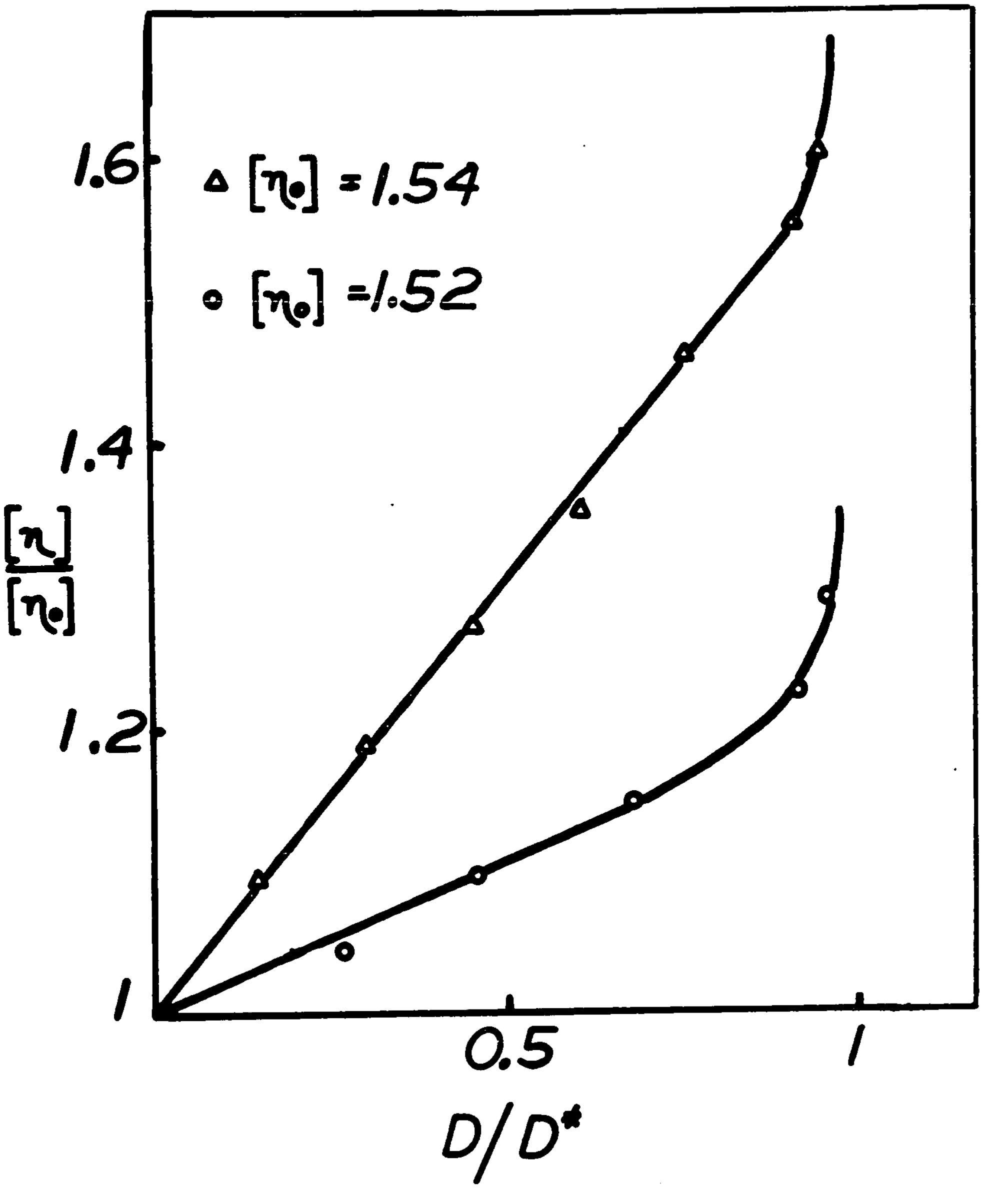

INTRINSIC VISCOSITY [η]
2.5
2.0
1.5
20
40
GAMMA RADIATION DOSE
[MEGARADS]
▲ [η₀] = 1.54
○ [η₀] = 1.52

FIGURE IV-13

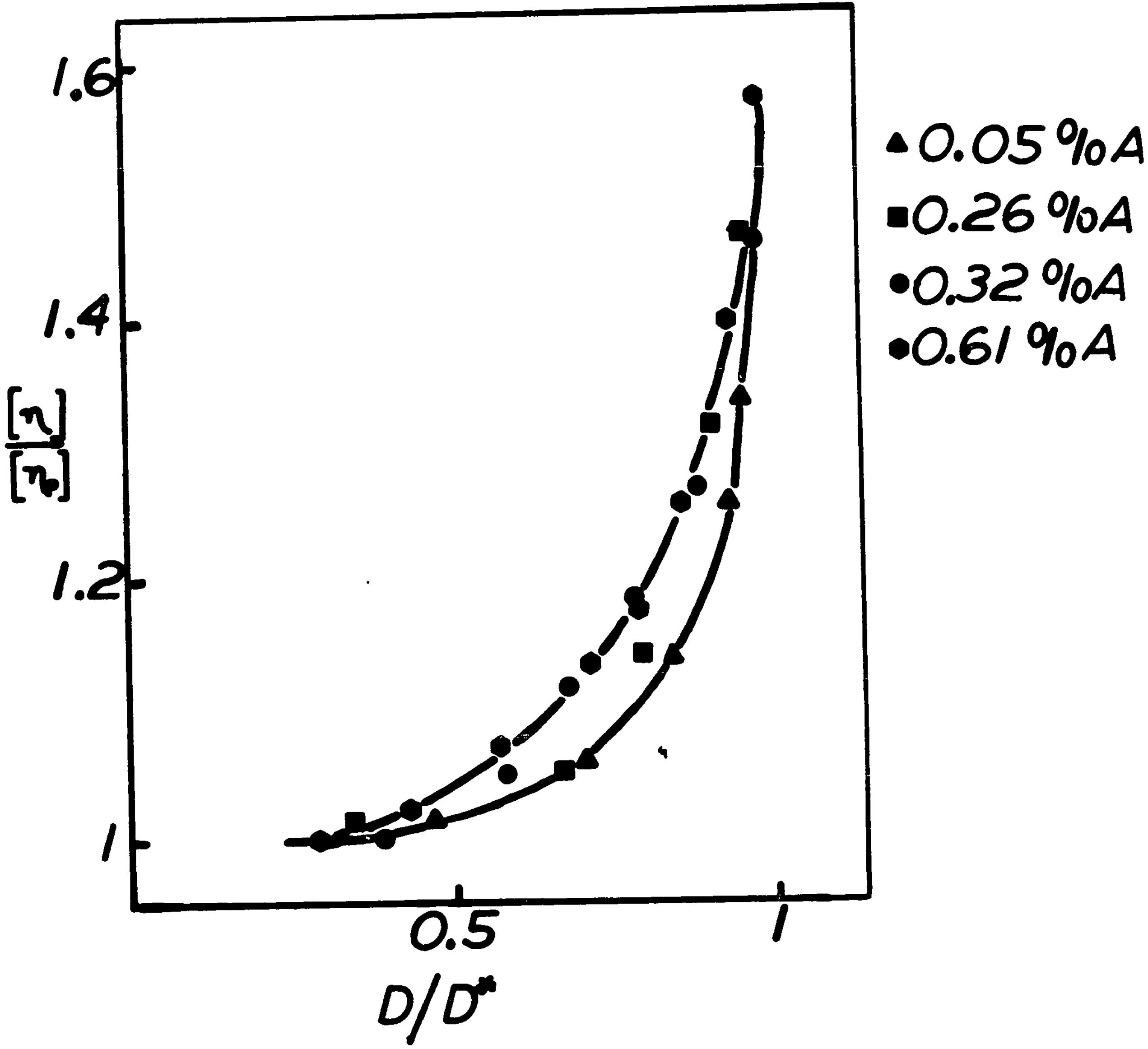
Ratios of Final to Initial Intrinsic Viscosity Versus
Ratios of Gamma Radiation Dose to Gelation Dose For
Pure Polystyrene



PURE POLYSTYRENE

FIGURE IV-14

Ratios of Final to Initial Intrinsic Viscosity Versus Ratios of Dose of Gamma Radiation to Gelation Dose For Polystyrene-Anthracene


1.6
1.4
1.2
1
[η]/[η₀]
0.5
1
D/D*
▲0.05 %A
■0.26 %A
●0.32 %A
⬢0.61 %A

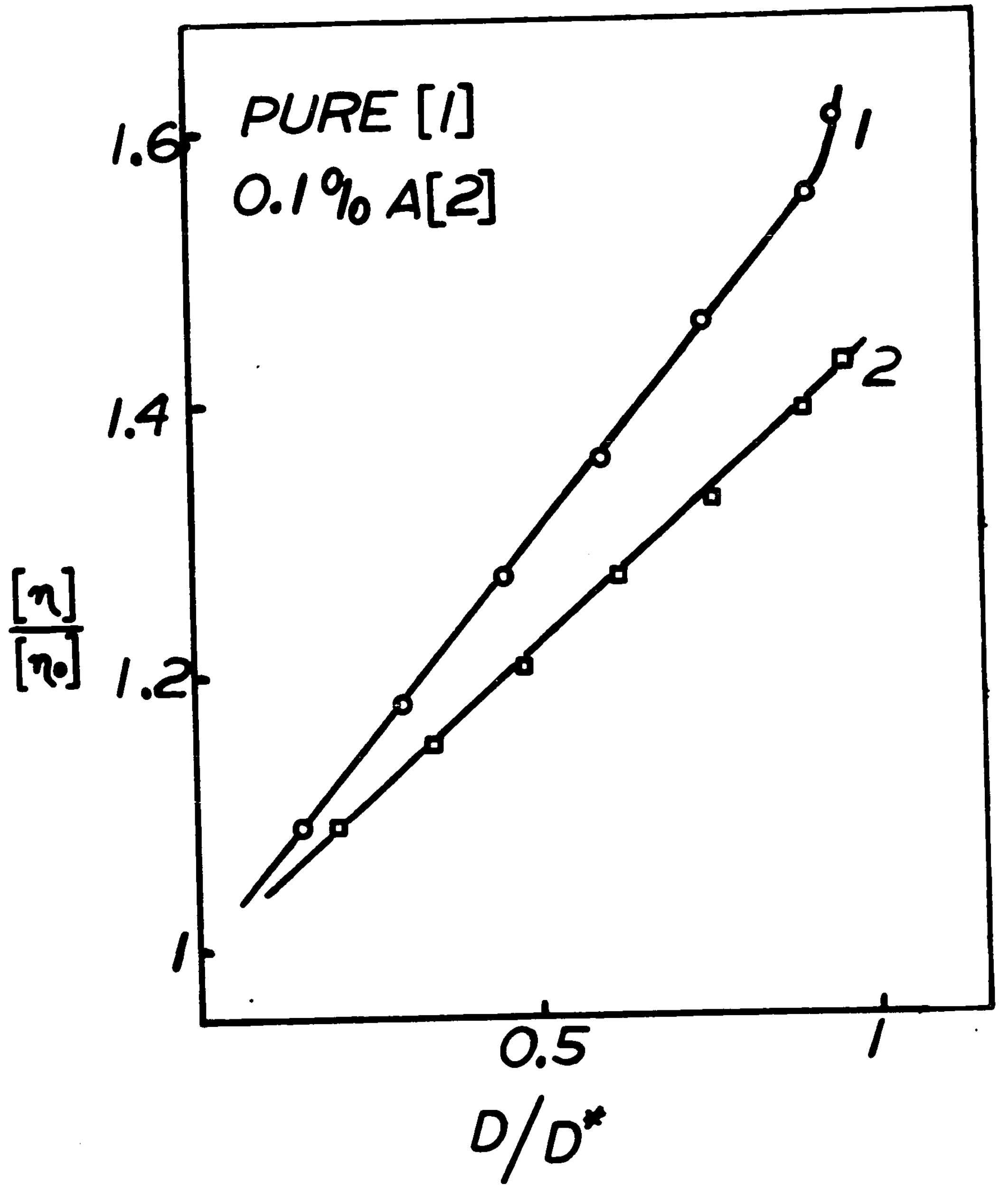
samples and increases somewhat for the 0.32% sample. We can assume therefore that the molecular weight distribution is similar for these samples and the the resulting gelation dose oberved is the result of the presence of anthracene and not to any difference in distribution of molecular weight.

Of course an easy way to get around the problem of molecular weight distribution is to add the anthracene after polymerization to the same batch of polymer in preparing all of the samples. The method however, as we have seen, results in the formation of microcrystals. Nevertheless samples were prepared at room temperature and the gelation dose determined. These values are plotted in Figure IV-11. The inaccuracy in the transfer measurements makes it pointless to draw a line or curve through the points. The transfer efficiency values used in plotting the points were those as estimated from Figure IV-3(solid circles).

In Figure IV-15 a plot of $(\eta)/(\eta_0)$ versus D/D* has also been made. For both curves the same molecular weight distribution polymer has been used. For samples containing more than 0.2% anthracene the curves are very close to that of curve (2). The greatest difference occurs between the pure polymer and the first sample investigated in the series, i.e. 0.14%. At D/D* = 0.8 the difference in $(\eta)/(\eta_0)$ for the two curves is 0.15. The difference is larger than that for anthracene added before polymerization for which the maximim difference is 0.09. The reason for

FIGURE IV-15

Ratios of Final to Initial Intrinsic Viscosity Versus Ratios of Dose of Gamma Radiation to Gelation Dose For Anthracene Added to Polystyrene at Room Temperature and For Pure Polystyrene

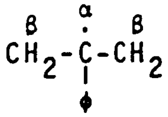

PURE [1]
0.1% A[2]
1
2
1.6
1.4
1.2
1
$\frac{[\eta]}{[\eta_0]}$
0.5
1
D/D*

the higher value in the former system may be that microcrystals of anthracene dispersed throughout the polymer disrupt the usual process of crosslinking. Radicals of anthracene in the microcrystal couple with polystyrene radicals formed in its vicinity. After a period of irradiation, the microcrystal has polymer chains emanating from it, as the spokes from the center of a wheel. The configuration of this crosslinked polymer has been altered from that of pure polystyrene crosslinked under the same conditions.

IV-3.3 Electron Spin Measurements

E.S.R. spectra of the thermally copolymerized solute-monomer samples were measured after gamma irradiation. The samples were ground to course powder on a Wiley Mill. The powder was irradiated in vacuum with gamma rays, and the spectra taken after every three hours of irradiation. Figures IV-16 and IV-17 illustrate some of the spectra obtained.

The e.s.r. spectrum obtained for pure polystyrene corresponds to that obtained by previous workers. The observed triplet structure (1:2:1) has been assigned to

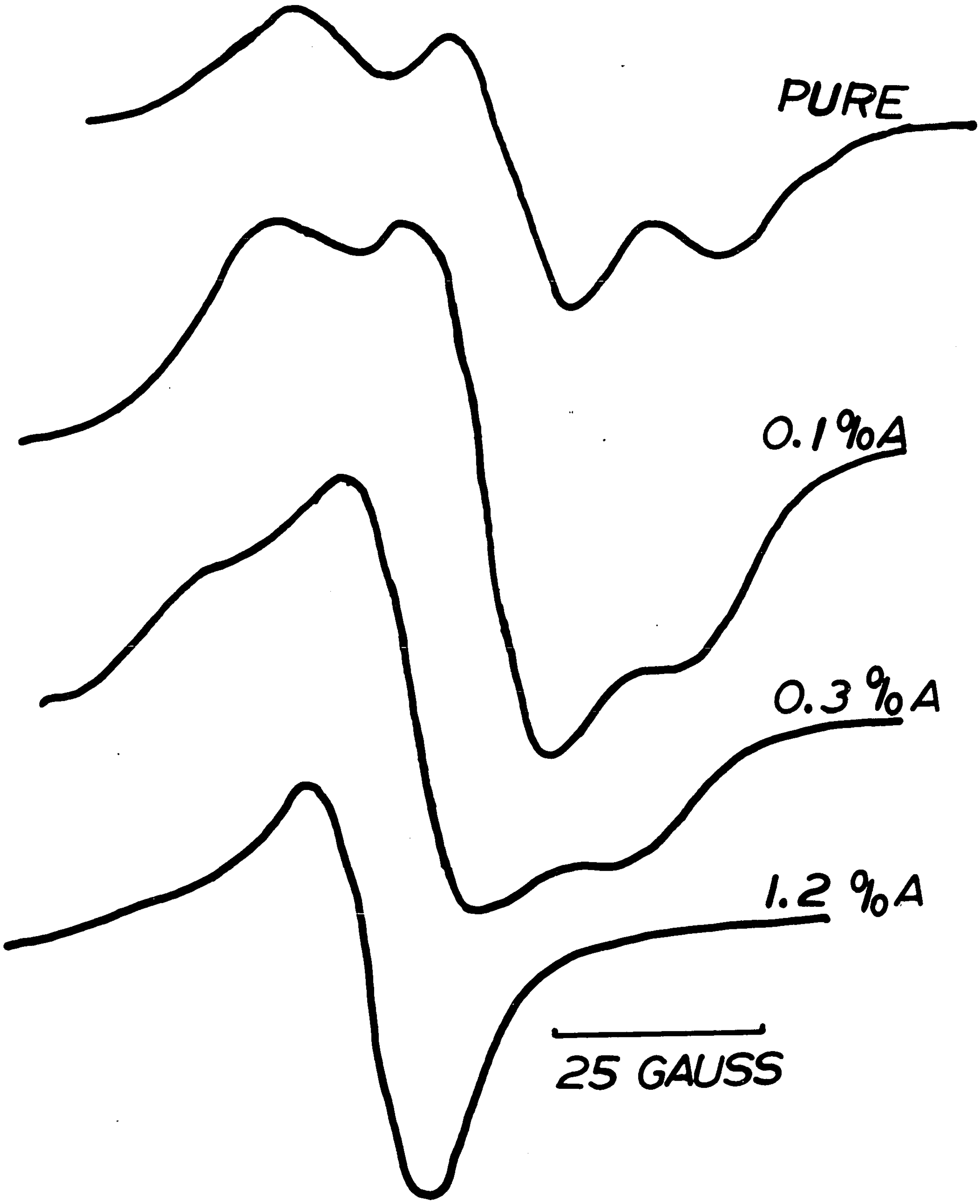


$$\overset{\beta}{\mathrm{CH_2}}-\underset{\phi}{\overset{\overset{\alpha}{\cdot}}{\mathrm{C}}}-\overset{\beta}{\mathrm{CH_2}} \qquad \text{(I)}$$

where hyperfine interaction due to only one of the two sets of β-methylene protons has been observed.(88-9)

FIGURE IV -16

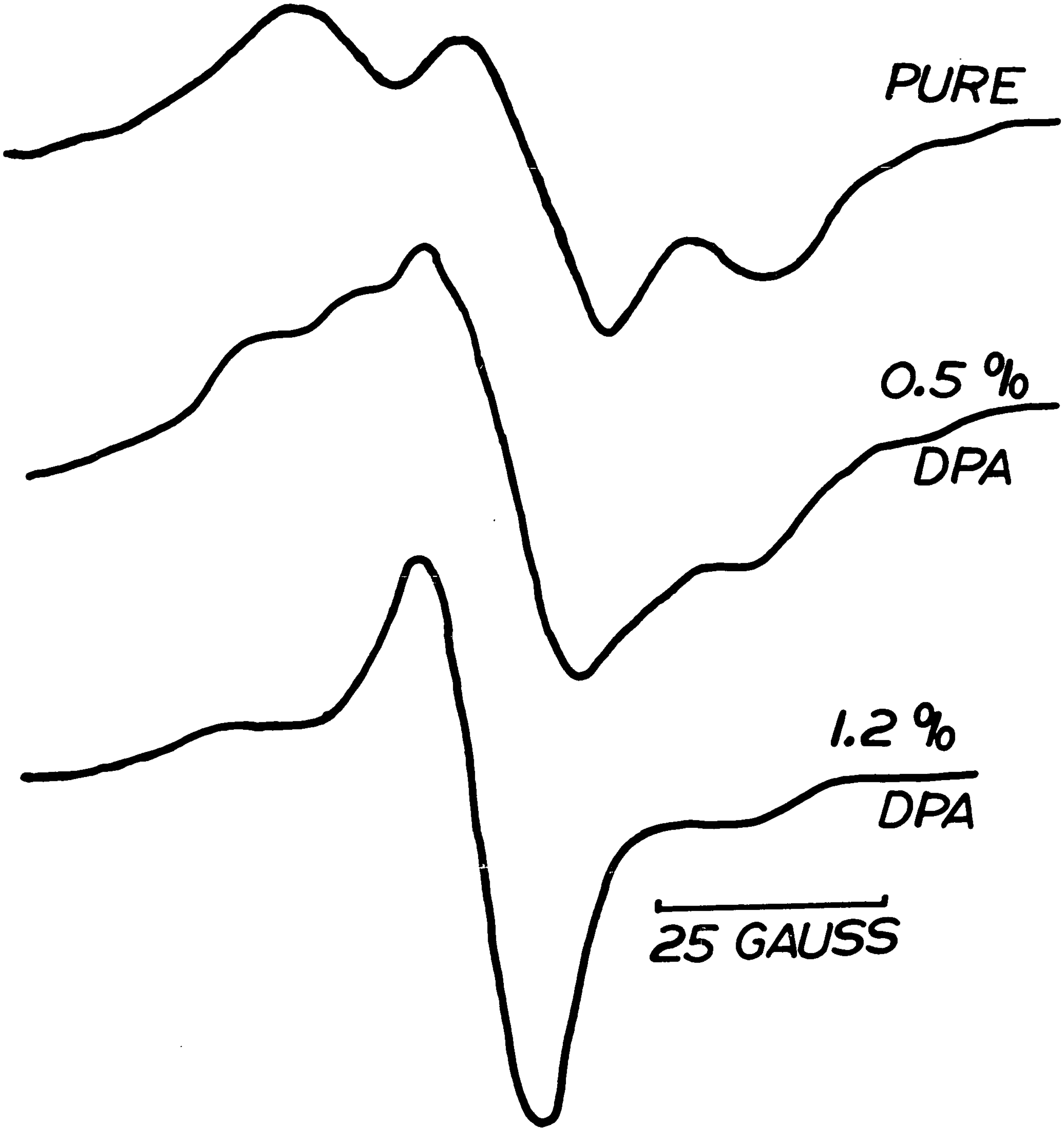
E.S.R. Spectra of Anthracene-Polystyrene Samples



E.S.R. SPECTRA

FIGURE IV-17

E.S.R. Spectra of 9,10-Diphenylanthracene-Polystyrene Samples

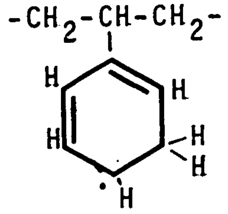


E.S.R. SPECTRA

According to Pravednikov and Shen-Kan(90) this radical is formed as a consequence of tertiary C-H rupture under the influence of high energy radiation. The resulting hydrogen atom can abstract hydrogen from the chain:

$$H\cdot + CH_2-\underset{\phi}{C}H-CH_2 \rightarrow H_2 + CH_2-\underset{\phi}{\dot{C}}-CH_2 \qquad (IV-9)$$

or add to the benzene ring to form the cyclohexadienyl-type radical (II)



(II)

Photolysis of concentrated solutions of polystyrene also results in radical (I) but under these conditions quite different spectra were observed and were interpreted in terms of different geometries of the radicals.(89)

The radicals present in the polymeric glasses after irradiation are stable at room temperature for months. At 30°C the number of radicals is reduced to 89% after one month according to Wilske and Heusinger.(46) After storage for one month at 11°C no decrease of radical concentration could be detected.

From Figures IV-16 and IV-17 one can see that as the amount of solute is increased the shape of the spectra changes. The curves are presented as the first derivative of the absorption curve. By taking the second moment of these spectra and comparing it with that obtained from a standard sample of DPPH, one can obtain the number of radicals. The number of radicals were determined for 3,6 ... etc. hours of irradiation. The data are given in Tables IV-6 and IV-7 and illustrated for several samples in Figure IV-18. The slope of the line drawn from the origin to the point was determined and the average slope determined for the set of points for each sample. This averaged out errors incurred in the packing of the samples in the e.s.r. tubes and also showed that the increase in radicals is linear with dose of gamma radiation.

The average slope determined for each sample was then taken as the value for spin generation per hour. These values for anthracene-polystyrene are plotted in Figure IV-19 and for 9,10-diphenylanthracene-polystyrene in Figure IV-20.

The G value obtained for pure polystyrene is 0.14. This value agrees closely with the value of Hurrah(64) of 0.102 and of Wilske and Heusinger(46) who obtained the value 0.2. As the percent of anthracene increases the total number of radicals increases and then decreases, falling below the value of pure polystyrene at high enough solute concentrations. We have seen that the presence of anthracene decreases the extent of crosslinking in polystyrene both with u.v. light and gamma radiation. The increase in radicals therefore, cannot be due to an increase in polystyrene radicals as this would have resulted in a

TABLE IV-6

TOTAL SPINS FOR POLYSTYRENE-ANTHRACENE AFTER GAMMA IRRADIATION*

%Solute	3 hours	6 hours	9 hours	12 hours	Average Value Spins/hour	
0	7.4		25.6	35.3	2.76	
0.05	7.4	16.1	25.6		2.66	
0.10	16.1	27.1			5.07	
0.15	11.3	32.5	42.4	45.3	4.42	
0.16						5.05
0.17	16.5	39.6			5.68	
0.21	16.5		46.2		5.31	
0.32	16.4	21.8	36.6		4.39	
0.34	16.8	26.8	33.0		4.57	
0.60	10.0	17.8	22.8		2.94	
0.80	6.8	12.6	25.2		2.44	
0.97	10.2	13.0	17.6		2.50	
1.10	7.8	7.0	12.5		1.71	

* The values for the total spins have been multiplied by 10^{-16}.

FIGURE IV-18

Total Spins For Polymer-Solute Samples After Gamma Irradiation

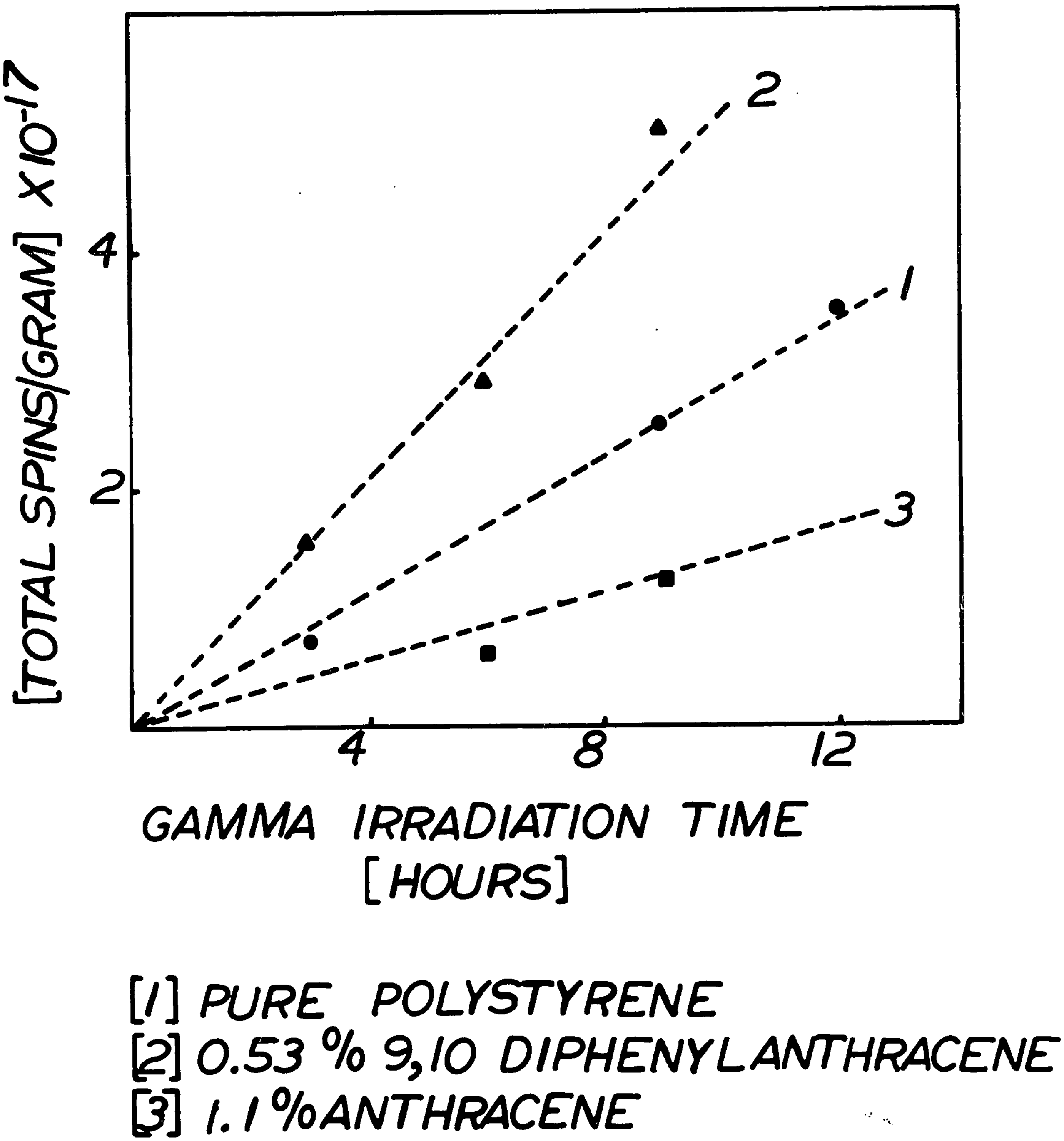

[TOTAL SPINS/GRAM] X10^{-17}
4
2
4
8
12
GAMMA IRRADIATION TIME
[HOURS]
2
1
3
[1] PURE POLYSTYRENE
[2] 0.53 % 9,10 DIPHENYLANTHRACENE
[3] 1.1 % ANTHRACENE

TABLE IV-7

TOTAL SPINS FOR 9,10-DIPHENYLANTHRACENE-POLYSTYRENE AFTER GAMMA RADIATION*

% Solute	3 hours	6 hours	9 hours	Average Value Spins/hour
0.2	9.0	25.0	46.2	4.79
0.53	15.5	29.1	50.6	5.18
0.75	17.0	24.5	34.6	5.15
1.23	11.9	12.4	16.2	2.02

* The values for the total spins have been multiplied by 10^{-16}

faster rate of crosslinking. We attribute the excess radicals measured to be due to that of the solute resulting from the transfer of energy from polymer to solute. In other words, at very low concentrations of solute, the energy transfer efficiency is not high so that you still measure a considerable number of polystyrene radicals. However some solute radicals have been generated as a result of energy transfer so that the summation of the number of polystyrene radicals plus solute radicals yields a value in excess of that for pure polystyrene. At higher concentrations of solute, the efficiency of energy transfer is high so that there are now few polystyrene radicals but many solute radicals. The sum of these two radicals now fall below that of pure polystyrene. This supposition is supported by the change in the shape of

FIGURE IV-19

Total Spins/Gram/Hour Versus Weight Percent of Anthracene in Polystyrene

Dose rate was 0.32 megarads/hour.

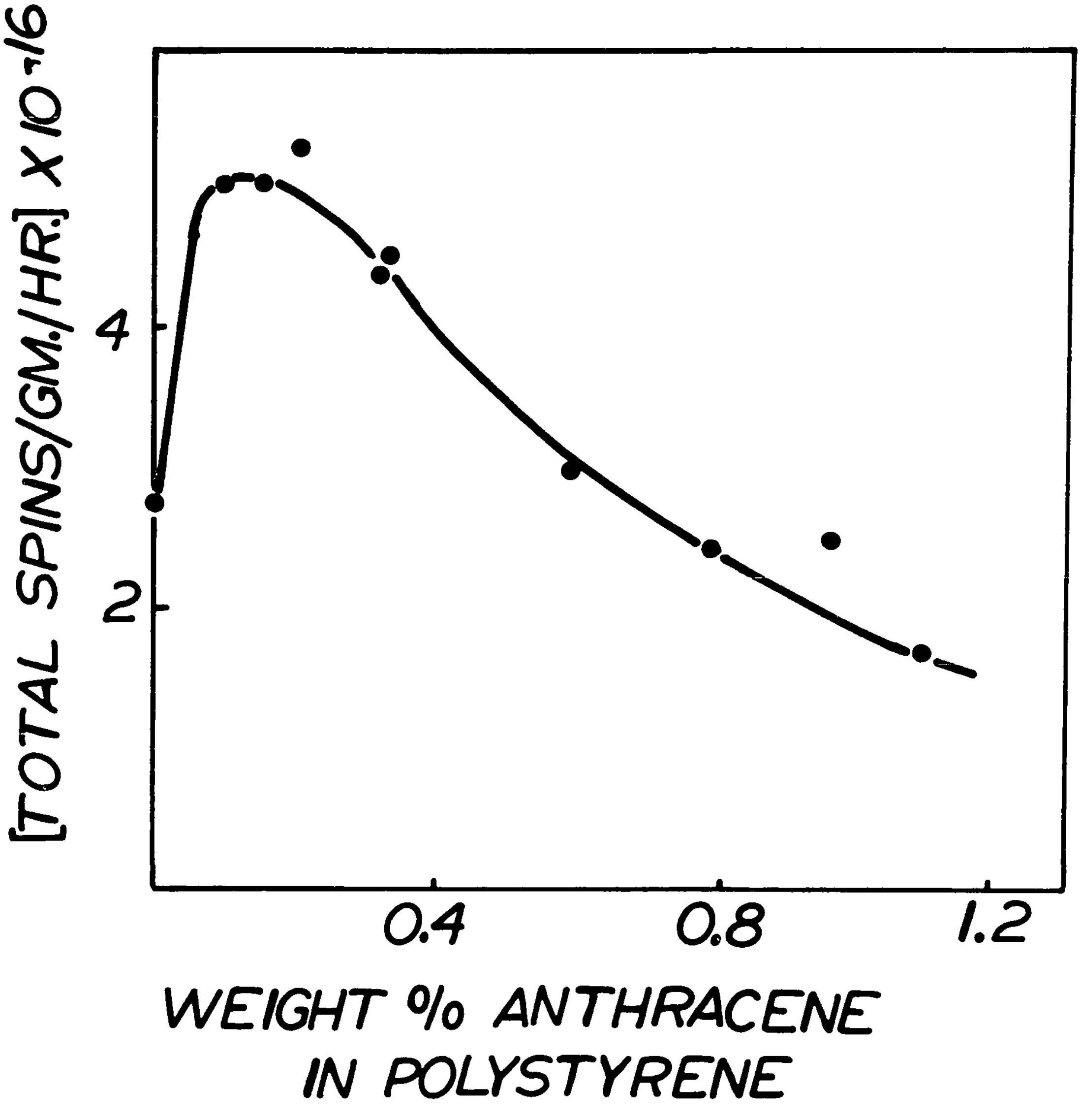
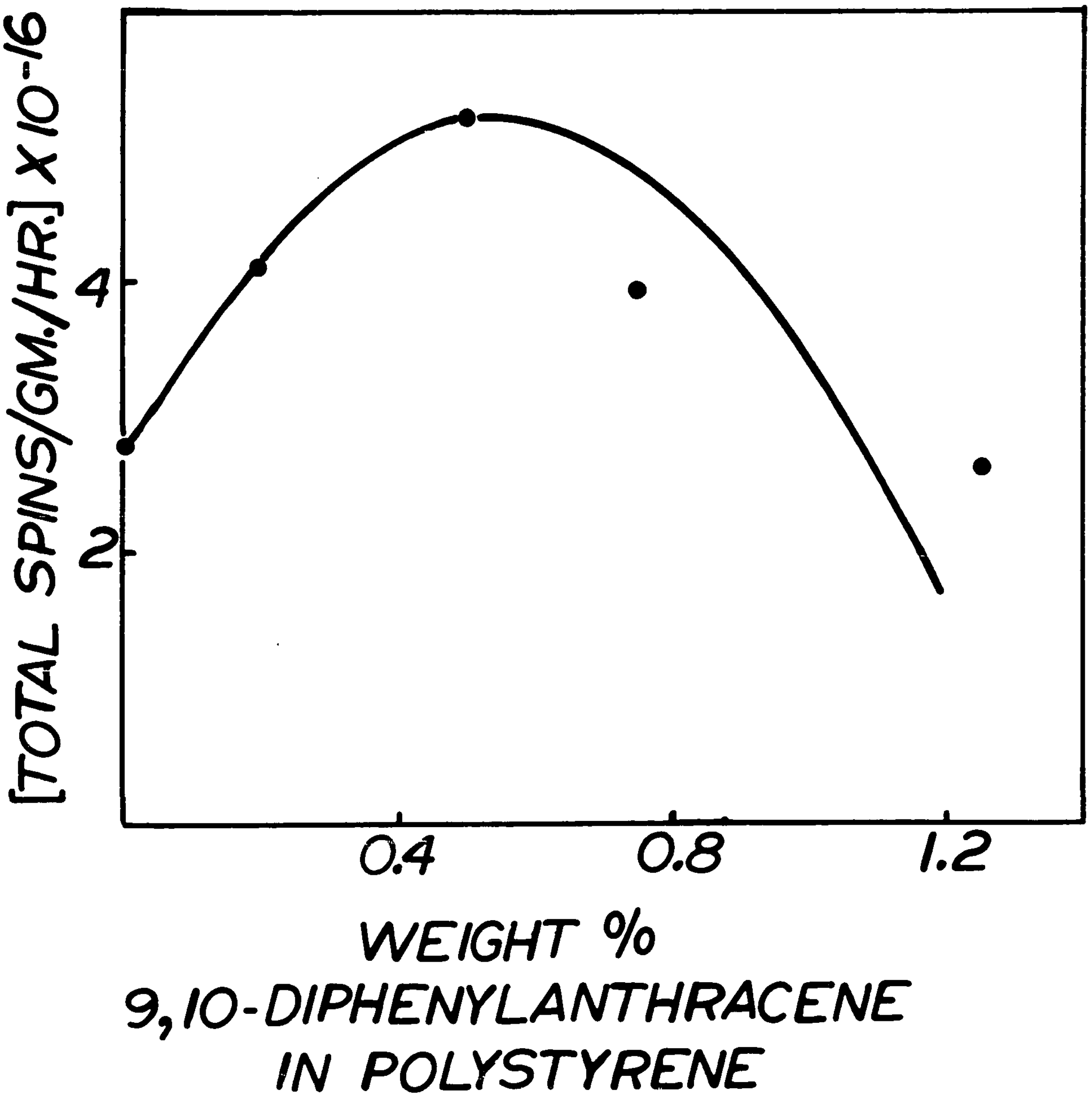

[TOTAL SPINS/GM./HR.] X 10⁻¹⁶
4
2
0.4
0.8
1.2
WEIGHT % ANTHRACENE IN POLYSTYRENE

FIGURE IV-20

Total Spins/Gram/Hour Versus Weight Percent of 9,10-Diphenyl-Anthracene in Polystyrene

Dose rate was 0.32 megarads/hour.


[TOTAL SPINS/GM./HR.] X 10^-16
4
2
0.4
0.8
1.2
WEIGHT %
9,10-DIPHENYLANTHRACENE
IN POLYSTYRENE

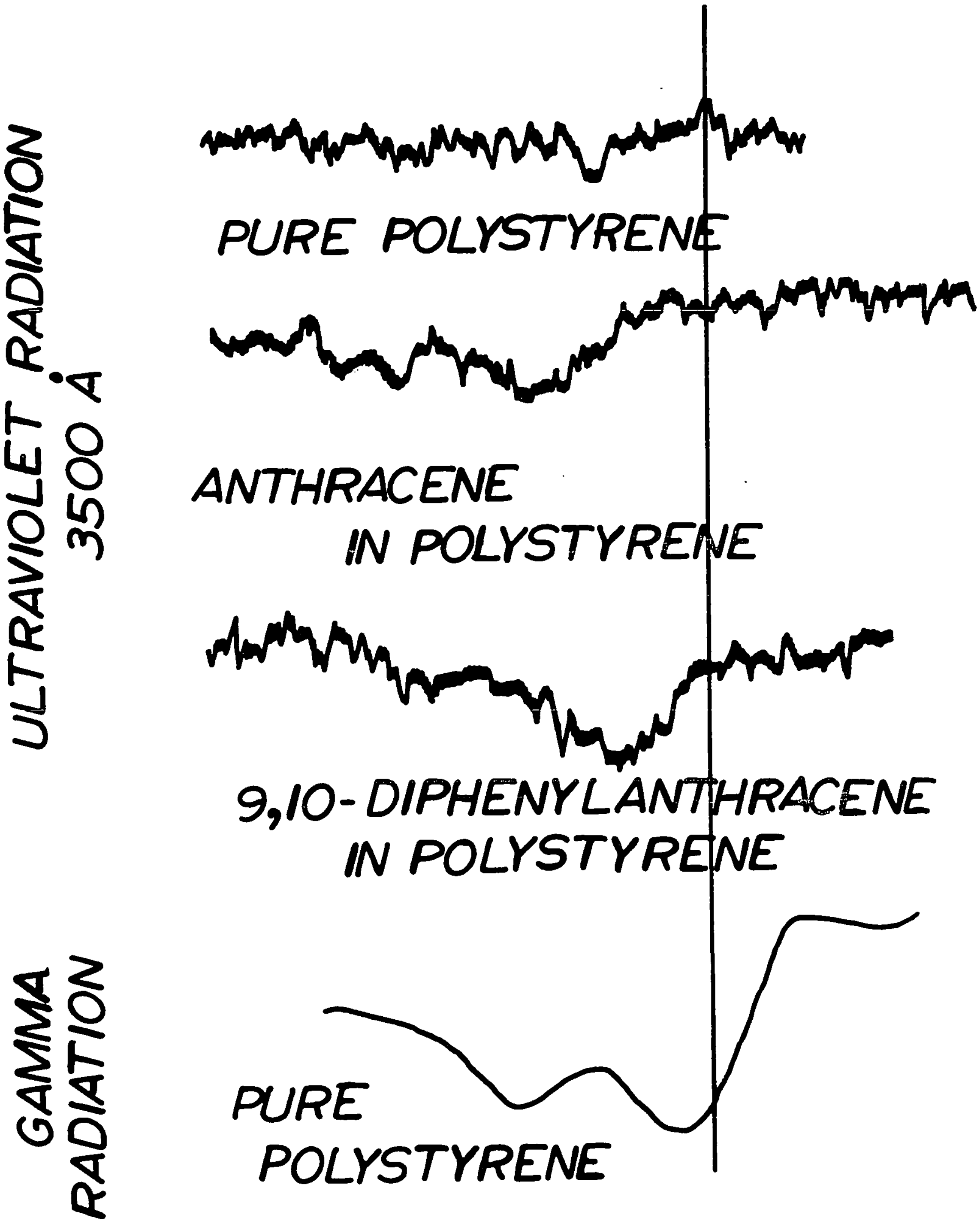
of the spectra as seen in Figures IV-16 and IV-17. At high solute concentrations we are in effect seeing only the solute radical.

To show that the solute radicals in a polymer matrix absorb at the same position in the e.s.r. spectrum as for polystyrene, transparent samples of polystyrene were prepared containing a high concentration of anthracene or 9,10-diphenylanthracene. They were irradiated with ultraviolet light at 3500 Å, a wavelength absorbed only by the solute, for 44.5 hours. The resulting spectra are shown in Figure IV-21. No signal is observed for pure polystyrene which was prepared and irradiated at the same time as the other samples. In the solute-containing samples weak signals are observed in the region for polystyrene absorption.

Since we know that for pure polystyrene the spin generation is 2.8×10^{16} spins/gm./hr. at a dose rate of 0.32 megarads/hour, we can calculate the expected value of polystyrene radicals that should be oberserved in the presence of solute if the systems follow the measured efficiency of energy transfer (Figures III-7 and III-8). These values are listed in column (1) of Tables IV-8 and IV-9. The difference between the observed values and the calculated values gives the number of anthracene or 9,10-diphenylanthracene radicals. These values are listed in column (2) of Tables IV-8 and IV-9. The values for the anthracene spins are plotted in Figure IV-22. It is seen that the

FIGURE IV-21

E.S.R. Spectra of Anthracene and 9,10-Diphenylanthracene Radicals in Polystyrene


ULTRAVIOLET RADIATION
3500 Å
PURE POLYSTYRENE
ANTHRACENE
IN POLYSTYRENE
9,10-DIPHENYLANTHRACENE
IN POLYSTYRENE
GAMMA
RADIATION
PURE
POLYSTYRENE

E.S.R. SPECTRA

TABLE IV-8

QUANTUM YIELD FOR LOSS OF ANTHRACENE RADICALS IN POLYSTYRENE WITH GAMMA RADIATION

% Anthracene	(1) Calculated Polystyrene Spins $\times 10^{-16}$	(2) Anthracene Spins $\times 10^{-16}$	(3) Initial Solute Spins $\times 10^{-16}$	(4) Loss of Anthracene Spins $\times 10^{-16}$	(5) Quanta Absorbed $\times 10^{-18}$	(6) Quantum Yield $\times 10^{2}$
0.025	2.46	1.29	1.29			
0.05	2.21	2.39	2.39			
0.075	2.10	2.90	2.90			
0.10	1.90	3.20	3.20			
0.15	1.68	3.42	3.42			
0.20	1.43	3.57	4.8	1.23	2.88	0.43
0.30	0.99	3.61	6.3	2.69	3.84	0.70
0.40	0.69	3.26	7.9	4.64	4.50	1.03
0.50	0.44	3.01	9.4	6.39	5.04	1.27
0.60	0.22	2.88	11.0	8.12	5.52	1.47
0.70	0.11	2.59	12.5	9.91	5.76	1.72
0.80	0	2.40	14.1	11.7	6.0	1.95
0.90	0	2.15	15.6	13.5	6.0	2.25
1.0	0	1.85	17.1	15.3	6.0	2.54

TABLE IV-9

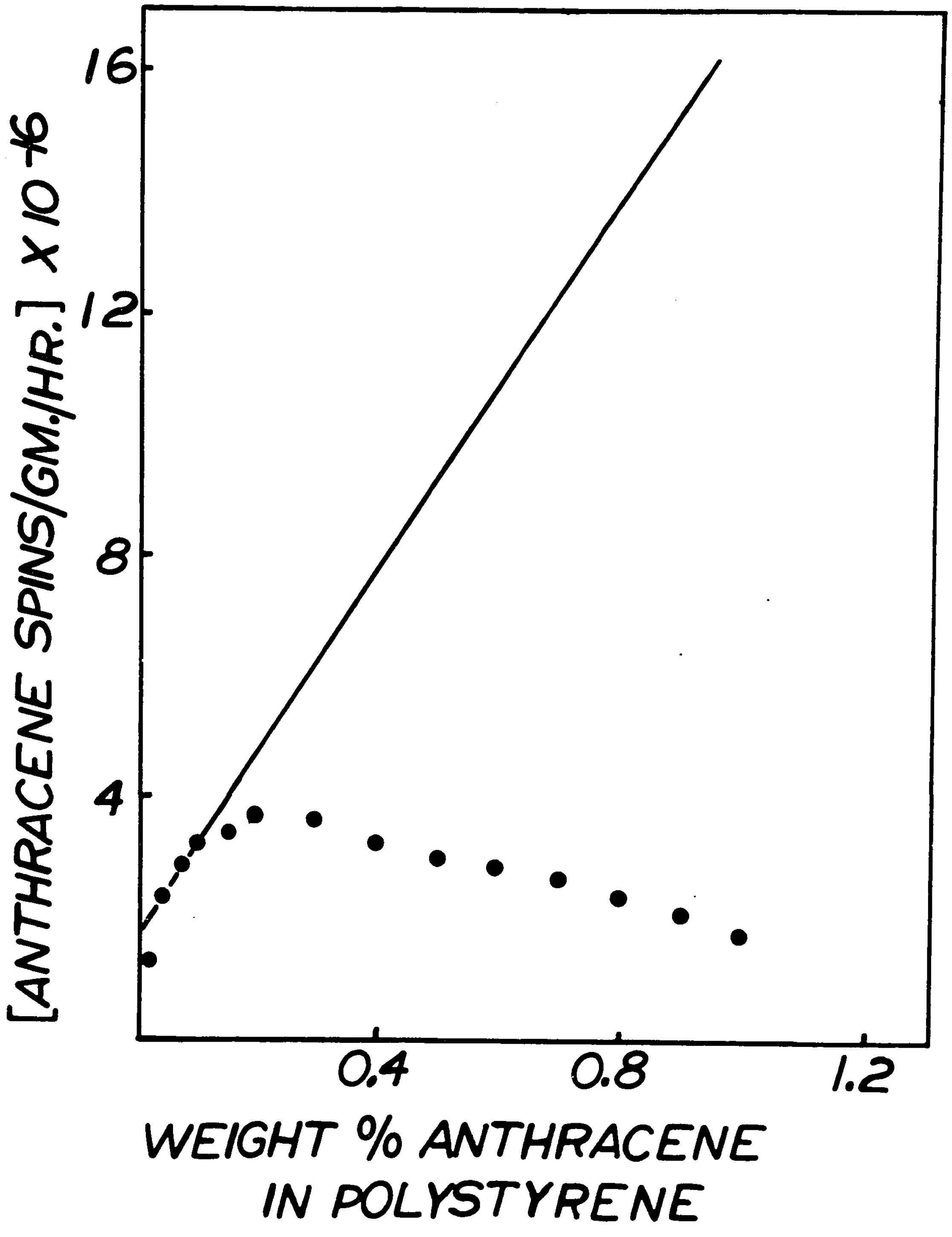
QUANTUM YIELD FOR LOSS OF 9,10-DIPHENYLANTHRACENE RADICALS IN POLYSTYRENE WITH GAMMA RADIATION

% 9,10 Diphenyl-Anthracene	(1) Calculated Polystyrene Spins $\times 10^{-16}$	(2) 9,10-Diphenyl-Anthracene Spins $\times 10^{-16}$	(3) Initial Solute Spins $\times 10^{-16}$	(4) Loss of Solute Spins $\times 10^{-16}$	(5) Quanta Absorbed $\times 10^{-18}$	(6) Quantum Yield $\times 10^{2}$
0.1	1.68	1.82				
0.2	1.30	3.00				
0.3	1.10	3.65	3.9	0.25	3.60	0.07
0.4	0.99	4.11	5.0	0.89	3.84	0.23
0.5	0.94	4.36	6.0	1.64	3.96	0.41
0.6	0.88	4.27	7.0	2.73	4.08	0.67
0.7	0.80	4.15	8.1	3.95	4.26	0.93
0.8	0.77	3.83	9.1	5.27	4.32	1.21
0.9	0.72	3.38	10.1	6.72	4.44	1.51
1.0	0.69	2.71	11.2	8.49	4.50	1.89
1.1	0.66	1.99	12.2	10.2	4.56	2.24

FIGURE IV-22

Anthracene Spins/Gram/Hour for Gamma Radiation Versus Weight Percent of Anthracene in Polystyrene

Solid Circles: Values Derived From Experimental Data


16
12
8
4
0.4
0.8
1.2
[ANTHRACENE SPINS/GM./HR.] X 10^-16
WEIGHT % ANTHRACENE IN POLYSTYRENE

concentration of anthracene radicals reaches a maximum of about 3.6x10^{16} spins/gram/hour and then decreases.

Let us assume that at low concentrations of solute, loss of anthracene radicals is negligible and therefore we can draw a straight line through the first few points of Figure IV-22. This line represents the value of anthracene radicals that would have been recorded had loss of anthracene radicals not taken place. These values are tabulated in column (3) of Tables IV-8 and IV-9. The difference in value between these extrapolated values and those calculated from the photophysical measurements [column (2)] give the loss in anthracene spins. These are listed in column (4) of Table IV-8 for anthracene and in Table IV-9 for 9,10-diphenylanthracene.

Each photon of 3660 Å has an energy of 3.34 e.v. The dose rate used in irradiating the samples with gamma radiation was 0.321 megarads/hour. Since one rad = 62x10^{12} e.v./gram, then 0.321 megarads is equivalent to 6x10^{18} u.v. photons at 3660 Å. The quantum yield in photochemistry in this case would be the number of anthracene radicals lost divided by the number of photons absorbed. The quantum yields calculated are tabulated in column (6) of Tables IV-8 and IV-9. The values are also plotted in Figure IV-23 together with the values of Cowell and Pitts.(91) The slopes of the lines are about the same but the quantum yield values for our system are higher by a factor of ten.

FIGURE IV-23

Quantum Yields for Loss of Anthracene and 9,10-Diphenyl-Anthracene in Polystyrene With Gamma Radiation

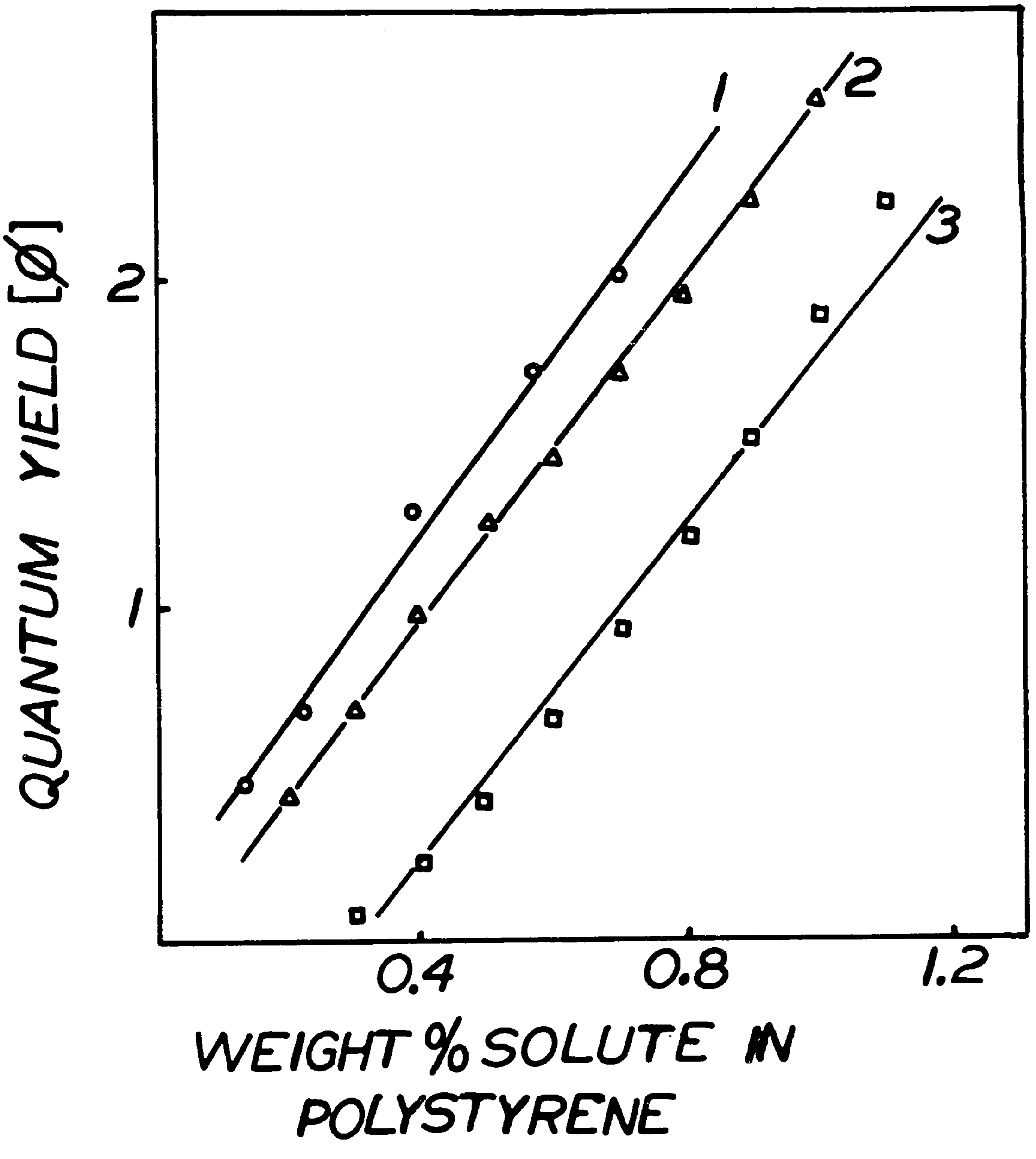
(1) Ultraviolet Radiation Data is taken from Ref. (91)

(2) Gamma Radiation --- Anthracene

(3) Gamma Radiation --- 9,10-Diphenylanthracene

$[\phi] = \phi_1 \times 10^3$ [U.V.]

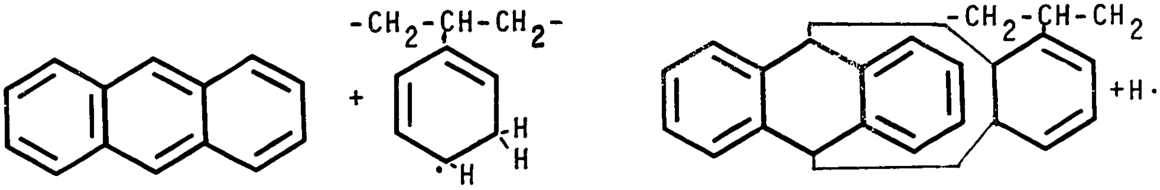
$[\phi] = \phi_{2,3} \times 10^2$ [GAMMA]



Cowell and Pitts(91) studied the diminution of anthracene concentration in polystyrene films with irradiation of light at 3660 Å, a wavelength not absorbed by the polymer. Thus any diminution of anthracene as evidenced by the decrease in the absorption band from 3000-3800 Å must be due to some reaction process involving only the anthracene molecules. The authors have stipulated that dimerization is the process that causes depletion of the solute concentration although they did not try to isolate the compound after ultraviolet irradiation of the polymer film. Now Cowell and Pitts prepared their samples at room temperature from a benzene solution and as we have seen this results in formation of microcrystals so that the probability of dimerization is high in these samples because of the proximity of the anthracene molecules.

In our samples however the anthracene is well dispersed since it was prepared by thermal copolyerization of the solute and monomer. Despite this our quantum yield for the loss of anthracene is about 10 times higher than that of Cowell and Pitts and indicates that loss of anthracene in our system is not through a dimerization process. (For the sake of argument we are assuming that every anthracene radical that is lost does not reappear as an anthracene molecule.) We propose the following mechanism to explain this result.

Since polystyrene is absorbing the gamma radiation excited polystyrene molecules as well as excited anthracene molecules, the latter by energy transfer, are produced. The polystyrene molecule forms a short-lived radical by the addition of hydrogen to its benzene ring forming a cyclohexadienyl-type radical (II). [See page 145] The radical is able to undergo a Diels-Alder-type of addition to anthracene in the following manner:



The reason for the maximum at 0.2% anthracene in Figure IV-22 can now be explained. At low concentrations of anthracene there is little energy transferred from polystyrene so that the number of excited anthracene molecules occurring close to a radical of type II is small. The excited anthracene molecules then form radicals at a constant quantum yield. This accounts for the straight line portion of the graph from 0 to 0.2% anthracene. Above 0.2% anthracene, the transfer efficiency is greater than 50% so that the number of excited anthracene molecules is large. The quantum yield for radical formation remains the same. However the probability of an excited anthracene molecule occurring near a cyclohexadiene radical is large. It appears that the Diels-Alder addition between these two species is spontaneous, occurring before the anthracene molecule can form a radical. Hence we see a decrease in radical formation of anthracene.

The fact that Cowell and Pitts(91) obtained a quantum yield of anthracene loss that is less than our value can also be explained. The loss of anthracene depends not only on the number of excited anthracene molecules but also on the number of cyclohexadienyl radicals. Because in their experiment, only the anthracene is absorbing the radiation, the hydrogen radical needed for addition to the benzene ring of polystyrene can only be derived from anthracene. Now the $G(H_2)$ for pure anthracene is 0.012, about half the value for pure polystyrene.(73) Assuming the same ratio would occur for ultraviolet radiation, we see that the anthracene produces less hydrogen. It follows that fewer cyclohexadienyl radicals will be formed and hence the quantum yield for loss of anthracene is less. If they had irradiated their samples with 2700 Å light, exciting the polymer, they would probably have seen higher values, comparable to the ones we have obtained by gamma radiation.

In short, the best conditions for high loss of anthracene is a large concentration of cyclohexadienyl radicals as well as a large number of excited anthracene molecules.

Probably a similar process operates for 9,10-diphenylanthracene. Since there is a dearth of data as to how this compound could react, it is pointless to speculate upon a mechanism.

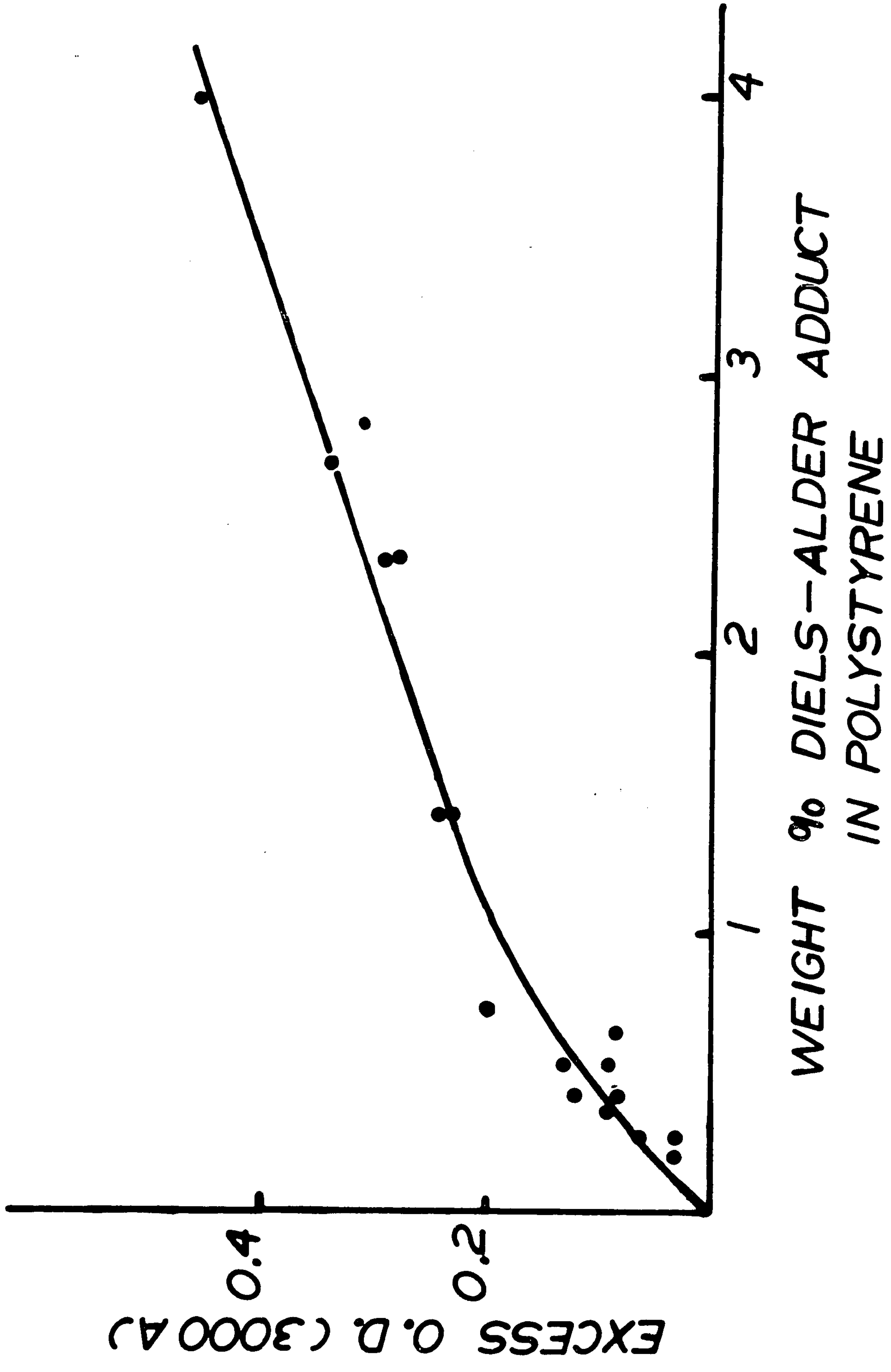
IV-4 CHANGES IN THE ULTRAVIOLET SPECTRA FOR ANTHRACENE-POLYSTYRENE WITH ULTRAVIOLET IRRADIATION

When polystyrene decomposes in vacuum upon absorption of ultraviolet light, there is a general increase in the optical density of the polymer. This is particularly noticeable from 2900-3100 Å in films 0.025 mm. thick. However when polystyrene containing some Diels-Alder adduct as well as anthracene was irradiated with u.v. light (2700 Å), it was noted that the film was much more yellow in appearance than the pure polymer used for comparison. The difference in optical densities at 3000 Å is quite large and is plotted in Figure IV-24. The increase in optical density at 3000 Å is attributed to the Diels-Alder adduct between styrene and anthracene for the following reasons:

1) Films of polystyrene to which anthracene has been added after polymerization show the same increase in optical denisty as for the pure polymer provided the reaction is not carried to the point where more than 30% of the initial amount of anthracene has decomposed.
2) Decomposition of anthracene in polystyrene film with ultraviolet light of 3660 Å (to which the polymer is essentially transparent) did not show any increase in optical density at 3000 Å. Decomposition of anthracene resulted only in a decrease in the long wavelength band absorption (3100-4000 Å)

FIGURE IV-24

Excess Optical Density Over That of Pure Polystyrene For Ultraviolet Irradiation of Polystyrene Films Containing Diels-Alder Adduct Plus Anthracene


WEIGHT % DIELS-ALDER ADDUCT
IN POLYSTYRENE
1
2
3
4
EXCESS O.D. (3000 A)
0.2
0.4

3) U.V. absorption spectra of polymer films containing anthracene and Diels-Alder adduct and irradiated by gamma rays do not show any excess increase in optical density at 3000 Å when compared to the increase in pure polystyrene. This means the Diels-Alder adduct must be selectively excited as with ultraviolet light in order to have its effect.

4) The purified Diels-Alder adduct was added to pure polystyrene and an increase in $O.D._{3000\ \text{Å}}$ was seen after ultraviolet radiation. This increase was larger than that for the pure polymer but not as large as for the thermally copolymerized samples of styrene-anthracene.

5) A similar effect as in (4) was observed with only dianthracene present in the polymer matrix. This explains the excess increase in $O.D._{3000\ \text{Å}}$ when more than 30% of the initial amount of anthracene added to the polymer at room temperature has decomposed. The dianthracene does however also decompose into anthracene so that with time some sort of equilibrium is set up:

$$2\ \text{anthracenes} \rightleftarrows \text{dianthracene}$$

The Diels-Alder adduct when present alone in the polymer was found experimentally to offer no radiation protection to the polymer. The dianthracene does however because of its decomposition into anthracene whereby some protection begins to occur via energy transfer.

6) The polymer films that were prepared from once-precipitated

thermally copolyermized samples of styrene-anthracene apparently still had an appreciable quantity of the Diels-Alder adduct present, especially in the higher concentration samples. Thus these samples of pure polystyrene (pure in the sense that they had no anthracene as dectected by u.v. spectroscopy) showed an unusually large $O.D._{3000\ \mathring{A}}$ after ultraviolet irradiation, but equal to that in the samples which had not been precipitated.

Thus the increase in optical density in excess to that of the pure polymer, is due to the decomposition of the Diels-Alder adduct in a manner that is not known at the present time.

IV-5 SUMMARY AND CONCLUSIONS

Crosslinking and e.s.r. data have shown that energy transfer is an efficient method of protection for polystyrene in the ultraviolet region. Wilske and Heusinger(46) found that although pyrene decreases the radical concentration, it does not decrease crosslinking. Our results show that crosslinking does decrease, at least for anthracene, with increasing efficiency of energy transfer whether by ultraviolet or gamma radiation. The method works well for gamma radiation but not as efficiently as for the ultraviolet as can be seen from the fact that the hydrogen gas yield is is not altered by the presence of anthracene solutes in the polymer matrix. This is because gamma radiation causes a high local concentration of the active species (that is, free radicals) in a spur so that recombination reactions are highly-favored. The primary recombinations in the spur may either rebuild the original molecule or else generate new chemical species, i.e. hydrogen and unsaturated polystyrene chains. Our results indicate that energy transfer cannot compete with such a process.

Since the experimental points for radiation protection from ultraviolet light fall very closely to the energy transfer curve, one can conclude that energy transfer by the Forster mechanism is an efficient method of photoprotection. Anthracene is not a good compound to use since it reacts easily through a Diels-Alder-type addition with polystyrene. 9,10-diphenylanthracene would be better since it is chemically more stable than anthracene. The reason it was not studied extensively in this thesis is that it screens the polymer in the region of ultraviolet absorption by polystyrene and hence could not be used for a rigorous conclusive proof of the efficiency of photoprotection via energy transfer.

With gamma radiation, the upper excited states play a role in the degradation of polystyrene. The rate of reaction from these upper excited states is faster than the rate of energy transfer by the Forster mechanism.

CHAPTER V

CLAIMS TO ORIGINALITY OF RESEARCH WORK AND SUGGESTIONS FOR FURTHER WORK

CHAPTER V

CLAIMS TO ORIGINALITY OF RESEARCH WORK AND SUGGESTIONS FOR FURTHER WORK

V-1 CLAIMS TO ORIGINALITY OF RESEARCH

1. The fluorescence and efficiency of energy transfer for the anthracene-polystyrene system was studied in the greatest detail to date. The previous values for efficiency of energy transfer are shown to be incorrect. The extent of formation of Diels-Alder adduct between anthracene and polystyrene has been shown to be appreciable at all concentrations of anthracene requiring large corrections for the energy transfer data.
2. A large difference between the thermally copolymerized system and that to which anthracene has been added at room temperature has been shown for transfer efficiency and concomitantly for radiation protection.
3. The constant production of hydrogen gas has been shown to occur up to a dose of 170 megarads, an amount of radiation not approached by other workers in the field.
4. Other workers have had to rely on theoretical caculations to estimate the amount of protection that would occur for a particular compound according to Forster's theory.

They then compared their results with these calculations. In our case the energy transfer efficiency was determined experimentally and then the ultraviolet and gamma radiation data were shown to agree for the polymer-solute system.

5. Crosslinking has been shown to decrease regardless of the nature of radiation absorbed by the polymer. This is in contradiction to Wilsk and Heusinger(46) who worked with gamma radiation for polystyrene-pyrene. No one previous to this work has given direct evidence for the decrease in crosslinking for polystyrene with ultraviolet light as a result of energy transfer.
6. E.S.R. studies have, for the first time, been conducted on polystyrene-anthracene and polystyrene-9,10-diphenyl-anthracene.

V-2 SUGGESTIONS FOR FURTHER WORK

1. Since the hydrogen gas yield does not change with concentration of anthracene, one must conclude that the reaction to form hydrogen occurs in the upper excited states. However there is also the possibility that the reactions occurs from the first excited singlet state of polystyrene but at a rate that is faster than energy transfer. To check this possibility it now seems worthwhile to set up sensitive equipment

and determine the gas yields for polystyrene under ultraviolet irradiation where only the first excited singlet state of the polymer is produced. Constant gas yields with increasing amounts of anthracene under these conditions would be conclusive proof of reaction from the first singlet state of polystyrene for hydrogen gas.

2. It has also been seen that the percent efficiency of energy transfer is much higher for the system in which anthracene is copolymerized with the styrene monomer than for the system where anthracene is added to a benzene solution of polymer at room temperature. The formation of microcrystals in the latter case had been cited as the reason for the decrease in the number of accepting centers for energy transfer. However another reason for the difference in energy transfer may exist.

Figure V-1 shows the fluorescence spectra (front-surface type). Curve 1 is for the thermally copolymerized system. Curve 3 shows the fluorescence spectrum of anthracene added to polystyrene at room temperature. Curve 2 is Curve 3 shifted several angstroms to match the peaks in Curve 1. Thus it is seen that the fluorescence spectrum of the thermally copolymerized system is a composite fluorescence

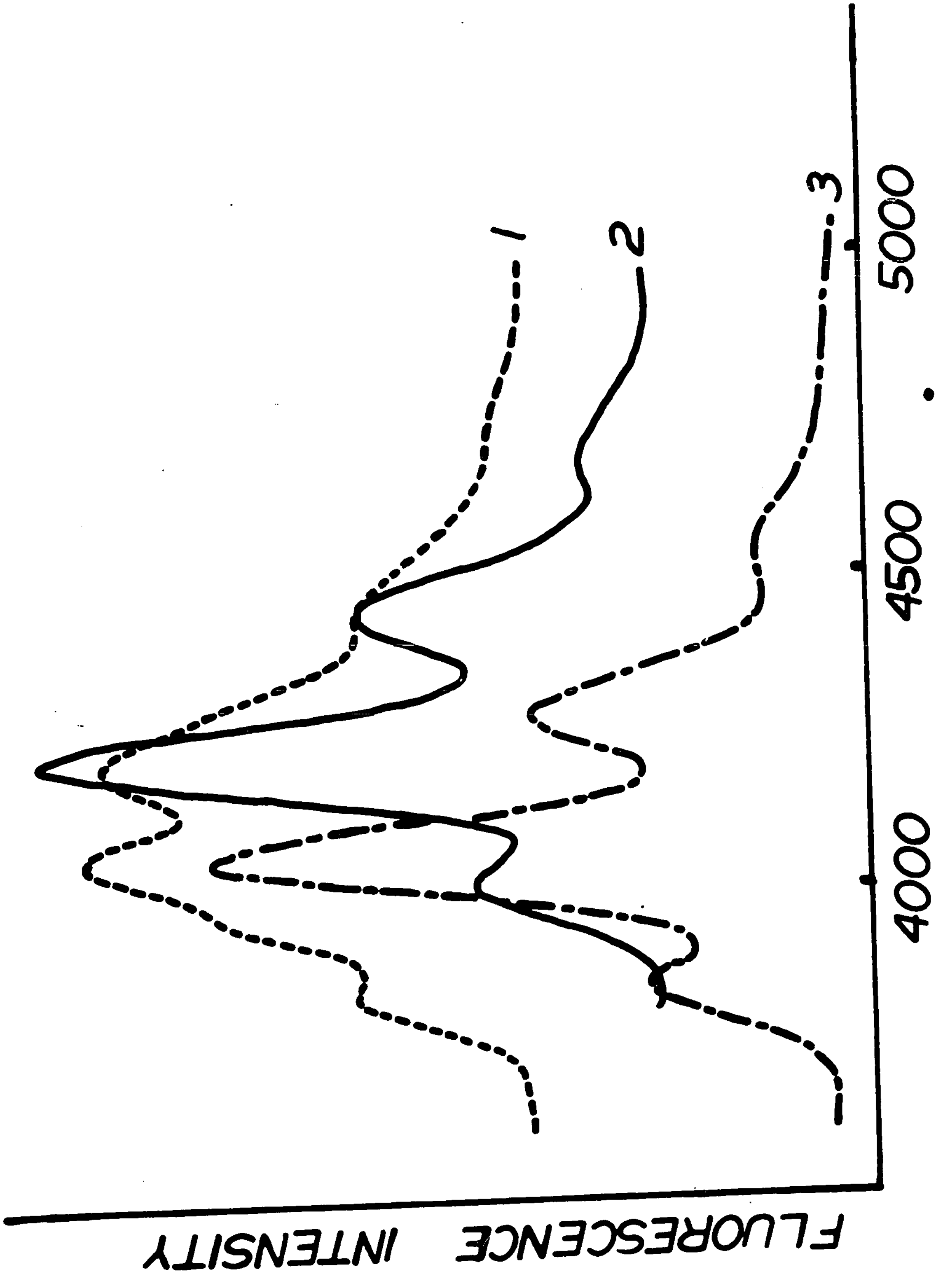
FIGURE V-1

Comparison of Fluorescence Spectra of Anthracene-Polystyrene For Anthracene Added to the System Before and After Polymerization

Curve 1: Anthracene Added to Styrene Monomer and Thermally Copolymerized

Curve 2: Curve 3 Shifted a Few Angstroms, Representative of Monosubstituted Anthracene

Curve 3: Anthracene Added to Polymer at Room Temperature


1
2
3
4000
4500
5000
WAVELENGTH Å
FLUORESCENCE INTENSITY

spectrum of two different kinds of anthracene. The normal fluorescence of anthracene is that of curve 2 whereas that of curve 2 is usually in agreement with monosubstituted anthracenes.(48) Monosubsubstituted anthracene occurs in the thermally copolymerized system as styrylanthracene(48) where the anthracene is substituted only at the 9 (or 10) position with styrene, the anthracene retaining its aromaticity in all three rings. It is also found bound to the polymer chain. Anthracene bound to the chain can probably participate very efficiently in intramolecular energy transfer. (We have seen evidence that energy migration occurs in polystyrene.) Hence the chemical bond of anthracene may cause a preferential migration to this particular kind of anthracene, resulting in a more efficient system for energy transfer. Gardner and Harper(73) found that polyethylene grafted with styrene had better radiation resistance than a polyethylene-polystyrene mixture. Thus the importance of intramolecular energy transfer as opposed to intermolecular energy transfer is not known at this time for polystyrene and anthracene.

Avivi and Weinreb(92) attempted to study these two systems in ethyl acetate. For a 1% solution of anthracene in polystyrene in ethylacetate he found a transfer efficiency of 19% for the thermally copolymerized system and 35% for anthracene added after polymerization. However we now know that in the thermally copolymerized system his value for the concentration of anthracene is more like 0.3% since he did not know of the formation of the Diels-Alder adduct. Since data has been obtained at only these two concentration it is pointless to form any strong conclusions although it appears that the thermally copolymerized system is the more efficient one. It is best to say that the fluorescence and energy transfer measurements should be repeated for both systems in solution. This would eliminate the problem of microcrystals being present in the system and would allow one to find the importance of intramolecular energy transfer in such a system.

3. The degradation measurements could also be investigated in the presence of air. This would give information as to whether oxidation occurs from the singlet or triplet state.

4. A project is also proposed whereby the the degradation of polystyrene is enhanced. As shown in Chapter I when a molecule absorbs electronic energy it is raised from its ground state to an upper singlet state. Through intersystem crossing the molecule passes

from the excited singlet state to the triplet state (spins unpaired). Now electric dipole transitions between pure singlet and pure triplet states are rigorously forbidden because of the orthogonality of the spin wave functions. Thus a perturbation, external or internal, is required to mix pure singlet and pure triplet states, thereby permitting transitions between impure singlet and impure triplet. This perturbation can be increased when a heavy atom or paramagnetic atom on one molecule interacts with the electronic structure of a second molecule. As a result of increased perturbation there will be greater population of triplet states, the state most responsible for chemical reaction because of its long lifetime.

It has been shown by researchers that diphenylmercury, hexacholorbenzene,(93)and cadmium octoate(94) diminish the fluorescence of polystyrene. However no one has observed the effect on the phosphorescence spectrum. The assumptions made by these workers is that the compounds act as quenchers of polystyrene fluorescence by acting as sinks for the migrating energy. The sinks are then incapable of fluorescence or energy transfer. If there is an increase in the phosphorescence intensity of polystyrene in the presence of these compounds , then one could proceed to show that the rate of degradation of the polymer is faster than for the pure polymer if the triplet state is important in the degradation of polystyrene. However if the compounds truly act as an energy sink then we should see a decrease in polymer degradation.

5. The importance of the triplet state in the degradation of polystyrene could be shown by choosing a sensitizer such that triplet-triplet energy transfer occurs. With increasing efficiency of such transfer an enhancement in the degradation of polystyrene should occur.

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APPENDIX

A-1 DATA FOR FIGURE II-2

Ratio of Fluorescence Intensities at 4200 Å for the Same Sample Versus the Ratio of Their Respective Slit Widths on the Beckman Unit

I_1/I_2	SW_1/SW_2
30.7	7.0
27.0	6.6
25.6	6.2
22.3	6.0
20.7	5.8
18.4	5.4
16.0	5.0
15.0	4.8
12.7	4.4
10.3	4.0
7.7	3.4
6.3	3.0
4.9	2.6
3.6	2.3
3.0	2.0
2.6	1.8
1.7	1.4
1.0	1.0

A-2 DATA FOR FIGURE II-3

Correction Factor of 1P28 Phototube Versus Wavelength

Correction Factor	Wavelength Å
0.20	3600
0.39	3750
0.64	4250
0.90	4500
1.00	4750
0.98	5000
0.93	5250
0.84	5500
0.55	5700

A-3 DATA FOR FIGURE II-4

Standard Calibration Graph for Potassium Ferrioxalate Actinometry

Concentration of $FeSO_4$(moles/litre)	Absorbance
8.1×10^{-6}	0.085
16.3×10^{-6}	0.180
24.4×10^{-6}	0.280
32.5×10^{-6}	0.360
40.7×10^{-6}	0.460
48.8×10^{-6}	0.547
57.0×10^{-6}	0.639
65.0×10^{-6}	0.722
81.4×10^{-6}	0.910

A-4 DATA FOR FIGURE II-6

Absorbance at 2700 Å of Thin Pure Polystyrene Films Versus Wavelength

Thickness (mm.)	Absorbance
0.010	1.08
0.008	0.92
0.006	0.72

A-5 DATA FOR FIGURE III-3

Final Weight % Anthracene in Polystyrene Versus Initial Weight % Anthracene in Styrene (Before Polymerization)

Final %	Initial %
0.086	0.23
0.120	0.12
0.158	0.42
0.196	0.49
0.196	0.64
0.239	0.76
0.216	0.84
0.307	0.92
0.295	0.98

Final %	Initial %
0.338	1.03
0.360	1.06
0.385	1.35
0.651	2.03
0.800	2.80
0.872	3.09
0.938	3.84
1.328	4.80

A-6 DATA FOR FIGURE III-4

Intrinsic Viscosity of Polystyrene-Anthracene Samples Versus Weight Percent of Initial Anthracene Concentration

Initial Weight % Anthracene	Intrinsic Viscosity
0.11	1.21
0.15	1.28
0.18	1.22
0.52	1.21
0.63	1.16
0.76	1.11

Initial Weight % Anthracene	Intrinsic Viscosity
0.92	1.14
1.06	1.07
1.36	1.09
3.10	1. 1
3.66	1.05

A-7 DATA FOR FIGURE III-7

Percent Efficiency of Energy Transfer Versus Weight Percent of Anthracene in Polystyrene

(Solute was added to monomer before polymerization)

Weight % Anthracene	$F_{2700\,\text{Å}}$	% Efficiency of Transfer
0.02	3.4	13.0
0.04	5.2	19.6
0.09	6.8	25.9
0.13	9.5	36.1
0.15	9.4	35.7
0.26	14.0	53.4
0.57	23.2	88.1
0.80	26.9	102.3
1.12	26.2	99.7

$F_{3340\,\text{Å}}$ was set at 100. The fluorescence of the samples was observed at 4200 Å. The ratio of the excitation wavelenghts was $I_{2700\,\text{Å}}/I_{3340\,\text{Å}} = 3.8$.

A-8 DATA FOR FIGURE III-8

Percent Efficiency of Energy Transfer Versus Weight Percent of 9,10-Diphenylanthracene in Polystyrene.

Weight % Solute	$F_{2900\,\text{Å}}$	% Efficiency of Transfer
0.20	29.4	55.0
0.53	33.8	63.1
0.75	39.4	73.7
1.23	39.1	73.1

$I_{2900\,\text{Å}}/I_{3340\,\text{Å}} = 1.87$.

A-9 DATA FOR FIGURE III-12

Weight % Anthracene in Polystyrene Versus Moles of Anthracene Per Litre of Polystyrene

% Anthracene	Moles Anthracene Per Litre	% Anthracene	Moles Anthracene Per Litre
0.15	0.0076	0.76	0.039
0.18	0.0080	0.92	0.046
0.39	0.020	1.06	0.054
0.52	0.027	2.03	0.103

A-10 DATA FOR FIGURE III-13

Relative Total Fluorescence Intensity Versus Moles of Anthracene Per Litre of Polystyrene (Indirect Excitation)

Anthracene Concentration*	Intensity**	Anthracene Concentration*	Intensity**
2.1×10^{-4}	10.7	4.5×10^{-3}	18.3
6.3×10^{-4}	11.1	6.5×10^{-3}	24.5
8.0×10^{-4}	10.8	8.3×10^{-3}	32.0
2.0×10^{-3}	10.9	1.05×10^{-2}	29 7
2.5×10^{-3}	14.5	1.25×10^{-2}	29.7
3.0×10^{-3}	18.1	1.6×10^{-2}	45.8

* Concentration of anthracene is in moles/litre of polystyrene.

** Intensity is given in arbitrary units.

A-11 DATA FOR FIGURE III-14

Radius of Sphere of Solvent Occupied by One Solute Molecule
Versus Moles of Solute Per Litre of Solvent

Moles of Solute Per Litre	R (Å)
0.5×10^{-3}	92.6
0.8×10^{-3}	79.1
1×10^{-3}	73.4
2×10^{-3}	58.2
4×10^{-3}	46.3

Moles of Solute Per Litre	R (Å)
7×10^{-3}	38.4
9×10^{-3}	35.3
12×10^{-3}	32.1
14×10^{-3}	30.5

See Page 186 for Data Corresponding to Figure III-17 (A-12)

A-13 DATA FOR FIGURE III-18

Efficiency of Energy Transfer (F) versus c(1 - F)
Plot is for equation(III-7).

F	c*	(1 - F)	c(1 - F)
0.15	0.20×10^{-3}	0.85	1.7×10^{-3}
0.20	0.30×10^{-3}	0.80	2.4×10^{-3}
0.25	0.40×10^{-3}	0.75	3.0×10^{-3}
0.30	0.50×10^{-3}	0.70	3.5×10^{-3}
0.35	0.65×10^{-3}	0.65	4.2×10^{-3}
0.40	0.85×10^{-3}	0.60	5.1×10^{-3}

* The concentration of anthracene, c, is in moles/litre

A-12 DATA FOR FIGURE III-17

Relative Total Fluorescence Intensities of Anthracene
Obtained by Direct and Indirect Excitation

Weight % Anthracene	Intensity (Direct Excitation)	Intensity (Indirect Excitation)
0.016	10.8	58.0
0.035	10.9	52.0
0.048	14.5	59.8
0.057	18.1	62.8
0.093	19.8	63.5
0.125	24.5	68.1
0.160	32.0	53.9
0.205	31.3	73.6
0.24	29.7	70.5
0.29	45.8	70.5
0.33	38.2	57.6
0.42	46.3	72.6
0.62	48.1	49.9
0.86	56.5	67.3
0.98	55.0	69.5
1.25	61.5	69.3

Wavelength used for indirect excitation was 2700 Å.
Wavelength used for direct excitation was 3340 Å.
Fluorescence intensities are given in arbitrary units.

A-14 DATA FOR FIGURE IV-2

Percent Photoprotection of Polystyrene Versus Percent of Anthracene as Determined From Insolubility Measurements (The anthracene was added to the monomer before polymerization.)

Weight % Anthracene	Weight of Insoluble Polymer (gm.)	Pure Polystyrene Weight of Insoluble Polymer (gm.)	% Photo-protection
0.06	0.0043	0.0084	49
0.09	0.0043	0.0084	49
0.09	0.0056	0.0088	37
0.13	0.0041	0.0076	42
0.21	0.0042	0.0082	51
0.29	0.0014	0.0049	70
0.33	0.0015	0.0054	72
0.62	0.0010	0.0079	88
0.86	0.0013	0.0074	85
0.98	0.0010	0.0101	90

For the values below pure polystyrene has been derived from precipitation of the corresponding anthracene-polystyrene samples.

0.06	0.0035	0.0045	20
0.13	0.0017	0.0025	32
0.29	0.0017	0.0031	45
0.33	0.0013	0.0025	48
0.62	0.0001	0.0016	94

A-15 DATA FOR FIGURE IV-3

Percent Efficiency of Energy Transfer for Thin Polystyrene Films Containing Anthracene

Anthracene Added Before Polymerization

% Anthracene	% Efficiency of Energy Transfer		% Anthracene	% Efficiency of Energy Transfer	
0.05	14.3	11.8	0.29	55.4	52
0.09	24.4		0.33	62.7	
0.12	35.3	17.0	0.42	74.6	
0.16	30.2	49.5	0.61	77.3	79
0.19	42.5		0.87	100.0	
0.20	26.0		0.98	100.0	
0.24	41.6				

Anthracene Added After Polymerization

% Anthracene	% Efficiency of Energy Transfer					
0.19	14.3	8.8	7.1			
0.31	31.9	31.1	20.8	20.5	16.5	15.1
0.49	60.5	48.7	39.5	31.8	16.8	
0.65	77.3					
0.80	39.5					
0.99	68.9	65.5	53.7	43.2	29.8	24.0
1.36	69.1	52.9	55.6	41.8		
2.37	73.8	69.7	59.1	59,4	47.9	47.1
2.94	100.0	87.2	70.1			
3.21	100.0	99.3	99.3	99.1	79.9	79.8

A-16 DATA FOR FIGURE IV-4

Percent Photoprotection of Polystyrene Versus Percent of Anthracene

The Anthracene was added to the polymer at room temperature.

Weight % Anthracene	Weight of Insoluble Polymer (gm.)	Pure Polystyrene Weight of Insoluble Polymer (gm.)	% Photo-protection
0.29	0.0058	0.0069	16
0.40	0.0039	0.0049	20
0.65	0.0036	0.0069	48
0.80	0.0034	0.0050	43
0.98	0.0056	0.0131	57
1.04	0.0023	0.0065	65
1.45	0.0006	0.0045	86
2.34	0.0016	0.0070	79
2.94	0.0010	0.0093	89

A-17 DATA FOR FIGURES IV-5 and IV-6

Gas Yields For Gamma Irradiation

	Dose (Megarads)			
	16.1	34.5	171.1	
Pure Polystyrene	4.1×10^{-7}	9.0×10^{-7}	5.4×10^{-6}	moles/gm.
1.23% 9,10-Diphenylanthracene	3.6×10^{-7}	7.8×10^{-7}	4.5×10^{-6}	moles/gm.

A-18 DATA FOR FIGURES IV-7, IV-8, and IV-9

Intrinsic Viscosities of Anthracene-Polystyrene Samples Versus
Dose of Gamma Radiation (Megarads)

Dose	Intrinsic Viscosity	Dose	Intrinsic Viscosity
	0.05% Anthracene		
0	1.28	19.9	1.54
7.4	1.33	21.1	1.84
11.2	1.31	20.7	1.88
15.9	1.38	21.7	1.94
	0.17% Anthracene		
0	1.31	43.1	1.76
7.1	1.33	34.6	1.73
21.1	1.41	36.7	1.87
25.0	1.49	37.0	1.58
30.5	1.44	38.0	1.91
31.4	1.67	38.2	1.84
	0.25% Anthracene		
0	1.29	35.8	1.74
6.3	1.31	39.2	1.66
14.5	1.29	44.0	2.40
26.7	1.49	46.0	2.02
30.5	1.29	48.2	1.91
33.2	1.56		

A-18 Continued

Dose	Intrinsic Viscosity	Dose	Intrinsic Viscosity
0.3% Anthracene			
0	1.34	40.1	1.67
6.3	1.36	48.9	1.80
24.2	1.39	50.3	2.47
28.9	1.50	52.1	2.61
33.0	1.54		
0.6% Anthracene			
0	1.25	57.8	1.55
12.9	1.15	61.9	1.62
20.3	1.25	66.4	1.95
30.4	1.31	69.0	2.00
50.8	1.62	71.8	2.00

A-19 DATA FOR FIGURES IV-10 AND IV-11

Gelation Dose Required for the Anthracene-Polystyrene Samples

% Anthracene	% Energy Transfer	Gelation Dose(Megarads)
Anthracene Added Before Polymerization		
0.05	17	21.5
0.17	42	40.0
0.26	52	44.5
0.32	64	51.5
0.61	92	73.0

A-19 Continued

% Anthracene	% Energy Transfer	Gelation Dose (Megarads)
Anthracene Added to Polymer at Room Temperature		
0	0	33.0
0.15	11	45.0
0.30	20	49.0
0.60	36	51.3

A-20 DATA FOR FIGURE IV-12

Intrinsic Viscosities for Two Different Polystyrene Samples
Versus Dose of Gamma Radiation(Megarads)

Pure Polystyrene		Pure Polystyrene	
Dose	Intrinsic Viscosity	Dose	Intrinsic Viscosity
0	1.52	0	1.54
3.7	1.59	9.21	1.80
7.0	1.64	30.7	2.42
10.0	1.57	33.14	2.65
17.4	1.78	15.1	1.88
21.1	2.05		
22.1	2.15		

A-21 DATA FOR FIGURE IV-13

Ratios of Final to Initial Intrinsic Viscosity Versus Ratios of Gamma Radiation Dose to Gelation Dose For Pure Polystyrene

(n)	D	(n/n_o)	D/D*
	$(n_o) = 1.52$	D* = 22	
1.59	5	1.05	0.23
1.67	10	1.10	0.46
1.74	15	1.15	0.68
1.90	20	1.25	0.91
1.95	21	1.28	0.96
	$(n_o) = 1.54$	D* = 33	
1.68	5	1.09	0.15
1.82	10	1.18	0.30
1.96	15	1.27	0.46
2.10	20	1.36	0.61
2.25	25	1.46	0.76
2.40	30	1.56	0.91
2.48	31.5	1.61	0.95

(n) is the intrinsic viscosity of the irradiated polymer at dose D, (n_o) is the intrinsic viscosity of the unirradiated polymer, D* is the gelation dose.

A-22 DATA FOR FIGURE IV-14

Ratios of Final to Initial Intrinsic Viscosity Versus Ratios of Dose of Gamma Radiation to Gelation Dose for Polystyrene-Anthracene

(η)	D	(η/η_o)	D/D*
0.05% Anthracene			
1.32	10	1.02	0.47
1.38	15	1.06	0.70
1.48	18	1.14	0.84
1.64	20	1.26	0.93
1.74	20.5	1.34	0.95
0.25% Anthracene			
1.31	15	1.02	0.34
1.36	30	1.05	0.67
1.48	35	1.15	0.79
1.70	40	1.32	0.90
1.90	42.5	1.47	0.96
0.3% Anthracene			
1.35	20	1.0	0.39
1.42	30	1.05	0.58
1.51	35	1.12	0.68
1.60	40	1.19	0.78
1.72	45	1.27	0.87
1.98	50	1.47	0.97

A-22 Continued

0.6% Anthracene

(η)	D	(η/η_0)	D/D*
1.27	20	1.00	0.29
1.30	30	1.02	0.43
1.36	40	1.07	0.57
1.44	50	1.13	0.71
1.50	55	1.18	0.79
1.60	60	1.26	0.86
1.78	65	1.40	0.93
2.00	68	1.57	0.97

For meaning of symbols see information under A-21

A-23 DATA FOR FIGURE IV-15

Ratios of Final to Initial Intrinsic Viscosity Versus Ratios of Dose of Gamma Radiation to Gelation Dose For Anthracene Added to Polystyrene at Room Temperature and For Pure Polystyrene

0.14% Anthracene

For Pure Polystryene see A-21

(η)	D	(η/η_0)	D/D*
1.68	9.4	1.09	0.21
1.77	15.6	1.15	0.35
1.86	21.8	1.21	0.48
1.96	28.0	1.27	0.62
2.05	34.3	1.33	0.76
2.15	40.6	1.40	0.90

A-24 DATA FOR FIGURE IV-24

Excess Optical Density Over That of Pure Polystyrene For Ultraviolet Irradiation of Polystyrene Films Containing Diels-Alder Adduct Plus Anthracene

Weight % Diels-Alder Adduct	Excess O.D.$_{3000\ \mathrm{\AA}}$	
0.20	0.03	
0.27	0.03	
0.42	0.08	
0.53	0.09	0.13
0.64	0.13	0.15
0.74	0.20	
1.43	0.23	0.24
2.36	0.28	0.29
2.69	0.34	
2.83	0.31	
4.05	0.46	

APPENDIX B

DISCUSSION OF EXPERIMENTAL ERRORS

1. Fluorescence Spectra

The spectra are of high accuracy, an error of ±1% being made in reading the intensities of the emitted light. Errors in calibration of the phototube are unknown since the manufacturer's data was used in this case.

2. Measurement of the Efficiency of Energy Transfer

For the solid cylinder the xenon lamp had $I_{3340\ \text{Å}}/I_{2700\ \text{Å}} = 4.3$ so that an error in intensity of ±1% would result in an error of ±4%. However this lamp, because of age had to be replaced by a new lamp for measurements on the the thin films and it had $I_{3340}/I_{2700} = 8.1$. Thus the error for the films would be ±8%. Corrections had to be made for absorption of 3340 Å since not all of it is absorbed by the thin films. In the very thin films, since absorption is logarithmic, the error for the low concentrations could be as high as ±20%.

3. Measurement of Insoluble Material

The amount of insoluble material for the pure polystyrene averaged about 0.0060 gm. The error in weighing the filter paper before and after filtration is ±0.0002 (0.0001 x 2). If water is not absorbed uniformly as in the blank filter papers then we could expect a further error of ±0.0005 gm. Thus in making comparisons between the pure polymer and polymer-solute samples a total possible cumulative error of ±0.0014 gm. or ±23% is possible.

4. Gas Measurements

The error in reading the McLeod gauge was ±2 mm. resulting in an error of $\pm 1.12 \times 10^{-9}$ moles. Thus the longer the period of irradiation, the smaller the percentage error.

5. Gelation Dose Measurements

As can be seen from the scatter in the graphs the gelation dose is off by not more than ±2 megarads.

6. Electron Spin Measurements

The impossibility of packing the e.s.r. tubes to the same density with the granulated particles of polymer causes some scatter of points for some samples in plotting concentration of spins versus hours of radiation. The possible slopes of the lines drawn did not exceed ±20% of the average value for most samples.