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Relief and Functional Imaging with New Chemically Amplified Resists

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Abstract

Several new families of chemically amplified photoresists were designed, synthesized and evaluated for microlithography. These materials were based on copolymers of the following but-2-enedioic acid derivatives: (i) maleic anhydride, maleic acid, fumaric acid; (ii) maleic or fumaric acid monoester; and (iii) fumaric acid di-*t*-butyl ester. Heating with photogenerated strong acid induced significant alteration of copolymer properties by acid-catalyzed reactions of, respectively: (i) dehydration, (ii) dehydroalkoxylation, and (iii) de-alkenation. Depending on the developing solvent, both negative-tone and positive-tone relief images were obtained with 1 micron resolution. The material alteration also allowed further patterned chemical modification ("functional development"), such as through sorption of various organic and inorganic species from contacting solutions or vapours into either exposed or unexposed resist areas.

Abstract

Plusieurs nouvelles familles de photorésistes par amplification chimique ont été synthesizées et evaluées pour la microlithographie. Ces materiaux ont été composés à partir de copolymères des derivés suivants de l'acide but-2-ènedioique: (i) l'anhydrure maléique, les acides maléique et fumarique; (ii) les monoestères de l'acide maléique et fumarique; et (iii) l'estère di-*t*-butylique de l'acide fumarique. La photogeneration d'un acide fort, suivi de chauffage, cause l'alteration significative des propriétés copolymères par acide par les reactions suivantes: (i) dés-hydratations, (ii) dés-hydroalkoxilation, et (iii) dés-hydroacyloxilation. Les images en relief (tones négative et positive) ont été obtenues avec les solvants variés à le résolution de 1 micron. L'altération de matériaux a aussi permi la modification chimique suivant un patron (developement functionnel), par example, en introduisant des molecules organiques ou inorganiques en solution ou les vapeures en contacte, dans les regions exposées ou non-exposées.

Foreword

This thesis is presented in seven chapters and an appendix. **Chapter A** is a general introduction and literature overview of Chemically Amplified microlithographic resists. The last section of **Chapter A** presents current problems in the field, and thus, demonstrates the necessity of the presented research. **Chapter B** presents the design, synthesis, characterization, and lithographic evaluation of new diester-type photoresist PDBFS. The next chapters introduce a concept of Functional Developing (or Functional Imaging). Using described in **Chapter A** photosensitive material as a template, metal ions (**Chapter C**) and organic molecules (**Chapter D**) were selectively placed into a micro-scale pattern. **Chapter E** describe the study of new monoester-type resists and completely water-processable diacid-type resists.

Overall conclusions and contributions to original knowledge are presented in **Chapter F**. This chapter has several summary tables for developed and optimized photolithographic procedures. Also presented general step-by-step approach for design and creation of functional images. In the end of **Chapter F** a reader will found several suggestions for further research.

To direct attention of a reader to the main ideas, experimental sections of each chapter provide complete, but condense description of used techniques. Detail description of TGA, FT-IR, UV-Vis, and fluorescence techniques is given in the **Appendix** in the very end of the thesis.

Chapters A-E feature several figures, schemes and tables from previously published articles [1-6]. There are copyright permissions from the CRC Press, ACS Publishing Division and SPIE Publishing Division for articles [1,2,5,6]. Articles [3,4] are copyrighted by the authors.

The literature overview (**Chapter A**), experimental work (**Chapters C-E**) and the first draft of articles [1,3-6] were done almost entirely by the thesis author under supervision of Prof. Darling. Part of synthetic work presented in **Chapter B** and the first draft of an article [2] were done by Dr. J. Zhang, while the thesis author performed most of the material characterizations, lithographic evaluation and the article revisions.

Acknowledgments

I wish to express my sincere gratitude to Prof. G. Darling for expert guidance, supervision, and encouragement throughout the course of this work.

I thank Dr. J. Zhang for intensive and fruitful collaboration in the first year and a half of my research, particularly for a part of experimental work in **Chapter B**, the writing of the first draft of article [2], and some ideas for sequential research.

Thanks also to the following people for valuable contribution to the presented research:

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- Dr. B. Wandelt and Dr. B. Tolloczko - training for fluoromicroscope.
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List of Abbreviations

4TS	4-(phenylthio)phenyl diphenyl sulfonium [cation]
CA	chemically amplified [resist]
CARL	chemical amplification of resist lines
DESIRE	diffusion enhansed silylation resist
DPI	diphenyliodonium [cation]
DSC	differential scanning calorimetry
DUV	deep ultra-violet [often denotes 254 or 248 nm]
mid-UV	300-350 nm
near-UV	350-450 nm
O_2-RIE	oxygen reactive ion [plasma] etching
OTf	triflic acid [anion]
PAB	post-apply bake
PAG	photo-acid generator
PDBFS	poly(di-*t*-butyl fumarate-*co*-styrene)
PEB	post-exposure bake
PolyTBOCST	poly(*t*-butyloxycarbonyloxystyrene)
PSF-acid	poly(styrene-*co*-fumaryl acid) [deprotected PDBFS]
PSF-ester	poly(styrene-*co*-fumaryl ester) [same as PDBFS]
RIE	reactive ion [plasma] etching
TBOC	*t*-butyloxycarbonyloxy [popular protecting group]
T_d	decomposition temperature
T_g	glass-transition temperature
TGA	thermo-gravimetric analysis
TMAH	tetramethylammonium hydroxide
TPS	triphenylsulfonium [cation]
VUV	vacuum ultra-violet [often denotes 193 or 173 nm]

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Chapter A

A Review of Chemistry and Processes of Chemically Amplified Resists

A-1. INTRODUCTION

Advanced microlithographic technologies use *Chemically Amplified* (CA) resists to produce electronic or photonic circuits and devices, including higher-density components such as 1 GB DRAMs, 150 MHz microprocessors or 10 GHz optical couplers.

Resist (photoresist, microresist) has become a general term for a polymer-based material that undergoes a chemical change following brief *Deep UltraViolet* (DUV) or other irradiation. It is typically applied by spin-coating the solution in casting solvent onto a silicon wafer or other substrate, followed by ***Post-Apply Baking*** (***PAB***) to produce a thin dry film. This, during exposure, captures a briefly-projected radiation image of a circuit pattern (or diffraction grating, etc.) as a *latent image* of altered/unaltered material (**Figure A-1**). Further steps may be done by liquid or plasma. *Relief development* removes either the exposed or unexposed areas of the latent image (and, in multilayer resists and top surface imaging, any planarizing layer of inactive polymer underneath) to produce a *relief image*. *Etching* then erodes or otherwise modifies the underlying substrate where no film is left to "resist". Stripping removes the last of the resist, leaving the image in the substrate as planned. Overall, *pattern transfer* has been accomplished from the projected image to the resist, then from the resist to the substrate. This is the general process of *photolithography*, also called photoengraving by the printing industry, where it was developed long before being adapted as microlithography to make integrated circuits. **Table A-1** lists some desirable properties of a resist for relief development, particularly for microlithography.

Alternatively, *functional development* after exposure removes neither exposed nor unexposed areas from the latent image, but selectively modifies one or the other (e.g. by adding some chemical species to its surface or bulk) to produce a *functional image* of modified polymer material as the final objective (**Section A-5** below).

In earlier generations of resists (often based on "novolak" phenol-formaldehyde polymers), each absorbed quantum of radiation induced on average less than one chemical reaction within the material. In CA resists however (**Figure A-2**), the primary photo-chemical event produces a mobile catalyst which, typically during later *Post-*

Exposure Baking (*PEB*), goes on to induce a cascade of material-transforming secondary catalytic events within a 5-25 nm radius. Such chemical amplification thus makes possible an overall quantum yield – number of material reactions divided by number of absorbed photons – of up to several hundred. Thus, a CA resist formulation must contain:

(i) a small amount (ca. 1-5 wt %) of radiation-sensitive catalyst precursor, generally a *PhotoAcid Generator* (*PAG*);

(ii) many chemical groups that can react by elimination, addition or rearrangement only in the presence of catalyst;

(iii) a polymer matrix able to disperse all other components in a smooth clear film;

(iv) optional additives to improve performance or processability; e.g. surfactants, photosensitizers, etch resistors.

(v) the casting solvent (removed during spin-coating and PAB steps).

Although in most reported compositions the catalyst-sensitive groups are polymer-bound and the catalyst precursors are free (i.e. i + ii~iii), components i-iii or iv can in principle be interconnected in any combination, as small molecules, homopolymers, copolymers or blends (e.g. i + ii + iii [1], i~ii + iii [2], i~ii~iii [3,4]). Along with their higher sensitivity and contrast in forming images, CA are also better than earlier resists in being more flexible in design and formulation, sensitive and often more transparent to a variety of radiation sources (including high-resolution but low-power deep- or vacuum-UV, X-ray, electron and ion beams), and compatible with dry (plasma), multilayer and other advanced pattern-transfer techniques.

"Photosolubilizable compositions" for photographic and photoresist applications with overall quantum yields greater than 1 were described by Smith (3M Inc.) as early as 1973 [5]. However, the idea was limited in practice until thermostable yet photosensitive onium salts of strong acids were developed by Crivello (GE Inc.) as PAGs for cationic photopolymerization [6]. The first CA resist for microlithography was reported by the university-industry team of Fréchet (University of Ottawa), Willson and Ito (IBM Inc.) [7], who combined onium salts with the acid-deprotectable poly-4-[*t*-butyloxy-carbonyl-oxy]styrene (PolyTBOCST; **Figure A-2**), and coined the term "chemical amplification". Since the late 1980's, IBM has been using proprietary CA resists in DRAM production. Several commercial CA resists are now available from Shipley, Hoechst-Celanese, BASF and other companies. Over 200 articles and several reviews [8-12] have appeared on this topic between January 1992 and June 1994 alone.

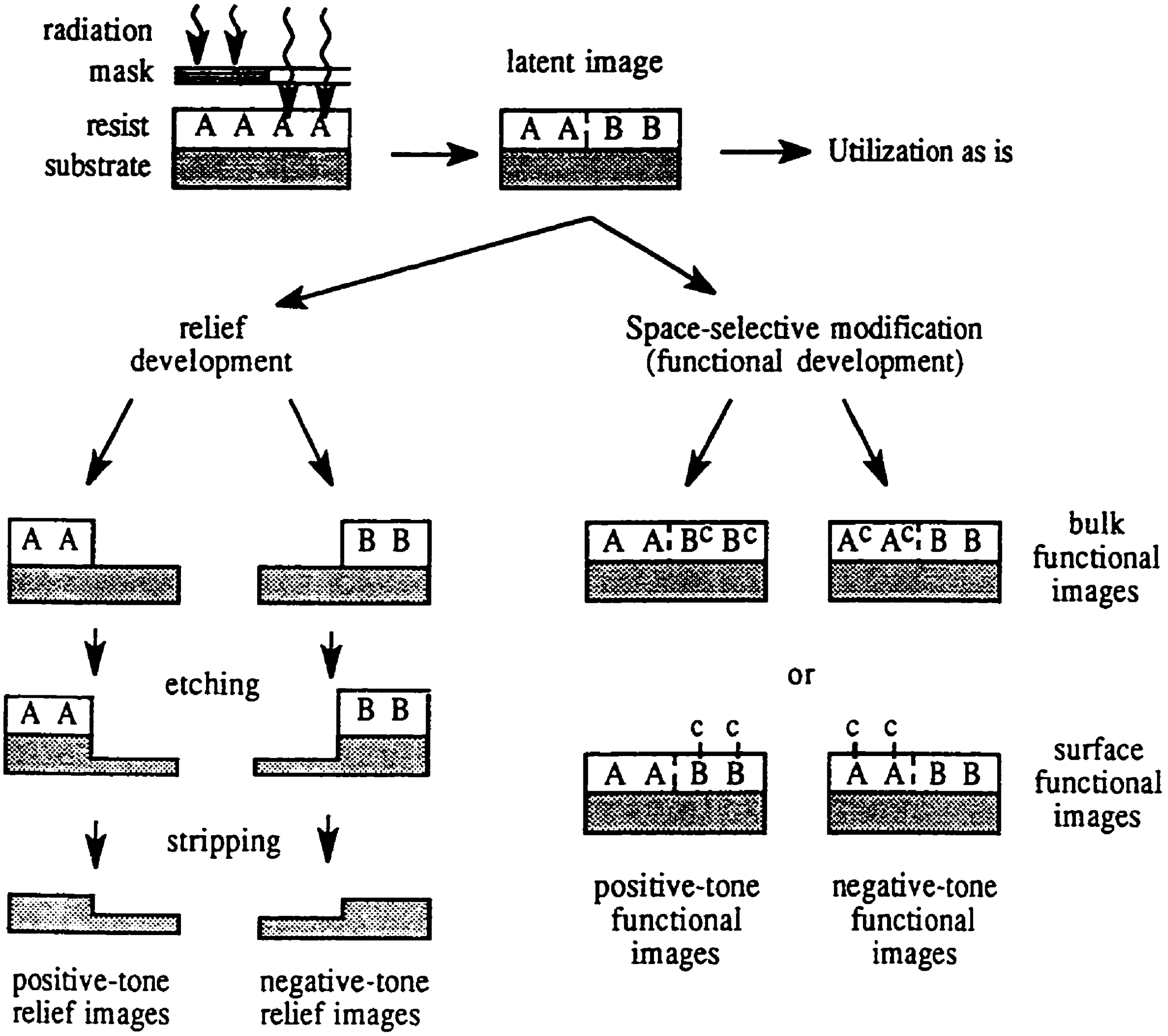
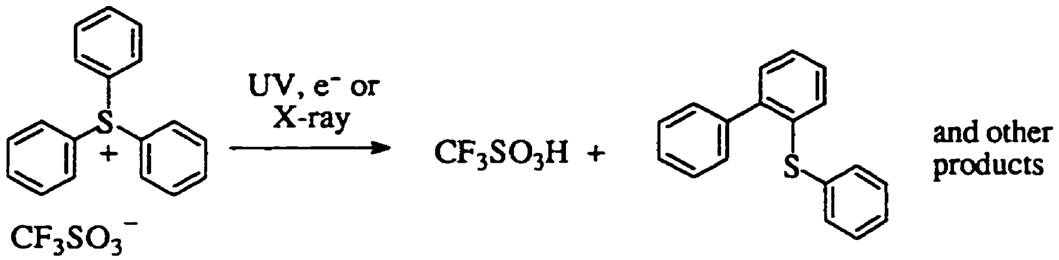


Figure A-1. Creation of relief and functional images with resists.

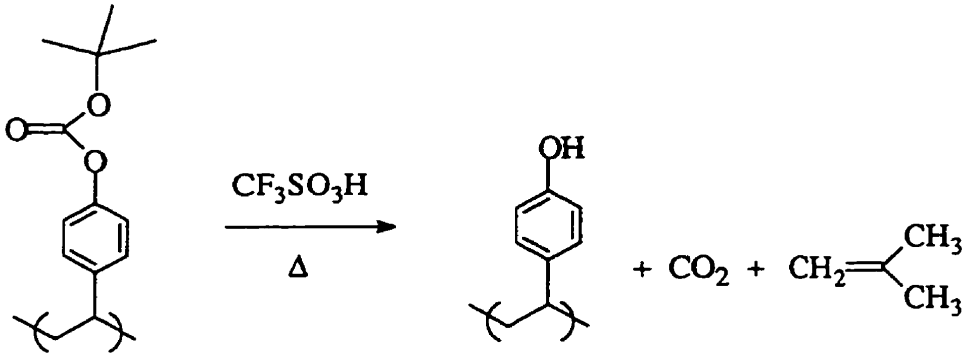
Table A-1. Preferred resist properties for microlithographic applications.

Property	Definition	Specifications	Comments
Transparency	Extinction coefficient at exposure wavelength.	0.3-0.6 μm^{-1}	Low enough for energy absorption; high for uniform exposure
Sensitivity	Minimal radiation dose to change film solubility.	< 50 mJ/cm^2	For high-resolution, but low-intensity beam sources.
Contrast	Steepest slope in curve of solubility vs. log(dose).	> 3-4	For vertical wall profiles in relief images, and best pattern transfer.
Thermostability: Deformation	Glass transition temperature (by DSC).	80-150 °C	Low to anneal and remove solvent; high that image won't flow during later heating steps.
Thermostability: Decomposition	Temperature for uncatalyzed mass loss; by TGA.	>200 °C	High, but not to prevent later plasma development or stripping.
Oxygen Plasma Resistance	Etching rate in anisotropic oxygen plasma.	Tenfold difference in exposed vs. unexposed areas.	High enough contrast to permit O_2-RIE development in multi-layer or top surface imaging.
Halo-Carbon Plasma Resistance	Etching rate in fluorocarbon plasma.	Comparable to novolac.	To protect selected areas of SiO_2 substrate during etching step.

a) Photogeneration of catalyst (strong acid)



b) Acid-catalyzed transformation of polymer.



Poly-TBOCST
(organic-soluble,
aqueous base-insoluble)

Polyhydroxystyrene
(organic-insoluble,
aqueous base-soluble)

Figure A-2. Example of a chemically amplified resist.

A-2. PHOTOCATALYST GENERATORS

The usual photo-supplied catalyst has been strong acid. Triarylsulfonium and diaryliodonium salts (**Figure A-3**) have become the standard PAG ingredients in CA resist formulations, because of their generally easy synthesis, thermal stability, high quantum yield for acid (and also radical) generation, and the strength and nonvolatility of the acids they supply [13]. Simple onium salts are directly sensitive to DUV, X-ray and electron radiations, and can be structurally tailored, or mixed with photosensitizers, to also perform well at mid-UV and longer wavelengths. An aromatic polymer matrix alone can also often act as a photosensitizer, presumably through electron transfer within 1.6-2.0 nm [14]. Mechanistic studies have shown onium salt photodecomposition to proceed via both homolytic and heterolytic pathways [15,16].

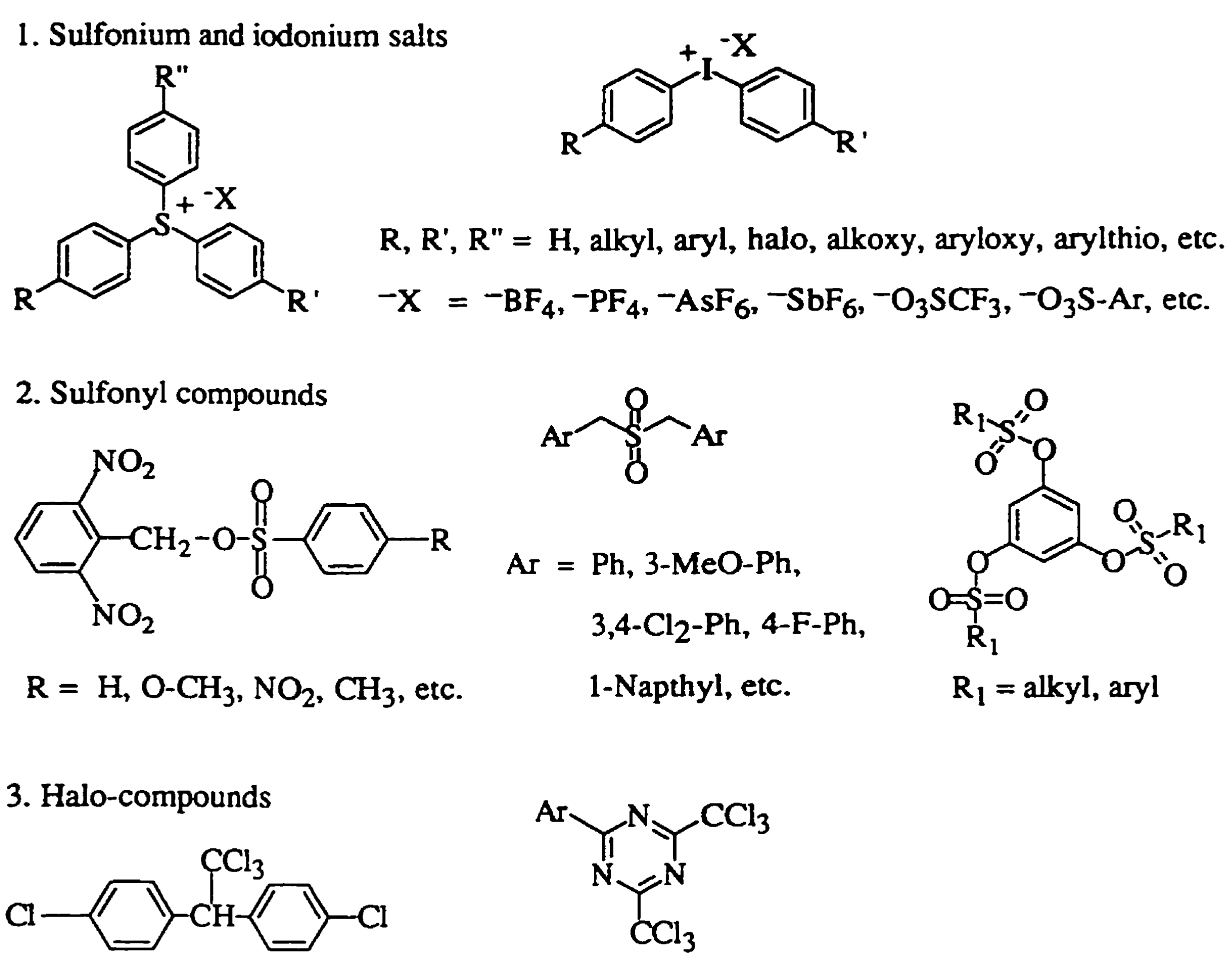


Figure A-3. Photoacid generators (PAGs).

However, onium salts are ionic and many will phase-separate from some apolar polymers, or not dissolve completely in some casting solvents. Nonionic PAGs such as phloroglucinyl and *o,o*-dinitrobenzyl sulfonates, benzylsulfones and some 1,1,1-trihalides (**Figure A-3**) are more compatible with hydrophobic media in general, although their thermal stabilities and quantum yields for acid generation are often lower [2,17-19].

Certain O-benzylic carbamates [20,21] or cobalt complexes with ammonia [22] can function as *photobase generators*. Photoradical generators are better known for photopolymerization applications than for microlithographic resists.

A-3. CATALYZED REACTIONS

A-3.1. Non-Polar-to-Polar Rearrangements

Many reactions can amplify the primary phototochemical event of catalyst generation. Besides photopolymerization, whose contrast is often insufficient for microlithography, these include rearrangement, crosslinking and chain scission/depolymerisation.

Rearrangements resulting in solubility changes can further be characterized as:
(i) nonpolar-to-polar; (ii) polar-to-nonpolar; and (iii) one of i or ii after the other (polarity reversal) [23]. Depending on the polarity of a developing liquid, either the exposed or unexposed areas can be finally removed to produce positive-tone or negative-tone relief images respectively (dual-tone developability).

Nonpolar materials can be transformed to polar ones by catalyzed cleavage if they contain ether, imide, ester or other oxycarbonyl functionalities capped with *t*-butyl, α,α-dimethylbenzyl [23], tetrahydropyranyl [24,25], adamantyl [26], or other acid-labile protecting groups. These may be derivatives of polymer units such as hydroxystyrene or other phenolics, maleimide [27] or N-hydroxymaleimide [28], acrylic, methacrylic [29], vinylbenzoic [23] or butenedioic [30] acids (**Figures A-2 and A-4**).

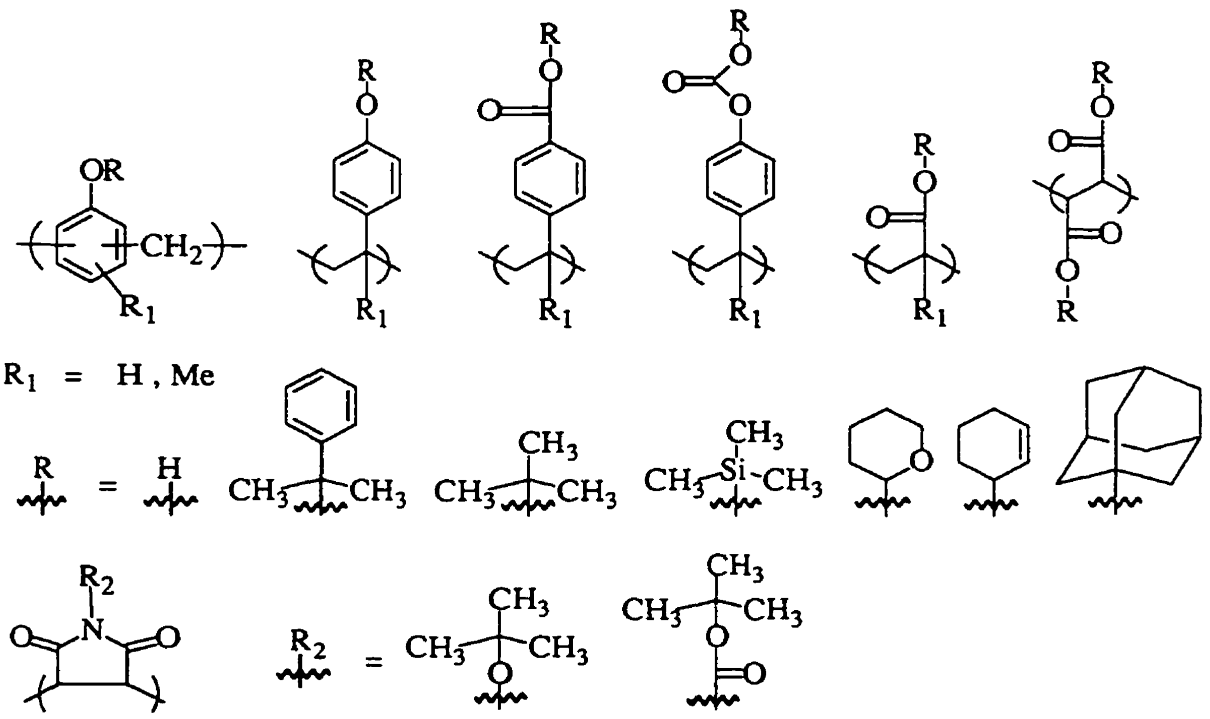


Figure A-4. Polymeric units for nonpolar-to-polar transformations.

Copolymers of TBOCST with SO_2 under X-rays [31], or with (2-nitrobenzyl)-styrenesulfonate under DUV [4] produce sulfinic and sulfonic acid groups, respectively, that both increase material polarity on their own as well as catalyze further deprotection of phenol groups. In contrast to the specialty polymers required for such single-component and many other resists, inexpensive novolaks and other phenolic polymers can make up the bulk of effective multi-component resists if combined with acid-sensitive small-molecule dissolution inhibitors as well as PAGs [1]. From one such a resist, Nakase [32] formed 0.25 µm patterns with mid-UV, achieving extremely high contrast through further hydrolysis of partially-deprotected polymer during development with aqueous base (self-solubility acceleration effect, which can also be termed Contrast Boosting [33]).

A-3.2. Polar-to-Non-Polar Rearrangements

Polar-to-nonpolar rearrangements include acid-catalyzed condensation of silanol [34,35] and carbinol [36] groups. Pinacol rearrangement from polar *vic*-diol to ketone moieties in polymers [37,38] or dissolution inhibitors [36] have been reported (**Figure A-5**).

The above modes of operation can also be imagined for base-catalyzed CA resists. Photogenerated amines catalyze decarboxylation of some polycarboxylic acids to nonpolar materials [20,21]. Decarboxylation of similar small compounds transforms them to dissolution inhibitors for development of novolak matrix in aqueous base [20].

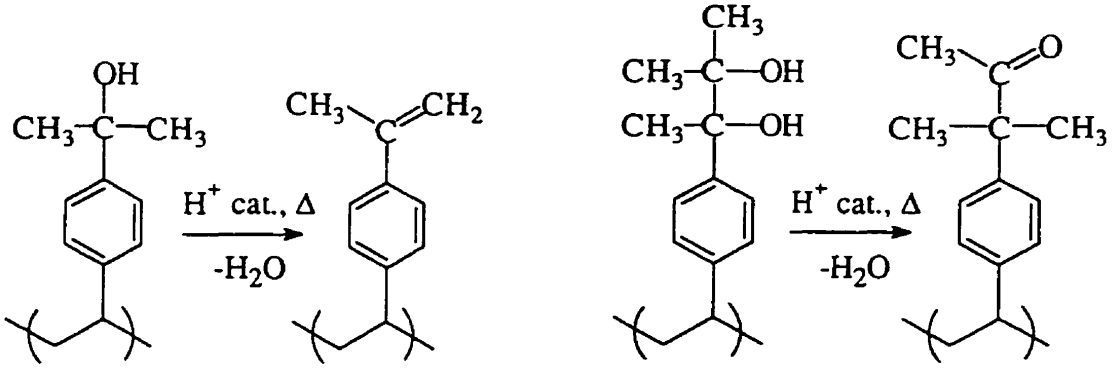


Figure A-5. Polar->nonpolar transitions by acid-catalyzed dehydration.

A-3.3. Crosslinking

Crosslinkable CA resists have formed negative-tone images, mostly through acid-catalyzed electrophilic aromatic substitution reactions, with remarkable DUV-sensitivities – well below 1 mJ/cm^2. Thus, protonation of small polyfunctional or polymer-bound benzylic ether, ester, alcohol [39-41], or 1,3-dioxolane [42] groups forms carbocations which readily attack polymer phenolic groups. Exposed areas thus become heavily crosslinked and insoluble, and sometimes, even unswellable (**Figure A-6**).

The crosslinking of unsaturated or epoxy monomers, oligomers or polymers by photogenerated cationic or radical catalysts has rarely been used for microlithography [43], but more for the lower-resolution applications of photocured coatings [44], and for ***Laser Directed Imaging (LDI)*** [45]. LDI offers direct transfer of image from design software into resist image by computer-directed laser beam without intermediate mask production.

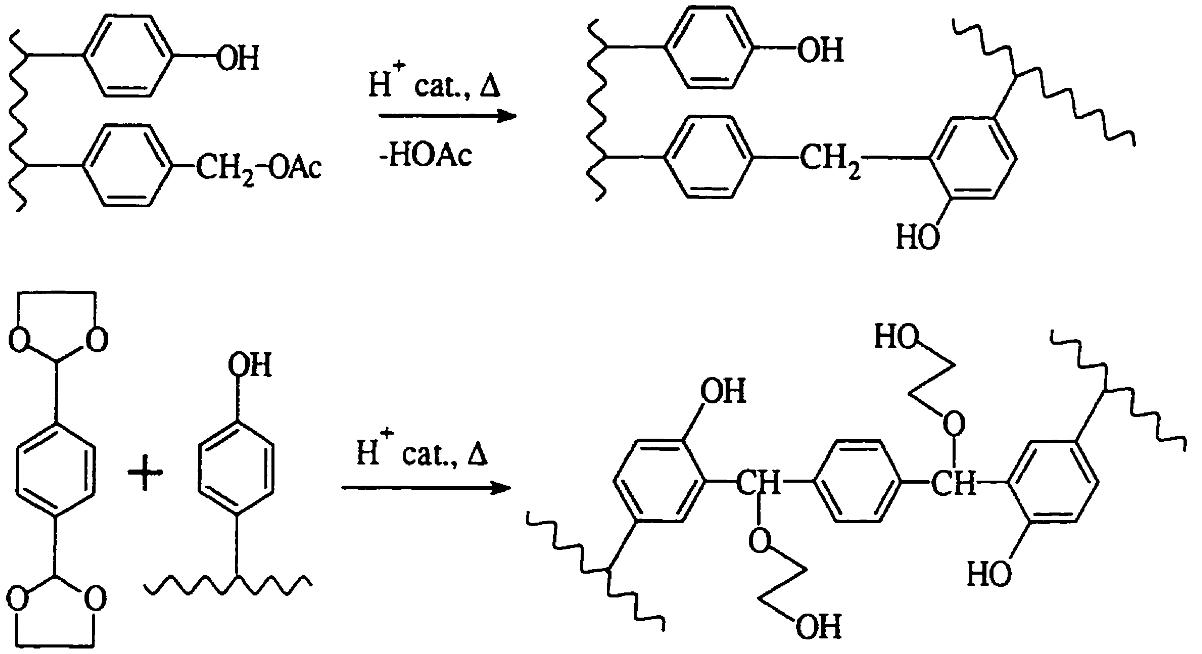


Figure A-6. Acid-catalyzed crosslinking by latent electrophiles that are (top) polymeric, or (bottom) small polyfunctional molecules.

A-3.4. Chain Scission and Depolymerization

Photoacid-catalyzed cleavage of tertiary or allylic ether, ester or carbonate moieties along a polymer backbone leads to chain scission that increases the solubility of exposed areas, for positive-tone images (**Figure A-7**). At the extreme, near-complete transformation of the resist to volatile compounds is possible: this would eliminate the need for liquid or plasma developers (self-developing resist), but premature evolution of condensable vapours can contaminate electron-beam or other exposure tools. Photolytic decapping of end-protected polyacetals with low ceiling temperature leads to a depolymerization cascade. Strong acid from irradiated PAG can also lead to simultaneous decapping, mid-chain scission and depolymerization of similar polymers [46,47].

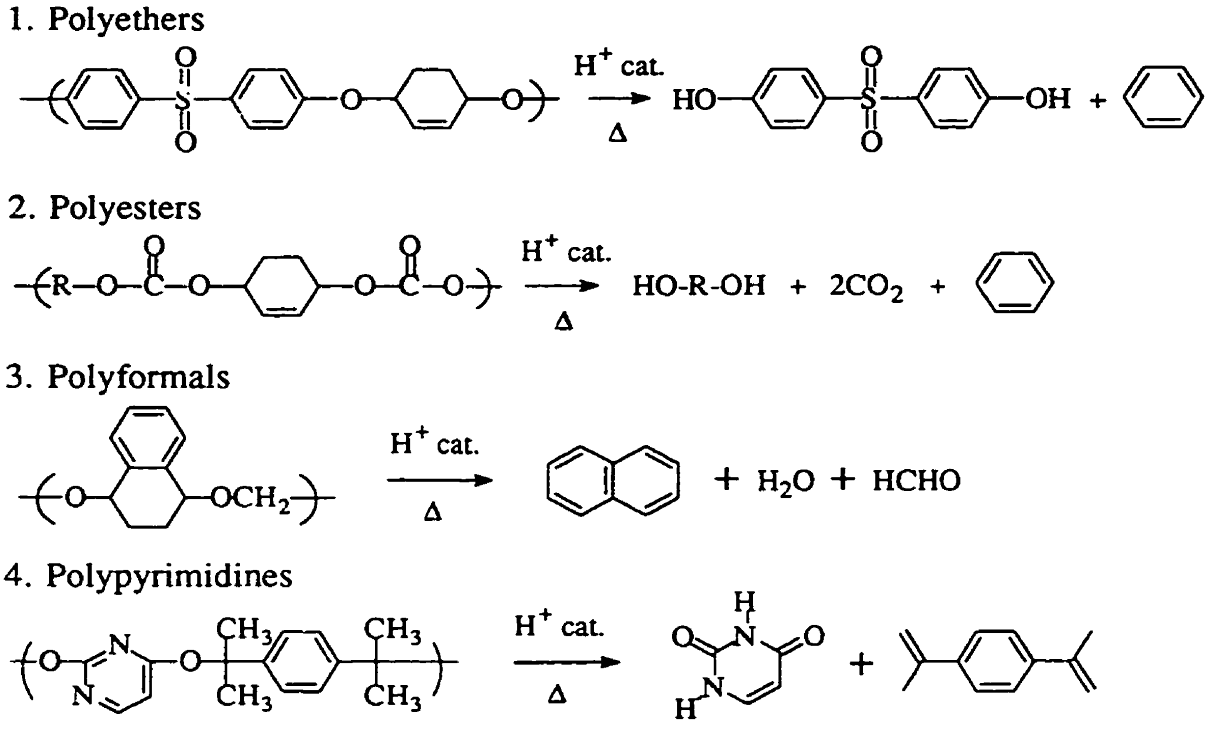


Figure A-7. Acid-catalyzed thermodecomposition of polymer backbones.

A-4. PROCESSING CONSIDERATIONS

The main advantage of CA resists, their catalytic nature, also causes their main troubles: extreme sensitivity to processing parameters and contamination. For each resist formulation, the conditions for exposure, PAB, PEB and developing must be optimized and made reproducible, since these factors greatly affect sensitivity, contrast and resulting pattern quality.

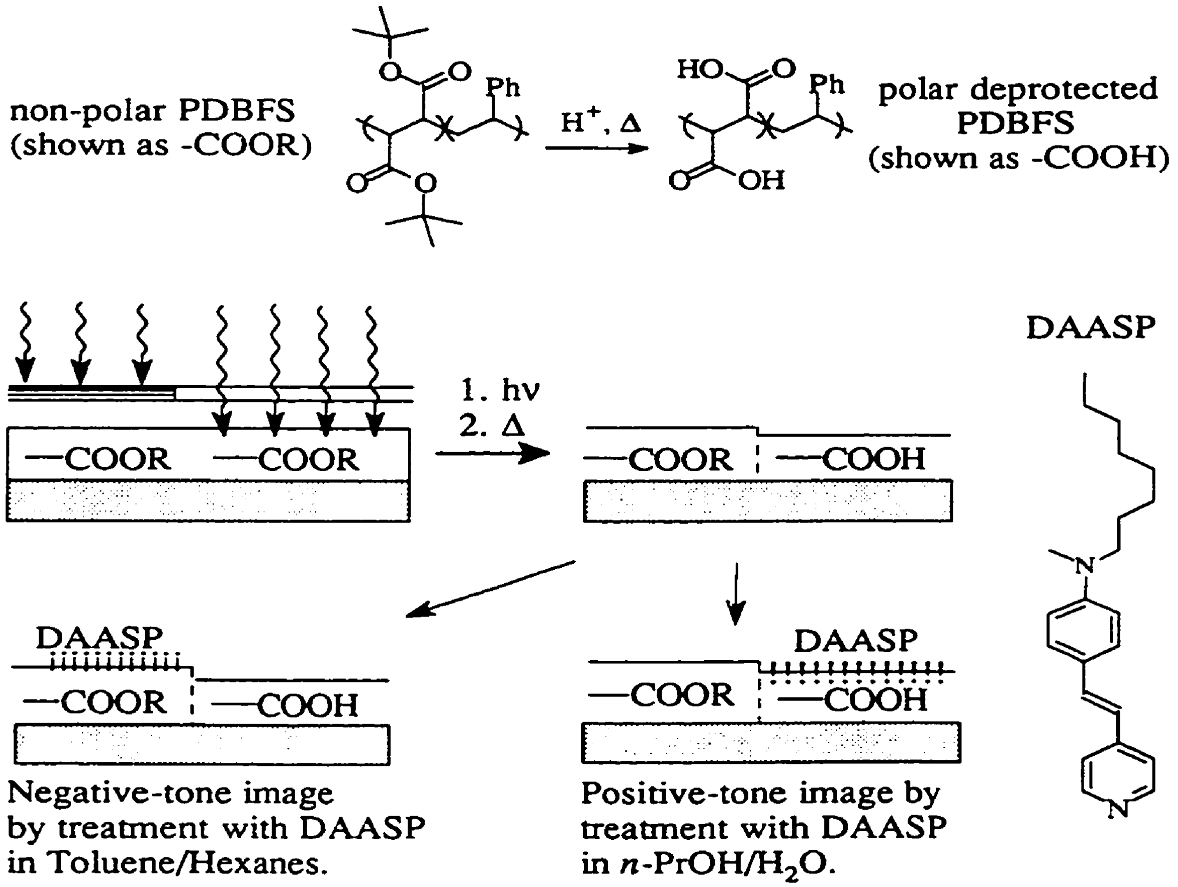
Any non-filtered laboratory or manufacturing environment contains trace amounts of ammonia, N-methyl-pyrrolidine, water, alcohols, and other relatively basic impurities [48,49]. Sorbed into resist films and substrate, these scavenge acid as it is photogenerated, thus decreasing sensitivity and image quality. The following suggestions have been made to reduce this problems:

- to minimize delay between resist spin-coating, irradiation and catalytic reaction steps;
- to eliminate contaminants by working in filtered air or in vacuum;
- to protect resists by transparent acidic or hydrophobic coating [50-52];
- to slow down absorption of contaminants by sufficient annealing near resist T_g (PAB) to remove casting solvent and close voids and microcracks [49,53];
- to design resists with components that are less affected by contaminants; e.g. stronger photo-generated acid, labile groups that are more basic than contaminants, special additives to repel or neutralize contaminants [27]; base-catalyzed resists.

A-5. FUNCTIONAL IMAGING WITH CA RESISTS

Drastically restructuring CA resists in catalyzed reactions not only alters their solubility, but the whole set of their chemical, physico-chemical and physical properties. These include: wettability, permeability, density, optical and thermal parameters, further reactivity, etc. Several microlithographic designs involve a functional development step to change etch resistance of either exposed or unexposed areas before relief development. In one, some silicon-containing species are selectively bound to catalytically deprotected phenolic or methacrylate moieies [54]. In another, the DESIRE process, silicon-containing vapours hardly penetrate acid-crosslinked areas, but selectively accumulate only in unexposed areas of novolak or poly-hydroxystyrene [55,56]. With all, subsequent relief development by *oxygen reactive ion etching* (*O_2-RIE*) then forms relief images due to differences in etching rates between silicon-containing and silicon-free areas. Electron microscopy shows that this anisotropic plasma treatment creates features of extremely vertical profile and high *aspect ratio* (resist thickness divided by minimum feature width). Many related designs using concepts of silylation (and multilayers, etc.) were reviewed recently by Gozdz [57] and Sebald [58].

As will be described in **Chapters C** and **D**, using photo-directed alteration in reactivity, wettability and permeability, selective space-resolved binding of various organic and inorganic chemicals were done with poly(di-*t*-butyl fumarate-*co*-styrene) resist (PDBFS) [59,60]. An example of control over physical properties is alteration of resist refractive index (for integrated waveguides): PDBFS before and after deprotection, and after further modification with calcium ions, shows refractive indices of 1.51, 1.55 and 1.58 respectively [60]. Micron-scale fluorescent pictures were created by treatment of this resist with various dyes in organic solvents (negative-tone) or in water:alcohol mixtures (positive-tone; **Figure A-8**).



Negative-tone image by treatment with DAASP in Toluene/Hexanes.

Positive-tone image by treatment with DAASP in n-PrOH/H_2O.

Figure A-8. An example of a dual-tone functional imaging with a CA resist and an amphiphilic dye 4-(p-dialkylaminostyryl)pyridine (DAASP).

A-6. CONCLUSIONS AND OBJECTIVES

Whatever new high-resolution radiation sources or techniques will occupy the market in the next decades, CA resists will continue to advance their important idea of amplifying by catalysis the primary events of irradiation [61]. Current opportunities for research and development in this area include:

- developing, understanding and applying new chemistry to CA resists;
- exploring "super amplification" resist designs, where acid-formation and/or resist development can be made auto-accelerating;
- engineering deep- and vacuum-UV, X-ray and E-beam exposure tools, and CA resists that best fit each;
- progressing in dry-developable, multilayer and top-surface resist techniques;
- developing environment-friendly water-castable and water-developable resists;

Along with their mainstream use in microlithography, the relief and functional imaging of CA resists can be useful in any field where submicron features need to be created. Possible novel applications include:

- micro-optical elements for waveguide circuits and other photonics (spatial control of material refractive index, optical rotation, nonlinear optical properties);
- holographic-, photo- and data-recording (photorefractive or photochromic) media, high-resolution color displays (precise positioning of dye spots);
- bioapplications (array biosensors and array biosyntheses);
- templates for space-resolved chemical and physico-chemical processes;
- patterned polymer-inorganic or polymer-organic composite structures.

Thus, in the beginning of the presented Ph.D. project several targets were chosen: design, synthesis and evaluation of new CA resists (**Chapter B**); exploration of a "Functional Imaging" concept, same as the space-selective modification of resist templates with metal ions (**Chapter C**) and with organic materials (**Chapter D**); and synthesis and evaluation of environmentally friendly water-processable CA resists (**Chapter E**).

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Chapter B

Poly(Di-*tert*-Butyl Butenedioate-*alt*-Styrene): Synthesis and Lithographic Evaluation

B-0. ABSTRACT

New photoimaging materials were formulated by dissolving photosensitive onium salts into the free-radical copolymer of di-*tert*-butyl *trans*-butenedioate (di-*tert*-butyl fumarate) and styrene. Exposure to mid- or deep- UV, followed by baking, drastically altered material solubility, absorbency and other properties, through mass cleavage of the polymer's numerous ester groups by photogenerated strong acid catalyst (chemical amplification). With aqueous base or organic solvent as developer, respectively positive-tone or negative-tone relief images could be obtained with submicron resolution. The materials also showed other good qualities for their application as microlithographic resists, such as sensitivity (14-38 mJ/cm^2), contrast ($\gamma = 4$-7), transparency (0.17 μm^{-1} @254 nm), and thermal stability against both flow-distortion (T_g of 139 °C for fresh copolymer; 199 °C after deprotection) and depolymerization (> 300 °C).

B-1. INTRODUCTION

As was described in **Chapter A**, the generation of images through photoinduced chemical changes in sensitive coatings remains a fertile field for fundamental and applied research. In particular, the prospect of fabricating ever smaller and faster microelectronic and microoptoelectronic devices has driven the search for new microlithographic resists of ever higher resolution, sensitivity and endurance. So far, relief images for microlithography with submicron resolution and excellent process latitude have been achieved by combining advanced technology with new chemistry [1]. Particularly fruitful has been the strategy of chemical amplification [2], in which a primary photochemical event produces a reactive species that goes on to catalyze extensive transformation of the resist material (see more details in **Section A-1**). Thus, in combination with onium salts or other acid photogenerators, certain functionalized novolak or styrene polymers have shown promising lithographic properties, PolyTBOCST being the well-known example [3].

The evolution of resists can be described as a progressive adjusting of materials properties towards simultaneously meeting all the requirements of the lithographic process, which are many and often conflicting: shelf-life vs. sensitivity, transparency at the short wavelengths needed for highest resolutions vs. plasma resistance requiring aromatic groups, ease of annealing vs. thermostability, etc. (**Table A-1**).

Many CA resists have been inspired by the use of protecting groups in synthetic organic chemistry, in which "capped" carbonate, ester or ether groups can undergo acid-catalyzed "deprotection" reactions to become much more polar carboxyl or hydroxyl groups. Carboxylic acids would be particularly attractive groups to permit both relief and functional development, via deprotonation and/or ion exchange (**Section A-3.1.**). Such are generated from co/terpolymers of *t*-butyl with other alkyl acrylates undergoing thermo-acidolytic deprotection with photogenerated acid, permitting their relief development with aqueous base [4]. These aliphatic polymers also possess excellent UV transparency down to 190 nm, but, without silicon or other plasma-resistant moieties, their films cannot later withstand conditions of the substrate etching step.

Alternatively, polymers of protected vinylbenzoic acid sufficiently resist such etching, however, conjugation between the carbonyl and aromatic ring results in strong optical absorbance below 320 nm [5]. A further improvement has been the copolymer of *t*-butyl methacrylate with α-methylstyrene, that combined etch-resistance with acceptable deep-UV transparency [6]. However, with only one ionizable group per 12 carbons, even the largely-deprotected matrix proved hard to dissolve in aqueous base without the addition of cosolvents such as *iso*-propanol. Recent similarly acidolyzable copolymers based on two or more nonaromatic methacrylate and/or acrylate monomers have also offered opportunities in designing sensitive resist materials for seminal near-vacuum UV (193 nm) lithography [4], their physical and chemical properties could be fine-tuned by manipulating ratios of the several comonomers [6]. The further incorporation of styrene or other vinylarene monomer into such acid-sensitive poly(meth)acrylate copolymers improved their resistance to fluorocarbon plasma etch and other harsh processing conditions without greatly decreasing transparency in the still-important deep-UV region (254 nm) [6]. We reasoned that a copolymer of an acid-sensitive diester of *cis* (maleic) or *trans* (fumaric) butenedioic acid could contain many such etch-resistant aryls, and still maintain a sufficient number of reactive ester groups for comparable or even improved photosensitivity, contrast and dissolution speed of the eventual resists. It was also expected that a generally greater number of pendant groups along the polymer backbone would also increase chain stiffness, thus raising T_g (from ca. 100 °C for styrene and 107 °C for *tert*-butyl acrylate homopolymers) [7] so that latent or developed images would be even less prone to soften or melt during processing.

B-2. EXPERIMENTAL SECTION

B-2.1. Materials and Instrumentation

Unless otherwise noted, chemicals were purchased in reagent grade from Aldrich Inc. and used as received. Styrene was distilled before use under reduced pressure. Toluene for polymerisation was dried overnight with calcium hydride and distilled before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Eastman Kodak Co. and purified by recrystallization. Diphenyliodonium, triphenylsulfonium and 4-(phenylthio)-phenyl diphenylsulfonium hexafluoroantimonates (DPI-SbF_6, TPS-SbF_6, 4TS-SbF_6), and diphenyliodonium triflate (DPI-OTf) were prepared according to reported procedures [8].

UV-visible spectra were recorded on a Shimadzu/Bausch & Lomb Spectronic 210UV spectrophotometer. Infrared analysis was performed on a Bruker IF-48 FTIR spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on either Gemini-200 or XL-200 Varian machines using tetramethylsilane as internal reference. Molecular weights were determined by gel permeation chromatography, relative to polystyrene standards and using chloroform as eluent, on a Waters-510 GPC instrument. Intrinsic viscosity was measured by dilution viscometry in chloroform at 25 °C using a 3 mL Ubbelohde viscometer. Differential scanning calorimetry (DSC) was done using a Seiko DSC 220 at a heating rate of 10 C°/min, with glass transition temperature (T_g) taken as the midpoint of a trace inflection. Thermal gravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 at a heating rate of 10 C°/min under nitrogen.

Substrates for coating were either pieces of Unisil silicon test wafers 3" x 330-432 μm <111>, or National Scientific GE 124 polished fused quartz plates 1" x 1" x 1/16". Polymer films were applied onto substrates from solution using a Headway Research spin-coater. Film thickness was measured using a Sloan Dektak profilometer. UV sources consisted of a Cole-Palmer 9815 Series 100 W DUV Hg lamp with a built-in 254 nm narrow bandwidth filter at 30 cm from samples, or an Oriel 87100 exposure system in mid-near-UV mode (90% 365 nm, 10% 313 nm); corresponding exposure doses were measured at 254 nm and 313/365 nm using Optical Associates powermeters OAI P306-001-002 and -008-002 respectively, and controlled with timers. Exposures were made with contact printing through a metallized quartz Optoline-Fluroware density photoresist step tablet REK/73 with resolution to 1 μm. Scanning electron micrographs were obtained on a JEOL JSM-840 or JSM-6100 at 15-20 KeV accelerating voltage after Au/Pd sputter coating.

B-2.2. Synthesis of Di-*tert*-Butyl Maleate (1)

From ref. [9]: maleic acid (20 g, 172 mmol), concentrated sulfuric acid (2 mL, 40 mmol), *tert*-butanol (40 mL, 430 mmol) and isobutylene condensed at -78 °C (50 mL, 530 mmol) were mixed in a pressure bottle that was then shaken mechanically at room temperature for 24 h. The bottle was then opened at -78 °C and the contents poured into a solution of NaOH (30 g, 750 mmol) in ice-water (150 mL). The resulting mixture was extracted with diethyl ether, and the organic phase dried ($MgSO_4$) and evaporated; Kugelrohr distillation of the residue gave colourless crystals of **1** (31 g, 79%): mp 65-66 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.0 (s, 2H, =CHCOOR), 1.5 (s, 18H, $-COOC(CH_3)_3$).

B-2.3. Synthesis of Di-*tert*-Butyl Fumarate (2)

From ref. [10]: to a solution of fumaryl chloride (56.6 g, 370 mmol) in THF (1 L) at 0 °C was added potassium *tert*-butoxide (83 g, 740 mmol). After stirring for 24 h at room temperature, the resulting mixture was filtered through silica gel (200 g), washing through with chloroform and methanol. The combined filtrate was evaporated to a black oil, from which Kugelrohr distillation produced **2** as white crystals (26 g, 31%): mp 67-68 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.6 (s, 2H, =CHCOOR), 1.4 (s, 18H, $-COOC(CH_3)_3$).

B-2.4. Synthesis of Poly(Di-*tert*-Butyl Fumarate-*co*-Styrene) (3a)

A flame-dried heavy-walled borosilicate glass tube was charged with **2** (25.6 g, 112 mmol), styrene (11.7 g, 112 mmol), dry toluene (55 mL) and AIBN (0.400 g, 2.44 mmol). The mixture was cooled to -78 °C in a dry ice/acetone bath, thrice degassed under vacuum then refilled with nitrogen, then the tube was sealed, heated at 60-70 °C for 24 h, then cooled to room temperature and its contents poured into methanol:water 1:2 v:v. The resulting precipitate was collected by filtration and redissolved into chloroform, then the solution was filtered through Celite, and the filtrate concentrated and poured into methanol:water 1:1 v:v to give fibrous white solid **3a** (13.5 g, 36%): GPC ($CHCl_3$, polystyrene standard) M_n 1.2 x 10^4, M_w/M_n 1.7; viscometry ($CHCl_3$, 25 °C) $[\eta]$ 0.10; ^1H NMR (200 MHz, $CDCl_3$) δ 7.5-6.2 (C_6H_5), 2.8-2.2 ($>CHCO_2-$), 1.9-0.5 ($-COOC(CH_3)_3$), with intensities corresponding to di-*tert*-butyl fumarate:styrene 0.75-0.80:1 mol:mol; ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.5-171 (C=O), 142.2 & 140.0 & 128.2 & 126.2 (C_6H_5), 81.1 & 80.3 ($-COOC(CH_3)_3$), 54.8 & 42.9 & 40.2 ($-CHPhCH_2-$, $>CHCOO-$), 27.9 ($-COO(CH_3)_3$).

B-2.5. Preparation of 3a-Based Photosensitive Coatings

Polymer **3a** was dissolved, together with 5-10% of its weight of DPI-OTf, DPI-SbF_6, TPS-SbF_6 or 4TS-SbF_6, into either propylene glycol methyl ether acetate (PM Acetate) or chlorobenzene, to 20 or 10 wt % respectively. The solutions were then filtered through a 0.2 µm Teflon membrane filter, then spin-coated onto silicon or quartz substrates at 1200 rpm for 60 s followed by Post-Apply Baking (**PAB**) on a hot plate at 100-135 °C for 60-300 s to form a ca. 1 µm thick film. FTIR (IR-transparent silicon substrate) and UV (fused quartz substrate) spectra were obtained therefrom in transmittance modes.

B-2.6. Development into Relief Images

3a-based photosensitive coatings on silicon substrate were exposed to UV radiation as described, generally through the step tablet, and then treated by Post-Exposure Baking (**PEB**) on a hot plate at 110-150 °C for 120-300 s, then developed using various solvents. Negative images resulted from several organic pure solvents or mixtures (typically, hexanes:toluene 3:1 v:v), and positive images from aqueous solutions of 1.5 wt % K_2CO_3 (with or without added *i*-propanol) or 1-5 wt % tetramethylammonium hydroxide (TMAH). Where dissolution was incomplete, the thickness of the remaining film was measured with the profilometer, normalizing with respect to the thickness before development, and a contrast curve was produced from which sensitivity and contrast were determined [1]. Appropriate portions of the images were then inspected and photographed through optical or scanning electron microscopes.

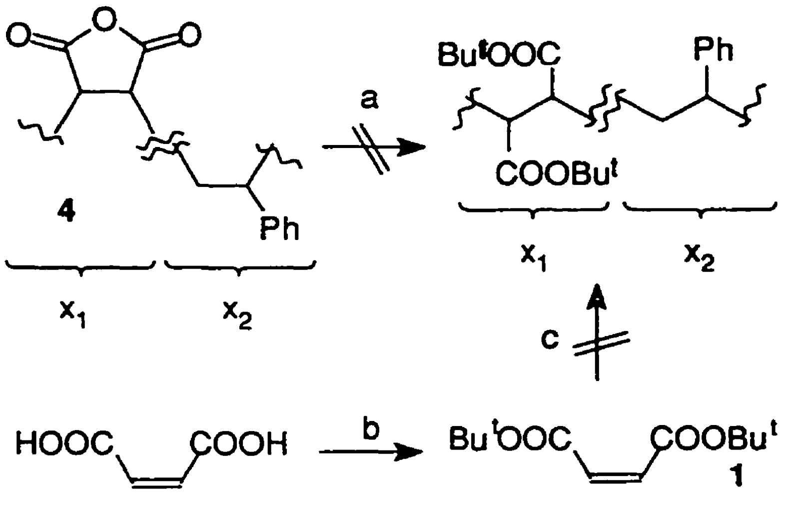
B-3. RESULTS AND DISCUSSION

B-3.1. Copolymer Synthesis

Possible synthetic routes to a dialkyl butenedioate-vinyl arene copolymer include: (i) esterification of pre-formed (even commercial) maleic acid or anhydride copolymer (**4**); (ii) copolymerization of dialkyl maleate with appropriate comonomer; (iii) copolymerization of dialkyl fumarate with appropriate comonomer. Although many procedures [11] for esterification of carboxyl-containing polymers are available, our attempts towards synthesis of acidolyzable poly(di-*tert*-butyl maleate-*co*-styrene) via route (i) were complicated by incomplete reactions and crosslinking or other side-reactions. The potential maleate monomer **1** was then synthesized, but its attempted copolymerization with styrene failed to give any copolymer product (**Figure B-1**).

Though very similar or identical products result from addition of a radical to either *cis* or *trans* isomers of dialkyl butenedioate, the transition state during the former is destabilized by loss of coplanarity through steric repulsion between the bulky ester alkyls: thus polymerizations involving dialkyl maleates such as **1** proceed only very slowly or not at all [12]. The much more polymerizable monomer **2** was prepared by modifying a reported method [10] reacting fumaryl chloride with potassium *tert*-butoxide (**Figure B-2**): substituting THF for benzene, and distillation for crystallization, gave a cleaner product in higher yield. Radical polymerization of equimolar quantities of **2** with styrene gave copolymer **3a** at a molecular weight range appropriate for spin-coating. ^{1}H NMR of **3a** showed that nearly half (ca. 40%) of the copolymer's repeating units came from monomer **2**. ^{13}C NMR of **3a** showed detectable carbonyl peaks characteristic of consecutive butenedioate units, as with spectra of dialkyl fumarate homopolymer [12]. This suggested a rather random distribution of styrene and butenedioate units in our copolymer. Other details of chain microstructure were hard to verify. Attempted copolymerization of **2** with other vinylarenes such as α-methylstyrene or trans-stilbene under similar conditions did not form copolymers **3b** or **3c**, possibly due to extreme steric interference with propagation.

Alone, copolymer **3a** showed only low absorbance (0.17-0.18 μm^{-1}) at such currently-interesting deep-UV wavelengths as 248 nm (from KrF excimer laser) and 254 nm (from Hg lamp), and even less at mid-UV above 300 nm (**Figure B-3**). DSC showed its T_g to be 139 °C, a good compromise between requirements for mild PAB conditions and for stability of images against thermal distortion during PEB and some dry etching procedures. A characteristic reaction of *tert*-butyl ester compounds, including di-*tert*-butyl butenedioate homopolymer [12], is cleavage to isobutylene gas and free carboxylic acid. With **3a**, results from DSC (**Figure B-4**), TGA (**Figure B-5, b-e**) and FTIR (**Figure B-6, a-b**) all showed this to occur only near 245 °C in the absence of photogenerated or other strong acid (thermolysis), yet below 100 °C in its presence (thermal acidolysis): a wide processing window for potentially good contrast. DSC of the deprotected polymer showed an even higher T_g at 199 °C, again good for dimensional stability of hot images. Whether or not acid was present, FTIR (**Figure B-6c**) and TGA (**Figure B-5d**) only showed extensive dehydration of the carboxylic acid groups to cyclic (and possibly some intermolecular) anhydride on heating above 200 °C. The resulting material, now quite similar to commercial styrene-maleic anhydride copolymer, further decomposed to volatile compounds only above 300 °C, indicating a chemical stability to high temperatures that could help it withstand plasma environments.

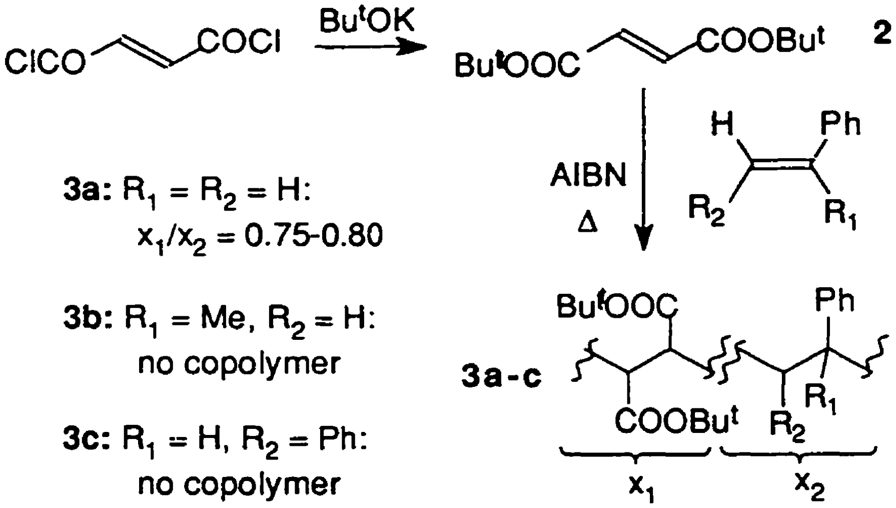


(a) $(Bu^tO)_2CHNMe_2$/toluene, or other reagents;

(b) 2-methylpropene/tert-butanol/acid catalyst;

(c) styrene/AIBN catalyst/ heat.

Figure B-1. Attempted syntheses of poly(di-tert-butyl maleate-co-styrene) through copolymerization and esterification



3a: $R_1 = R_2 = H$: $x_1/x_2 = 0.75$-0.80

3b: $R_1 = Me$, $R_2 = H$: no copolymer

3c: $R_1 = H$, $R_2 = Ph$: no copolymer

Figure B-2. Synthesis and copolymerizations of di-tert-butyl fumarate

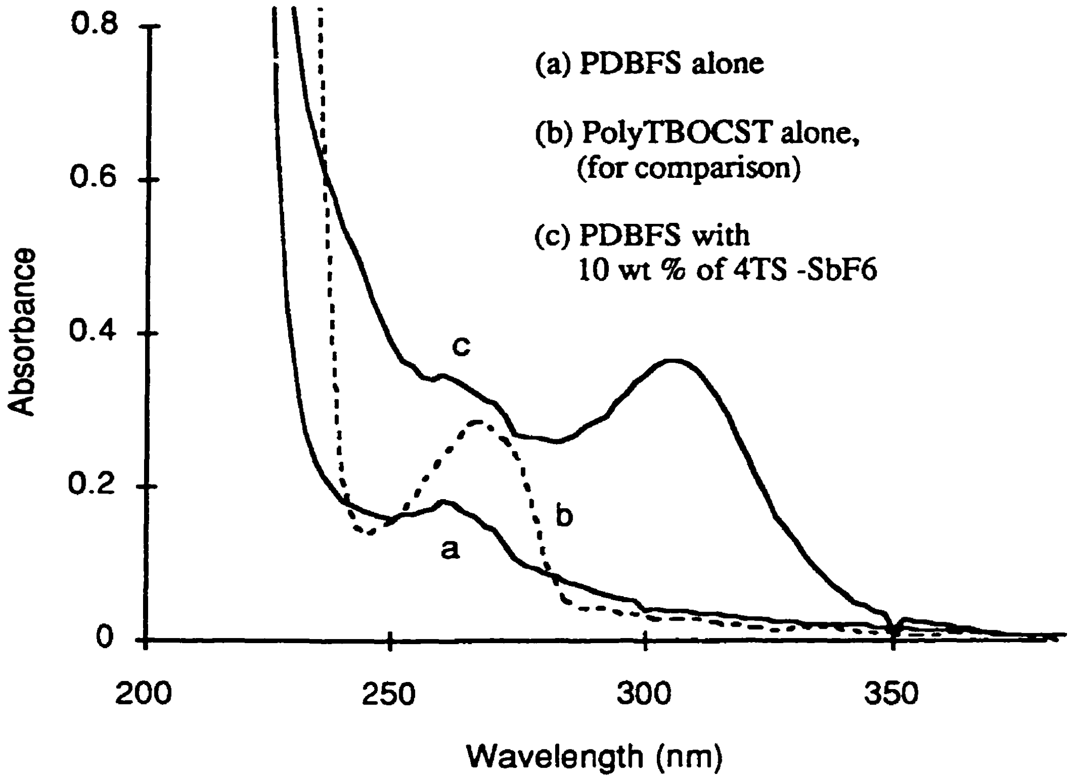


Figure B-3. UV spectra of 1 μm films

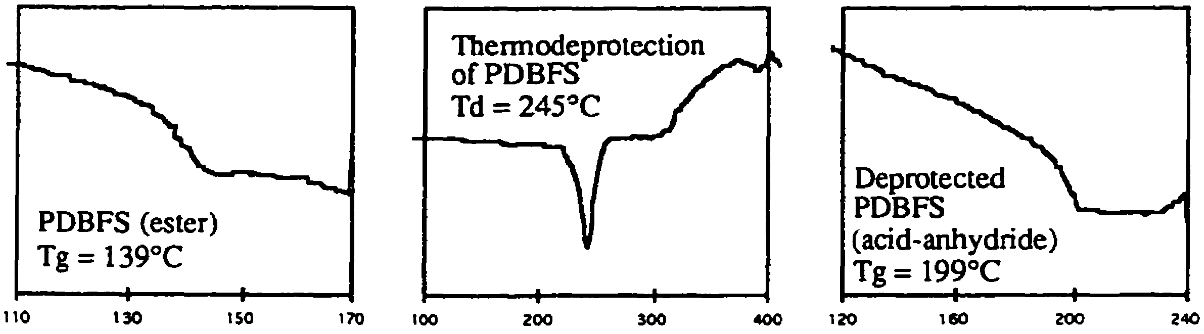


Figure B-4. DSC curves of PDBFS (dM/dT vs. temperature)

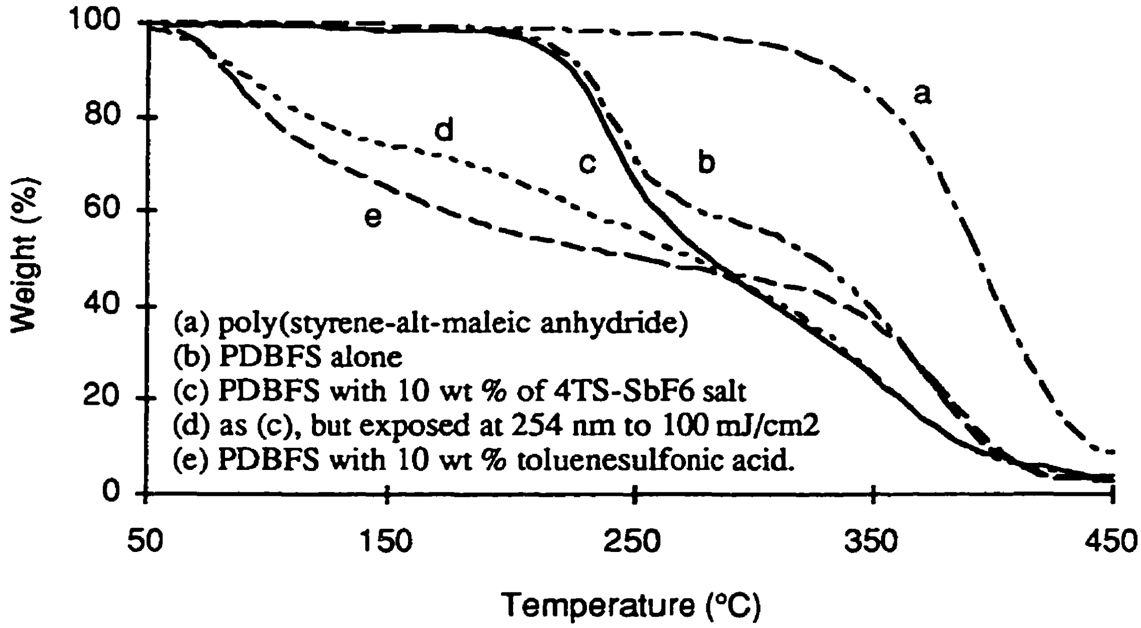


Figure B-5. TGA curves of polymers

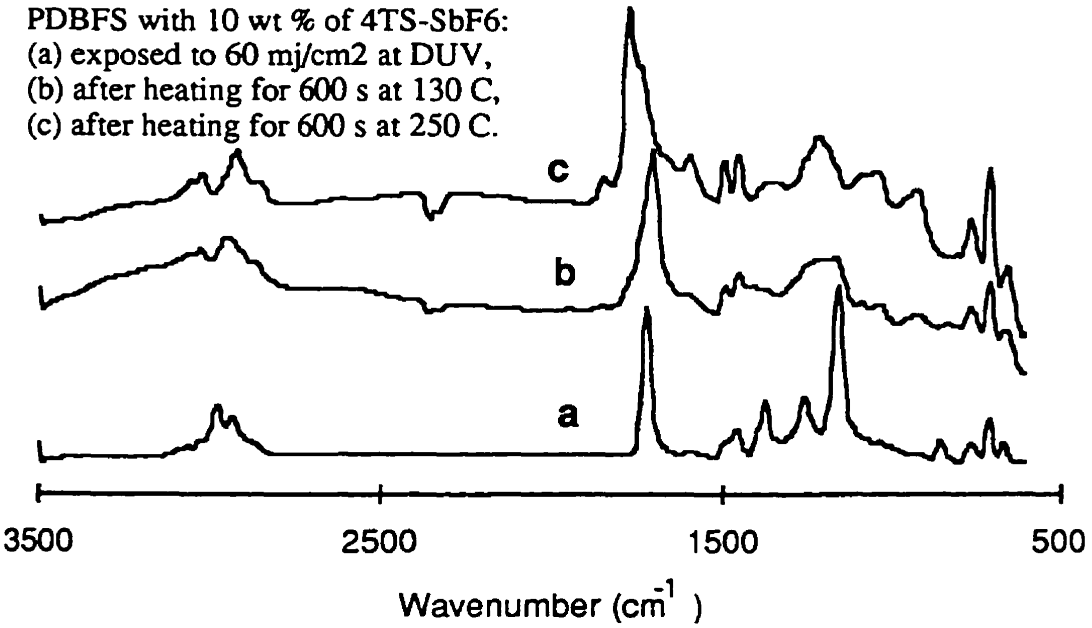


Figure B-6. FTIR spectra of PDBFS resist

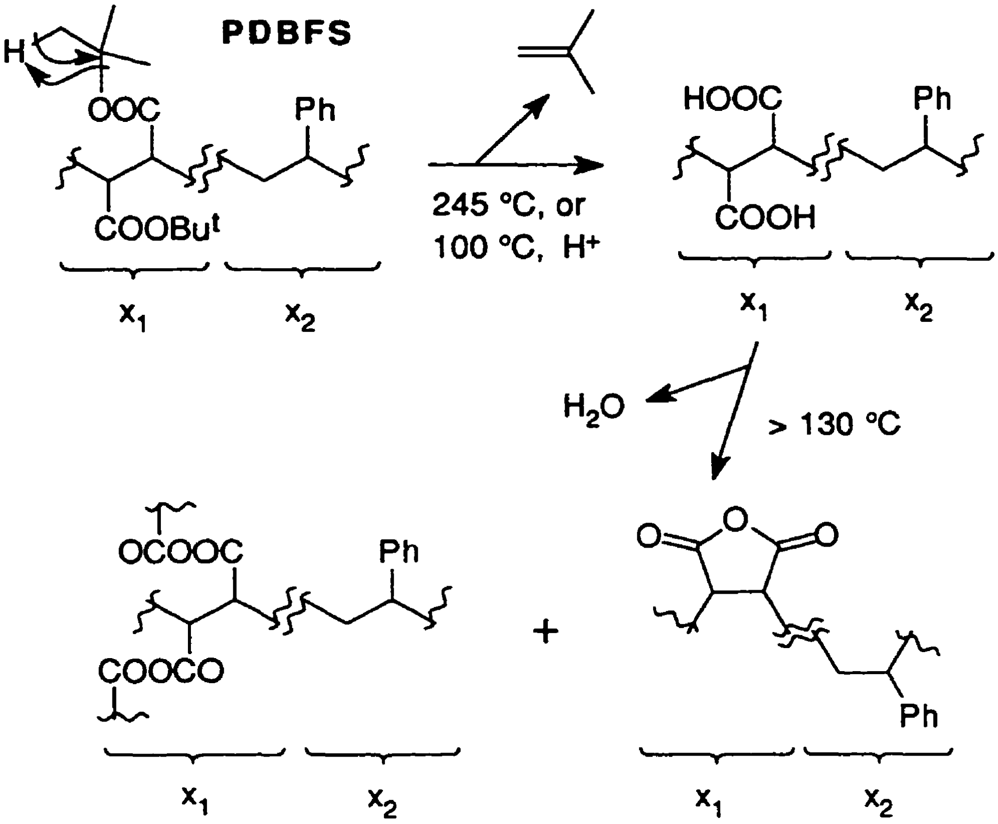


Figure B-7. Reactions of di-tert-butyl fumarate copolymer.

B-3.2. PEB Reactions and Relief Development of PDBFS

In the previous section we estimated the appropriate conditions for relief developing of PDBFS-based resists:

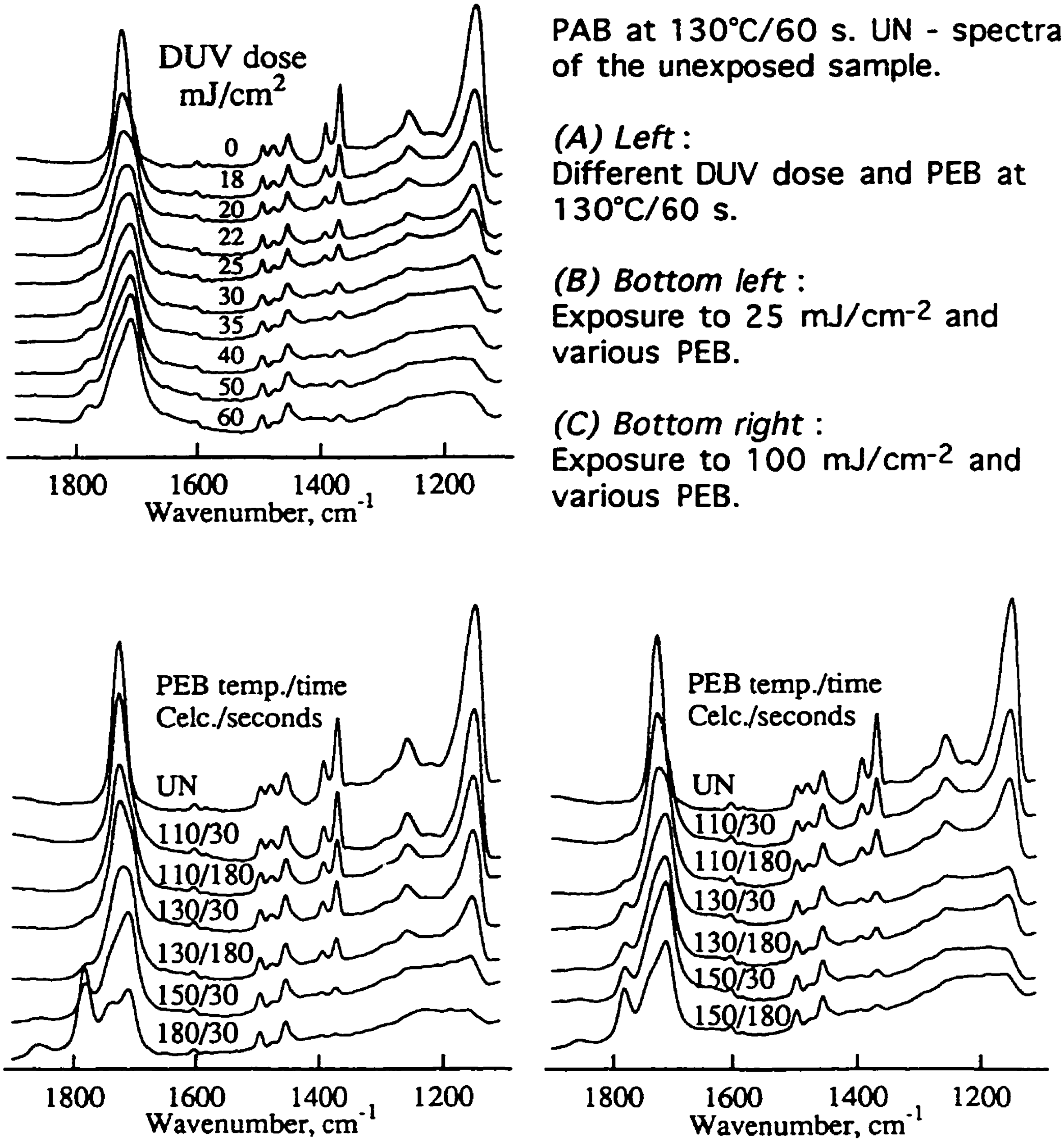
- PAB at 130-140 °C for > 60 s;
- exposure at deep- or mid-UV to > 14 mJ/cm^2;
- PEB at >100 °C for > 30 s;
- developing in aqueous base (positive tone relief image) or in some organic solvents (negative tone relief image).

But, for fine tuning of process parameters, more information is required about polymer matrix transformations, especially about acid-anhydride ratios after processing under different conditions.

Figure B-8 shows a representative set of IR spectra taken from PDBFS:4TS-SbF_6 films after different exposures, and PEB for 60 s at 130-135 °C. All characteristic ester peaks gradually disappeared with increasing UV dose: 1145 cm^{-1} (s, C-O-C, sym), 1254 cm^{-1} (m, C-O-C, antysym), 1367 cm^{-1} and 1392 cm^{-1} (m, CH_3), 1728 cm^{-1} (vs, C=O), 2977 cm^{-1} and 3003 cm^{-1} (m, CH_3). Formation of H-bonded carboxylic acid dimers was evident by a detectable C=O peak shift to 1708 cm^{-1}. With more heating, a new peak at 1780 cm^{-1} and a small satellite at 1855 cm^{-1} appeared, corresponding to the formation of sterically favorable cyclic anhydride (by comparison with succinic anhydride's 1790 cm^{-1} (s) and 1870 cm^{-1} (m), and maleic anhydride-*alt*-styrene polymer's 1779 cm^{-1} (s) and 1856 cm^{-1} (m) [13]).

The assignment of a distinct peak at 1745 cm^{-1} is debatable. It can hardly be an intermolecular anhydride, because generally this is a doublet, as in butanoic acid anhydride: 1820 cm^{-1} (vs) and 1700 cm^{-1} (s) [13]. The region around 1700 cm^{-1} is already occupied by the carboxylic acid peak, but we have never detected any 1820 cm^{-1} peak. A second explanation is that this C=O signal also originates from an acidic moiety, but which is positioned in an microenvironment different from that producing the 1708 cm^{-1} peak. To compare: IR spectra of different mono- and di-carboxylic acids often have a similar doublet signal at the C=O region, with a definite absence of anhydride signal pattern [13]. Distinct isolated, or dimeric, or polymeric H-bonded associates may be responsible for such kind of doublets. Working with somewhat similar resists, Ito et al. [14] have assigned the 1740 cm^{-1} peak to the "free" non-H-bonded carboxylic acid. There is no IR evidence of theoretically possible phenylketone groups.

As was expected, all processing parameters affected the eventual chemical composition of irradiated resist. 30 mJ/cm^2 of deep-UV is enough to remove almost all *t*-butyl groups after mild PEB. The immediate main products are carboxylic acid (1708 cm^{-1}) and "probably acid" (1745 cm^{-1}, see discussion above) groups in comparable amounts, although higher doses give slightly more of the 1708 cm^{-1} signal (**Figure B-8a**). Spectra after fixed UV dose and PEB at various temperature and time (**Figure B-8b**, 25 mJ/cm^2 and **Figure B-8c**, 100 mJ/cm^2) revealed that baking longer than 30 s at the same PEB gave little further changes. A more important factor was the PEB temperature: at 110 °C, deprotection was not complete even after 100 mJ/cm^2 and 180 s; while 130 °C and 150 °C baking gave massive deprotection to -COOH; but at higher temperatures (180 °C) and longer times more and more anhydride was formed.



PAB at 130°C/60 s. UN - spectra of the unexposed sample.

(A) Left :
Different DUV dose and PEB at 130°C/60 s.

(B) Bottom left :
Exposure to 25 mJ/cm^{-2} and various PEB.

(C) Bottom right :
Exposure to 100 mJ/cm^{-2} and various PEB.

Figure B-8. FTIR spectra of PDBFS/4TS-SbF$_6$ resist after different processing conditions

A preliminary comparative study, using different onium salts as PAG, showed these also to affect the product acid-anhydride ratio. At PDBFS:PAG 10:1 wt:wt loading, and identical PAB, PEB, and UV dose, the amount of anhydride gradually increased in the presence of 4TS-SbF_6, TPS-SbF_6 and DPI-OTf. Assuming a complete conversion to acid at such a high dose, TPS-SbF_6 and DPI-OTf release more acid for their mass, as their molecular masses are lower. Also, the stronger triflic acid from DPI-OTf may better promote eventual dehydration, compared to hexafluoroantimonic acid from 4TS-SbF_6 and TPS-SbF_6: indeed, we found that triflic acid from DPI-OTf intensively promotes condensation of vicinal carboxylic acid groups, while $HSbF_6$ from other onium salts was inactive under similar conditions (see **Chapter E** and ref. [15]).

Thus, this IR study has revealed a range of composition and processing conditions (the "processing window") for controling ester-acid-anhydride ratio. For example, based on these results, we chose PDBFS:4TS-SbF_6 10:1 wt:wt formulation , 100 mJ/cm^2 exposure, and PAB and PEB for 60 s at 130-135 °C, as standard conditions for binding experiments (see **Chapters C and D**). Thus, we have minimized any effects of slight variations of these conditions on the resist reactions.

B-3.3. Properties Alteration within CA Resists

Whatever mode of its development, an effective resist must show high contrast for sharp demarcation between exposed and unexposed areas. For reasonable concentrations of PAG, the amount of strong acid produced in a CA resist increases only in gentle linear fashion with the UV dose supplied. Even after subsequent PEB treatment of PDBFS/onium salt resist, the relationship between the content of its remaining *t*-butyl ester groups, and its previous UV dosage, typically appeared as a still shallow sigmoid curve (**Figure B-9**). The slow start here of ester cleavage at lower doses may be due to basic contaminants, such as perhaps this polymer's -CN end groups from the AIBN, that deactivated the first few units of acid that had been photogenerated. By 15 mJ/cm^2, increasing exposure had a stronger effect on further alteration of material, possibly because the new -COOH groups assisted in further *t*-butyl cleavage (autocatalysis). Beyond 30 mJ/cm^2, the curve leveled off again, perhaps because some ester groups were in regions of low onium salt or acid concentration, either through bulk heterogeneity (i.e. microphase separation), or uneven vertical distribution (i.e. relating to the less-soluble "skin" often seen in positive-tone relief development of CA resists [16]).

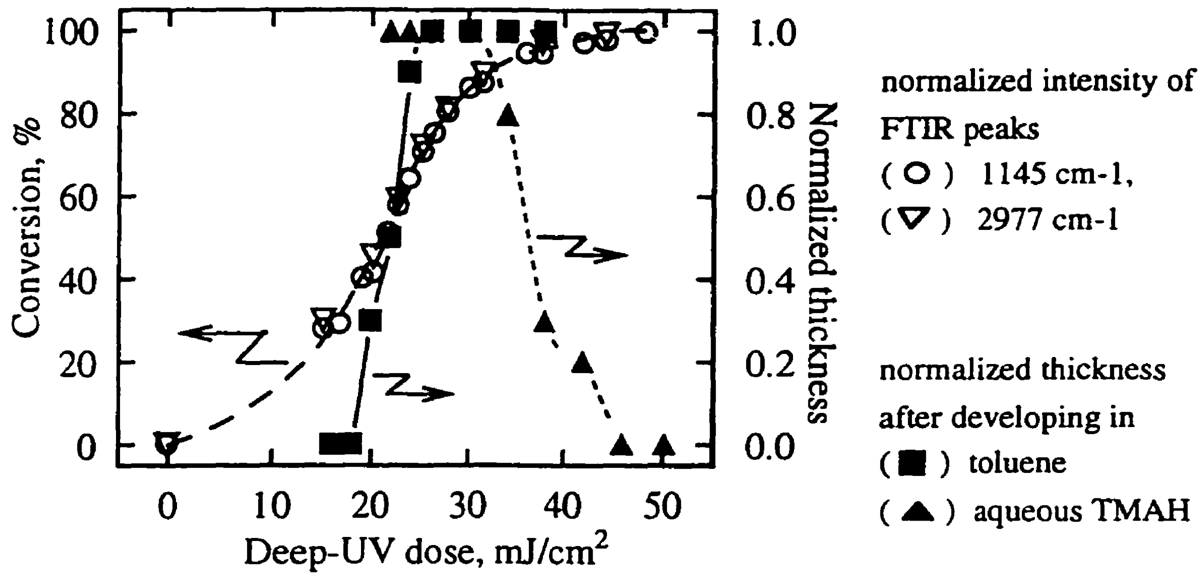


Figure B-9. Ester-to-acid conversion and developing of PDBFS resist vs. DUV dose (see Appendix for details on plotting normalized thickness and conversion curves)

Even the steepest slope of this "% ester vs. dose" curve was rather low. Similar low contrast between more- and less-exposed areas would also be expected for material properties which vary rather linearly with material composition, such as density, refractive index, or dielectric constant. However, for other material properties or processes that depend more on composition being above or below a critical threshold, contrast may be much higher. Thus, film dissolution of PDBFS/onium salt resist varied between nil and complete within a range of 7 mJ/cm^2 of UV energy and 40 mol % *t*-butyl ester content for negative-tone development with organic solvent, and 15 mJ/cm^2 and 10 mol % for positive-tone with aqueous base (**Figure B-9**). Indeed, the complete mechanism of film dissolution involves consecutive steps whose thermodynamics and/or kinetics can be highly cooperative:

- wetting - solvent or other solution components must penetrate the liquid/solid interface;
- permeation - these must then diffuse into the film to surround a given chain;
- (optional) reaction - polymer may have to be transformed, for example by deprotonation, to a more solvent-compatible form;
- solvation - chains are completely separated from each other and transported away into the liquid phase.

Even without eventual dissolution, the further alteration of a CA resist material during liquid functional development would also require at least the wetting then penetration of the resist, if not further reaction of its polymer, and thus would also be critically dependant on the composition of the "latent image". Thus, even though a steadily increasing UV dose only gradually produces more acid and acid-cleaved polymer product, the onset of new or greatly altered materials properties upon functional development could also be remarkably sudden. This suggests that the same resist that shows high contrast in relief development would also be a good candidate for many forms of functional development as well. **Chapters C and D** will describe use of PDBFS resist templates for space-selective immobilization of metal ions and some organic molecules.

B-3.4. Photolithographic Performance

Copolymer **3a** was able to dissolve and disperse several acid photogenerators that are typically employed in chemically-amplified resist systems. Thus, mixtures of **3a** with 5-10 wt % onium hexafluoroantimonates (DPI or TPS for deep-UV, and 4TS for mid-UV exposures) could be dissolved in organic solvents, and the solutions spin-coated onto flat substrates (ex. silicon wafers), followed by PAB near the T_g of the polymer to dry and anneal it [17], to give films that were smooth and clear. Contrast curves (ex. **Figure B-9**) showed how UV dose affected the solubility of these complete resists for similar PEB (again, optimized to near or slightly below the polymer's T_g) and relief development conditions.

Good sensitivities of 27-40 mJ/cm^2 were achieved from positive-tone relief development with either tetramethylammonium hydroxide (TMAH) or potassium carbonate (K_2CO_3) in pure water, though additional isopropanol (*iso*-PrOH) improved contrast with the inorganic base (**Table B-1**). For negative-tone relief development, enough carboxylic groups were deprotected with even 14-25 mJ/cm^2 for resists to become insoluble in common organic solvents (**Table B-1**), with the remaining COOH-containing polymer adhering particularly well to SiO_2/Si substrate. For either tone, liquid relief development happened with rapid dissolution (10-30 s) and high contrast ($\gamma = 4$-7). With even very modest optic systems, relief images to 1 μm resolution (the mask limit) could be produced (**Figure B-10**), providing at least 5 wt % onium salt had been employed, and PEB done promptly after exposure (to avoid the surface "skin" known [16,18] to complicate positive-tone development by aqueous base).

Table B-1. Development of PDBFS-based resist into relief images (a)

PAG	exposure	PEB, °C*min	developer(b)	sensitivity, mJ/cm^2	contrast(c)
5% 4TS	254 nm	135*5	2.5% TMAH:H_2O	42	7.6
5% 4TS	mid-UV	135*5	1.5% K_2CO_3:H_2O	40	4.5
5% 4TS	mid-UV	135*5	1.5% K_2CO_3:H_2O(d)	30	7.0
10% 4TS	mid-UV	135*5	1.0% TMAH:H_2O	36	6.1
10% 4TS	mid-UV	135*5	5.0% TMAH:H_2O	27	6.0
10% 4TS	mid-UV	135*5	1.5% K_2CO_3:H_2O	38	4.0
10% 4TS	mid-UV	135*5	1.5% K_2CO_3/H_2O(d)	32	7.0
10% DPI	254 nm	110*7	1.5% K_2CO_3:H_2O	40	4.0
10% TPS	254 nm	110*7	1.5% K_2CO_3:H_2O	38	4.0
5% 4TS	254 nm	135*5	toluene:hexanes 1:3	24	4.6
5% 4TS	mid-UV	150*5	toluene:hexanes 1:1	20	5.0
10% 4TS	mid-UV	135*5	toluene:hexanes 1:1	14	7.1
10% 4TS	mid-UV	135*5	n-butyl acetate	22	5.1

(a) 1.0± 0.1 µm of 3a:PAG; (b) developing for 10-30 s; (c) value of slope of contrast curve between normalized thicknesses of 0 and 0.7. (d) with 33 vol % of *i*-prpanol

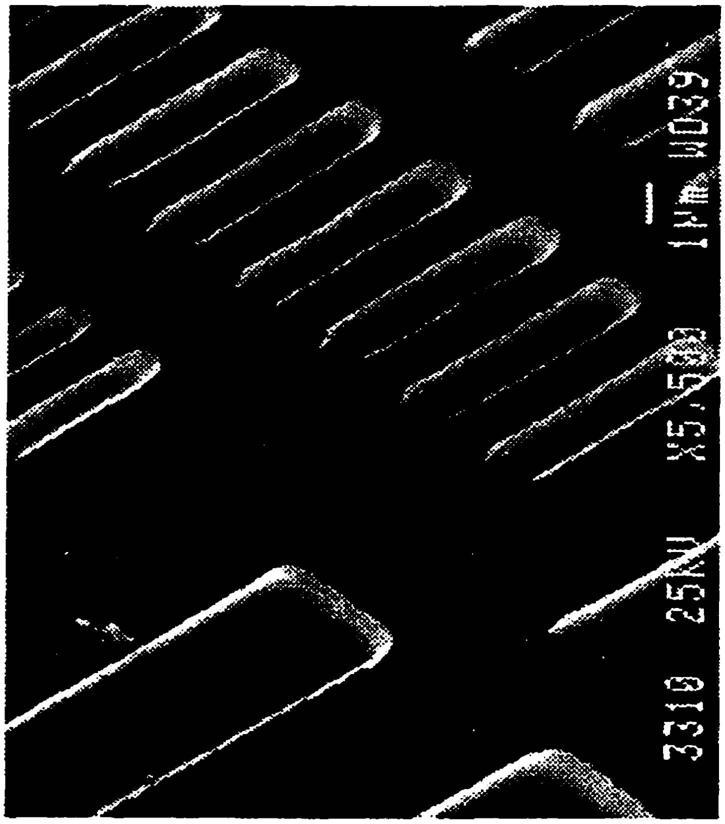
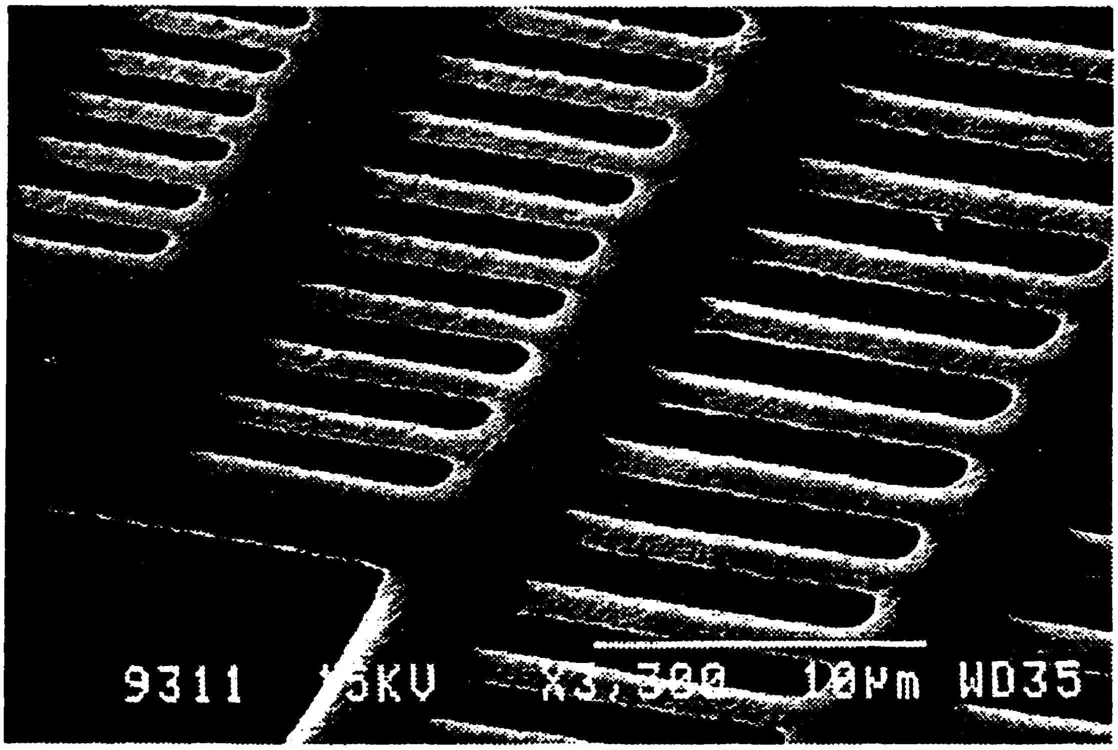


Figure B-10. SEM of relief images from 3a and 10 wt % 4TS -SbF$_6$ resist:

top:
negative-tone image
(i) 25 mJ/cm^2 at mid-UV,
(ii) PEB 300 s at 135 °C,
(iii) developingv in
toluene:hexanes 1:1 v:v.

bottom:
positive-tone image
(i) 40 mJ/cm^2 at mid-UV,
(ii) PEB 300 s at 135 °C,
(iii) developing in
1.0 wt % TMAH/H$_2$O.



Relief images were further tested to withstand higher temperatures such as might accompany some plasma or other processes. After heating a negative-tone relief image (mostly consisting of butanedioic acid/anhydride copolymer; T_g = 199 °C) for 0.5 h at 170 or 190 °C, SEM showed no noticeable distortion; image edges began to flow only at 210 °C or higher. The heat stability of developed positive-tone relief images (still containing -$COOBu^t$) could be improved to this range by further flood-exposure before baking to 135 °C or higher.

Thus, synthesised PDBFS appeared to be an excellent acid-sensitive matrix for CA microresists. Relief images were obtained in both negative- and positive- tone with micron resolution. The next two chapters will describe using the same resist for space-selective immobilization of metal ions (**Chapter C**) and organic molecules (**Chapter D**).

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Chapter C

Space-Selective Binding of Inorganic Materials into Chemically Amplified Resists

C-0. ABSTRACT

The same dramatic photosensitivity shown by films of chemically amplified resists that permits their patterned removal ("relief development", typical of microlithography), can also instead allow their further patterned chemical modification ("functional development"), such as through exposure-controlled sorption of various species from contacting solutions or vapours. For example, radiation-defined deprotection of nonpolar poly(di-*t*-butyl fumarate-*co*-styrene) produced a pattern of polar and reactive carboxylic acid and anhydride moieties. Conditions were found for only these exposed areas of resist material to take up Ca(II), Ni(II), Co(II), Pb(II) from the corresponding aqueous solutions, without being dissolved. Modes and mechanisms are discussed in terms of resist, solute and solvent properties. Possible applications of such functional imaging strategies and techniques are presented as well.

C-1. INTRODUCTION

As was described in the review (**Chapter A**), sensitive CA resists have been designed and tested to rapidly produce fine patterns of materials, such as in the manufacture of high-density DRAM devices and microprocessor chips by microlithography [1]. The traditional role for a resist in such applications has been to capture a projected radiation pattern as a "relief image" of removed and remaining areas of resist film (see **Figure A-1**), which is then translated into an underlying inorganic substrate through an etching process [2]. However, in microlithography-like techniques for making fine-scale optical waveguides, couplers, and recording media, or array sensors, displays and supports for solid-phase (bio)chemical analysis or synthesis, or other useful patterned structures, it would be often better not to remove either the exposed or unexposed areas of resist material ("relief development"), but instead to further modify one or the other to achieve the physical, chemical or biological properties whose patterning would be useful for some final application ("functional development"). Such patterned material properties could include density, refractive index (n), color, fluorescence, hyperpolarizability, reflectivity, heat capacity, dielectric constant, adhesiveness, liquid crystallinity, electrical or thermal conductivity; together with wettability, permeability, sorbtion or catalytic activity or chemical reactivity towards various liquid or gas-phase species; along with dissolution and etch resistance that would be relevant to later relief development steps as well.

Upon or following exposure, the polymers within CA resist materials can become altered in three general ways: i) polymerization or crosslinking that increase average molecular weight; ii) scission or depolymerization that decrease average molecular weight; iii) functional group transformation, that does not affect chain length, but drastically alters polarity, solubility and reactivity of chain units. This last mode (see **Sections A-3.1. and A-3.2.**), is not only the most attractive for relief development because of the lack of swelling in undissolved material and the possibility of dual-tone imaging, but the one that is most adaptable towards functional development. Indeed, both solubility and many other immediate or potential properties (including, tendency to further chemical modification) are critically dependant on the exposure-controlled functional composition of such resists, through highly cooperative behaviour of functional groups.

Unlike relief development, a functional development step by definition does not remove any of the solid polymer film, and can be a heterogeneous reaction that produces a stratified product. Patterned modification exclusively at a surface has been done to adsorb catalysts for further metallization [3,4], or biomolecules for DNA sequencing [5]; non-photochemical surface imaging has also been reported by a stamping technique [6]. In near-surface imaging, only the upper 10-100 nm of material is transformed due to low penetration of the initial imaging radiation (ex. low-energy electron or ion beams, or UV in relatively opaque materials [7], or due to low diffusion of chemical species during a later functional development step (ex. in the "diffusion enhanced silylated resist" = DESIRE processes [8,9]). Modifying species can also enter and diffuse deeper into the bulk of the polymer. The rate and extent of such uptake can depend on the polymer-solution interface, or on bulk polymer-polymer (ex. crosslinking), polymer-solvent (ex. plasticization), and polymer-solute interactions, covalent or not, often involving polymer functional groups [4,10-13]. The understanding and design of functional development would benefit from the study of relevant chemical and physico-chemical phenomena, similar to what has been done on airborne contamination of resists [14,15], and miscibility of their components [16].

One general way of modifying a thin film of material is by controlled uptake of ions or molecules from a contacting liquid or gas. We discuss here the functional development, through exposure-controlled sorption of various inorganic metal ions, of a model CA resist based on poly(di-*t*-butyl fumarate-*co*-styrene) (PDBFS, see **Chapter B**).

C-2. EXPERIMENTAL SECTION

C-2.1. Instruments

Instruments for spin-coating, exposure and baking were described in the **Section B-2**. The pH of aqueous solutions was measured with a Cole-Palmer Digi-Sense 5938-00 pH-meter with 5992-40 combination electrode, which had been calibrated using commercial buffer solutions (Caledon Inc.) of 0.05 M potassium hydrogen phthalate (pH 4.00) and 0.01 M sodium borate (pH 9.22). FTIR spectra were obtained with a Brucker IF-48 spectrophotometer with microscope accessory. Reactive ion etching (**RIE**) was performed in a custom-built Large-volume Microwave Plasma (**LMP**) apparatus [17].

C-2.2. Chemicals

Preparation, evaluation and general lithography processing of the PDBFS resist were described in **Section B-2**. Metal salts of >99% purity were used as received: $CuCl_2$, $NiCl_2$, $CoCl_2$, $AlCl_3$, $FeCl_2$ and $FeCl_3$ from Alfa Inc.; $Pb(OAc)_2$ and $PdCl_2$ from Aldrich Inc. Each of these was dissolved in H_2O to ca. 0.1 M, except for $PdCl_2$ which was almost insoluble. $Ca(OH)_2$ was prepared [18] from calcium oxide (Anachemia Inc.), and the saturated solution was freshly filtered before use. 0.1 M HCl/H_2O and 5 wt % NH_3/H_2O were prepared by dilution of the commercial concentrates (Caledon Inc. and BDH Inc., respectively).

C-2.3. Functional Development with Metal Ions

Samples for binding experiments were prepared by dissolving 50 mg of PDBFS, together with 5 mg of either triphenylsulfonium or 4-(phenylthio)phenyldiphenylsulfonium hexafluoroantimonates [19] as PAGs, into 250-350 mg of propylene glycol methyl ether acetate; then filtering this solution (0.2 µm) and spin-coating it at 1000-1200 rpm onto a silicon wafer; then performing a PAB at 130 °C for 60 s, to give a 0.8-0.9 µm film that was optically clear. This was later irradiated with 0-100 mJ/cm^2 of deep- (254 nm) or mid-near-UV (mainly 365 nm) through an Optoline-Fluroware density photoresist step table REK/73 with resolution to 1 µm, or while half-shading the sample with an opaque object, before being subjected to a PEB at 135 °C for 60 s.

30 ml of solution containing metal ions was placed in a beaker with pH electrode and continuous magnetic stirring. As needed, drops of 0.1 N HCl/H_2O or 5 wt % NH_3/H_2O were then added to adjust the pH of the medium. Silicon wafers containing irradiated-

PEB resist were then introduced for 10-180 s, then quickly rinsed for 30 s with distilled water, and air-dried before FTIR and other evaluation.

C-2.4. Reactive Ion Etching

Samples were prepared and exposed at mid-near-UV through the step tablet (0-100 mJ/cm^2), dipped in saturated $Ca(OH)_2/H_2O$ for 90-180 s, dried, then later exposed to O_2 plasma reactive ion etching (O_2-RIE) in the LMP apparatus under conditions of 10 sccm O_2 flow, 50 mtorr pressure, 120 W power, and -500 V bias.

C-2.5. Refractometry

The refractive index (*n*) of a resist thin film on a slide of fused silica was measured by a known wave-guiding technique [20], in which a laser beam was coupled by a prism into the resist layer, then decoupled ca. 1 cm further on by another prism. The relationship between coupling and decoupling angles and output light intensity gives both average *n* and film thickness. As the technique requires multi-mode wave-guiding, relatively thick films (1.1-2.0 μm) were prepared using a more concentrated resist solution and lower spin rate.

C-3. RESULTS AND DISCUSSION

C-3.1. Functional Development of the Resist with Metal Ions

Metal cations can be captured and held inside a polymer material by ion-ion or ion-dipole interactions, or may simply remain after swelling the polymer with solution then evaporating the solvent. Since an ion-exchange mechanism seemed to promise the best rate and capacity for metals loading, we explored the formation of insoluble polymer-supported metal carboxylates from the carboxylic acid moieties of deprotected PDBFS. Other candidates for strong metal binding would be acrylic co- and ter-polymers [21-23], protected phenolic resins (Novolac or hydroxystyrene) with possible formation of metal phenolates, or any metal chelating resins capable for photo- or catalyst-transformation.

C-3.2. Exposure-Controlled Sorption of Calcium Hydroxide

As expected, beyond a critical UV dose (30 mJ/cm^2), aqueous solutions of either sodium or potassium hydroxides quickly dissolved exposure-deprotected areas of PDBFS resist, presumably due to formation of a water-soluble monocation-polycarboxylate polyelectrolyte. However, the same treated resist did not dissolve in even highly basic, saturated solutions of calcium hydroxide in water, though FTIR of the still-solid films (**Figure C-1**) showed the appearance of peaks corresponding to carboxylate anion (ca. 1415 and 1565 cm^{-1}, sym and asym COO^-) and water (3000-3500 cm^{-1}) within the polymer matrix. Their increasing height with prolonged contact of $Ca(OH)_2/H_2O$ correlated with further shrinking of remaining carboxylic acid and anydride peaks (1700-1850 cm^{-1}). The broad shapes of these peaks suggested the formation of a variety of carboxylate-water-metal ion complexes in different microenvironments.

Since no other cation is present at such high pH, it is obvious that at least one Ca^{2+} is being taken up into the polymer for every two COO^- being formed, to give proportions of styrene:fumarate:calcium of 55:45:45 (14 wt % calcium, by calculation) from completely deesterified PDBFS resist. Each divalent cation would thus ionically link two carboxylate groups, either intramolecularly (forming at least a 7-membered ring – not particularly favoured), or intermolecularly to crosslink the polymer and keep it from dissolving. **Figure C-2** depictes such binding. The literature reports instances of similar polycarboxylic acids being precipitated through ionic crosslinking by polyvalent cations: depending on pH, gels formed this way contained tetra- or hexadentate complexes, with up to 1/3 of the carboxylic groups still remaining un-ionized [24,25].

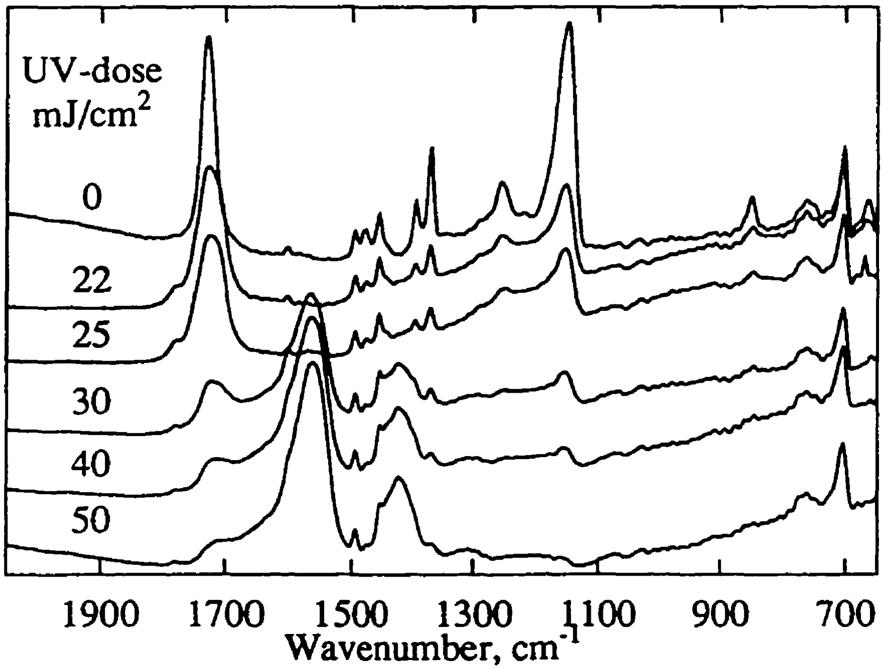


Figure C-1. FTIR spectra of PDBFS/PAG resist after different exposure and treatment with saturated aqueous $Ca(OH)_2$ solution for 20 s.

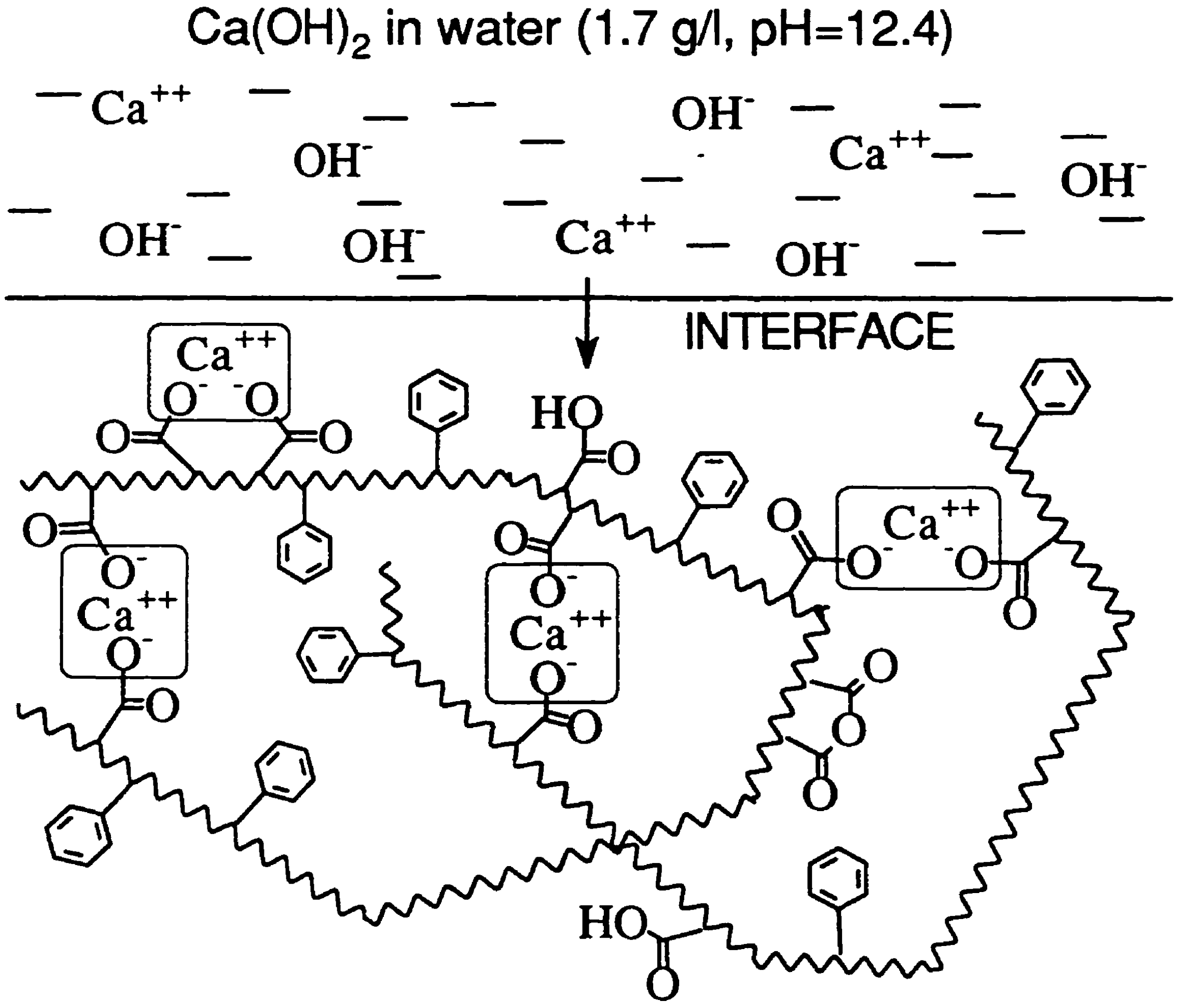
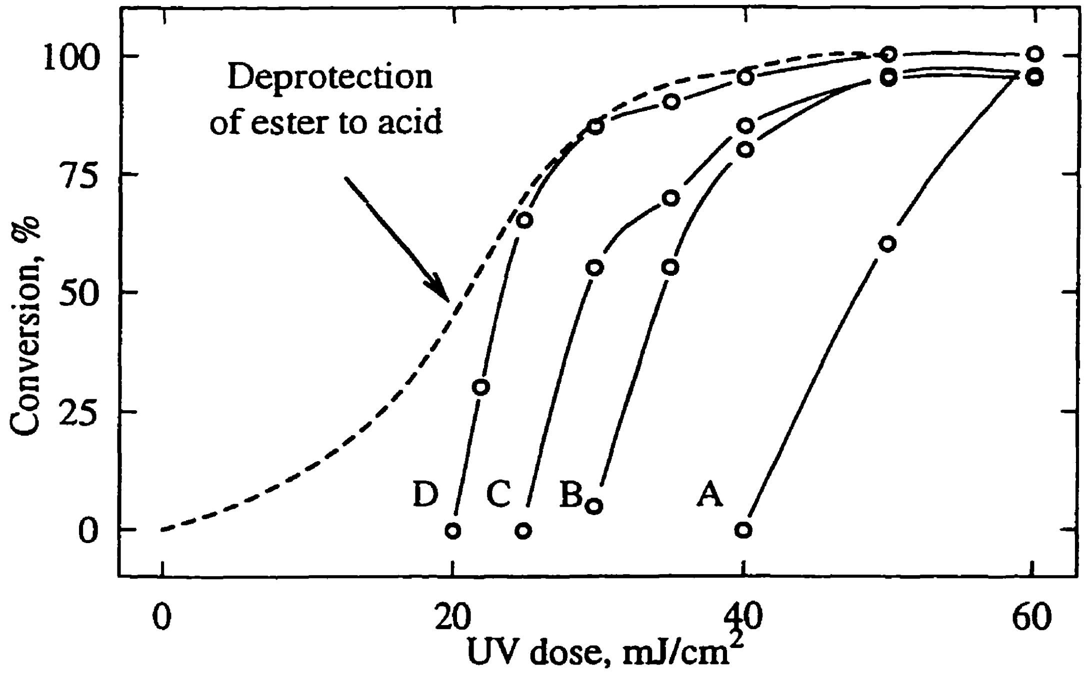


Figure C-2. Binding of Ca++ ions into deprotected PDBFS

In our thin films, rough kinetics of $Ca(OH)_2/H_2O$ loading showed (**see Figure C-3**) an initial delay without detectable formation of carboxylate anion, probably for the material surface to become sufficiently ionized and wetted, and possibly relating to the annoying "skin" often seen in positive-tone relief imaging [15]. Once begun, reaction proceeded until, within a time comparable to or shorter than the induction period, all carboxylic acid and anhydride groups made available by UV/PEB had been converted to carboxylate, without hydrolysis of any more *t*-butyl ester groups. Even with this crosslinking species, the rate of material alteration was probably more limited by propagation of the reaction front than by ion movement into and through the now-hydrophilic polymer matrix, as has been suggested for other, even oligomeric crosslinkers entering similar maleic anhydride copolymers [11]. More complete initial deesterification shortened both these times and thus the total time for maximum functional development (180 s for 30 mJ/cm^2, to 10 s for 60 mJ/cm^2), and increased too the ultimate ion-exchange capacity of the film. As with relief development of the same resist, this abrupt infiltration of solute beyond critical exposure and developing times benefited the contrast of the resulting functional images (maximum slopes of curves in **Figure C-3**).

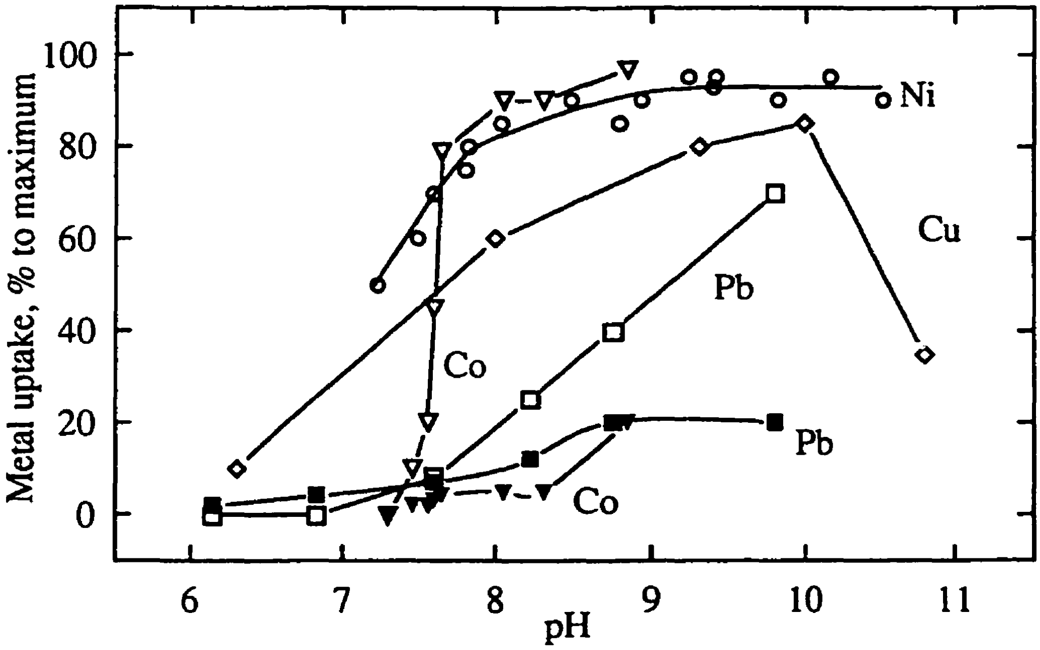
Figure C-3. Conversion of -COOH into -COO⁻ after treating the deprotected resist with aqueous saturated $Ca(OH)_2$ for 10 s (A), 20 s (B), 30 s (C) and 180 s (D). Ester-to-acid and acid-to-salt conversion curves are produced from FTIR data; e.g., curve (B) is derived from Figure C-1 (as described in the Appendix).



C-3.3. Exposure-Controlled Sorption of Other Metal Ions

0.1 M aqueous solutions of $CuCl_2$, $NiCl_2$, $CoCl_2$ or $Pb(OAc)_2$ did not even wet a film of PDBFS resist, even after its complete photo-deprotection. These solutions were neutral or acidic (pH 4-7): it was expected that more basic conditions could help deprotonate the polymer films for better wetting and influx of metal cations. Precipitation of metal oxides with rising pH was often largely forestalled by using NH_3 as base, since this is also a good ligand for many cations. Actually, aqueous ammonia alone was an effective relief developer for deprotected PDBFS. However, many of its mixtures with crosslinking polyvalent metal ions (likely containing NH_3, NH_4^+, M^{n+}, $(NH_3)_mM^{n+}$ and OH^- species) did not dissolve even fully-deprotected resist at higher pH, though FTIR peaks near 1550 and 1400 cm^{-1} showed increasing conversion to carboxylate anion with increasing contact time and pH (**Figure C-4**). Ammonia or ammonium hydroxide probably forms ammonium carboxylate first, but then metal would displace the ammonium ion for a thermodynamically more favourable association (lattice energies for acetates: 725 kJ/mol for NH_4^+, but 2835 for Cu^{2+} and 2247 for Pb^{2+} [26]). With increasingly higher ammonium ion concentrations (as reflected by increasing pH), monocation carboxylate groups eventually predominate within the material, ultimately leading to its dissolution.

***Figure C-4.** Uptake of metals by the resist at different pH after 30 s. Hollow and filled dots represent uptake by -COOH and -COOR areas.*



Thus, at pH 6-7, Ni^{2+} and Cu^{2+} began to penetrate exposed areas, which dissolved at pH 10-10.5. At pH 8 Ni^{2+} or Cu^{2+} ammonia solution does not cause any IR-detactable alteration within unexposed areas. With Co^{2+}, dissolution occured at pH 9, and was accompanied by transformation of even unexposed areas of resist (new FTIR peaks at 3500-3000, 1480 and 1380 cm^{-1}). Pb^{2+} only slowly penetrated exposed areas even up to the point of dissolution at pH 10, while clearly causing hydrolysis of *t*-butyl ester groups in unexposed areas at all pH (new FTIR peaks at 1540 and 1390 cm^{-1}). Overall then, pH 8 seemed best for exposure-selective binding of these metal ions, though contrast was poor for Pb^{2+}. Brief attempts to introduce FTIR-detectable quantities of Fe^{2+}, Fe^{3+}, Al^{3+} or Pd^{2+} failed, due to their precipitation in basic solutions, even with NH_3.

C-3.4. Metal Ion-Developped Resist: Reactive Ion Etching

Mainly silicon [9,11,12,27], and some other elements that form refractive oxides (boron [28], tin [29] germanium [30], nickel and zirconium [4]), have been used in microlithography in "dry development" processes, in which their compounds are selectively introduced either in exposed or unexposed areas of resist. The stable oxide layer produced under plasma bombardment protects polymer below. This technique gives excellent wall profile and high aspect (depth/width) ratio [8]).

Preliminary tests showed that introducing of Ca^{++} into 0.8 μm films of exposed resist did indeed reduce the rate of its O_2-RIE plasma etching from 7.0 nm/s (ester without Ca) down to 1.5 nm/s (carboxylic Ca salt), to create 1 μm relief images. Sensitivities were 40 mJ/cm^2 for 90 or 120 s of immersion in $Ca(OH)_2/H_2O$, and 25 mJ/cm^2 for 180 s, similar to sensitivities associated with wet development (see **Table B-1**).

C-3.5. Metal Ion-Developped Resist: Refractive Index

A waveguide consists of a channel of material with high refractive index (*n*), surrounded by one with low. The value of *n* depends on material composition, being higher in materials containing more polarizable atoms (such as heavier atoms or ions) or groups (dipoles, delocalized charges). Exposure/PEB, then development with inorganic cations, each significantly and progressively increased the refractive index of PDBFS resist, as measured in different regions of the same film, through the formation of increasingly polarizable functional groups: -COOR > RCOOH or $(RCO)_2O > (RCOO^-)_nM^{n+}$. In principle, patterns of sharply- or gradually- varying refractive index could thus be generated, to 1 μm resolution and below (**Figure C-5**).

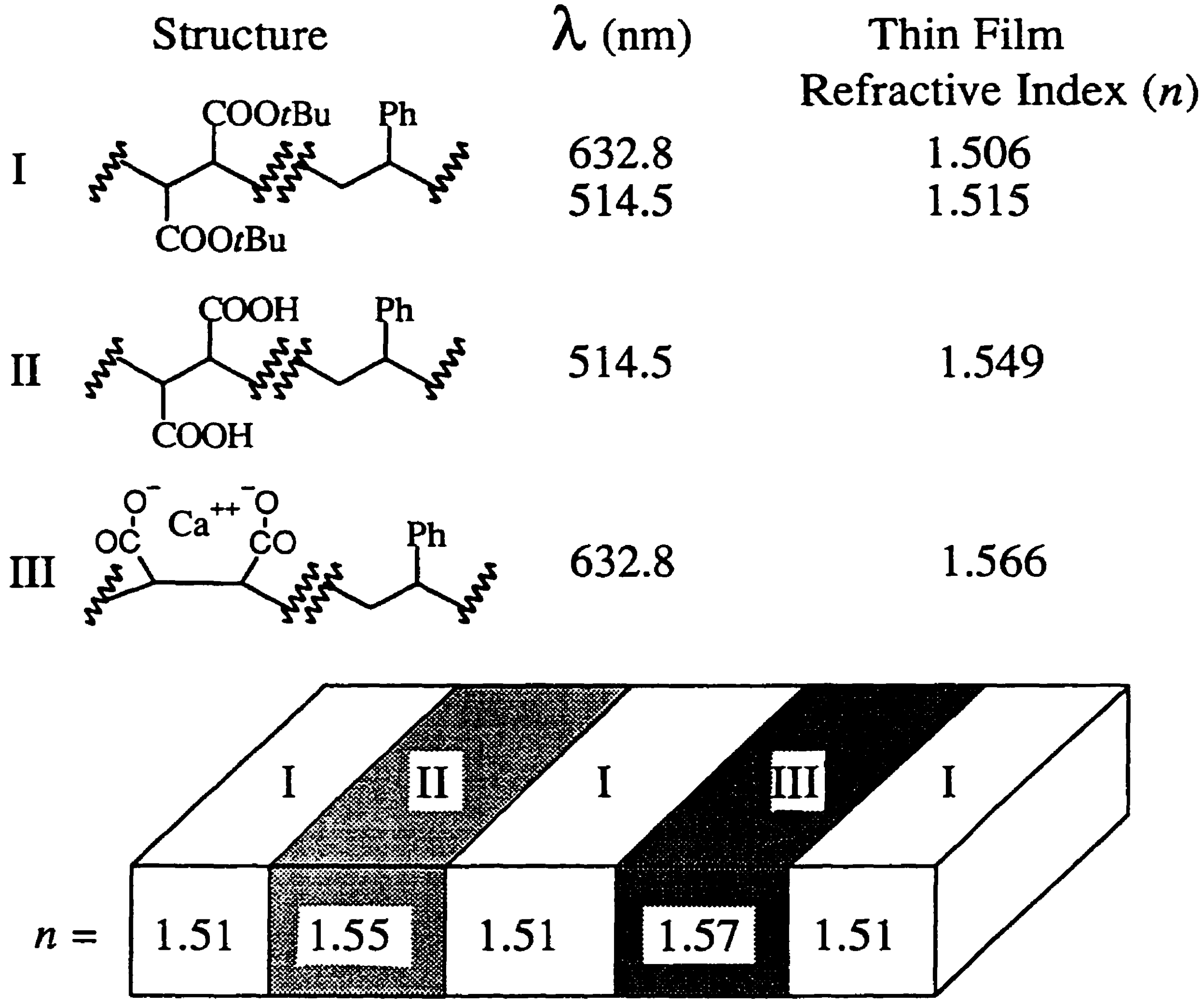


Figure C-5. Refractive indices of unexposed, deprotected and Ca^{2+}-developped resist thin films, and possible patterned features.

C-4. CONCLUSIONS AND ACKNOWLEDGMENTS

As electrical, optical, bio- or chemo- devices and their features continue to shrink, demand will continue to grow for micron-scale patternable systems. One way to create such structures is by a relief image and fill back holes with inert or contrasting material. Another way is to space-selectively modify resist-like system by multiple transformation and by further inclusion of active materials with valuable properties.

The pH of solutions and the nature of metal ions were found to be the main factors controling space-selective binding of metal ions from aqueous solution into deprotected PDBFS areas. At acidic and neutral pH, salt solutions did not even wet the polymer. Solutions with monovalent cations cause fast dissolution of deprotected PDBFS at pH > 7.5. But in the presence of polyvalent cations, like Co(II), Ni(II), Pb(II), etc., instant ionic crosslinking preserved the integrity of the matrix at pH 8-10. Several experiment have proved potential suitability of such metal-patterned polymer structures for plasma-etch developing and for wave-guiding applications. **Chapter D** will present binding of various organic molecules into similar PDBFS-based templates.

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Chapter D

Functional Imaging with Chemically Amplified Resists and Organic Molecules

D-0. ABSTRACT

Chemically amplified resists were tested for preparing universal templates to bind various organic species in micron-scale patterns (functional images). UV exposure and heating of a poly(di-*t*-butyl fumarate-*co*-styrene):onium salt resist produced alternating areas of non-polar ester and polar acid/anhydride polymers. Various compounds that were fluorescent dyes or amines could then be placed selectively either into or onto exposed or non-exposed areas, according to the nature of solvents and binding species. The ease and extent of immobilization were found to depend on (i) resist composition; (ii) matrix wettability and permeability by a solvent; and (iii) covalent, ionic, dipole-dipole or other sorbate-matrix binding interactions.

D-1. INTRODUCTION

As was described in **Chapter A**, the simplest CA resists consist of a photosensitive catalyst generator and a polymer matrix with catalyst-labile groups. After irradiation, an initial photochemical event -- the formation of a small amount of catalyst -- is amplified hundred of times by a cascade of thus catalyzed reactions of crosslinking, scission or rearrangement.

Along with mainstream use in microlithography, microresist ideas and technologies can benefit any application involving micron-scale features. In microoptics, polymer resists have been used to create interconnected channel waveguides and grade coupler elements [1]. The production of optical storage media and liquid crystal displays (LCD) also involves a resist technology. Another example is the creation of array biosensors: subsequent binding of different biomolecules onto a polymer surface has been accomplished employing photodeprotection of hydroxyl groups [2].

In microelectronics manufacture and other processes to date, photoresists have usually played only brief roles, in translating images into an underlying substrate through the following steps: i) a pattern-wise irradiation of the photosensitive polymer coating; ii) a development of the irradiated polymer into a "relief" image, revealing areas of an underlying (usually inorganic) substrate; iii) an etching or a modifying of the substrate in such denuded areas; iv) a stripping away of the remaining polymer. The substrate surface thus eventually is made to bear an image as areas of contrasting materials, e.g. of insulating vs conducting areas in a circuit pattern. *Alternatively, the polymer coating itself, which has been irradiated and heated to contain a pattern of micron-scale alterations of properties, can be considered a useful structure.* Thus, a resist that bears a pattern of altered chemical, physico-chemical and physical properties can be used either directly (e.g. making use of contrasting refractive indices for waveguiding), or indirectly through its ability to further space-selectively sorb, release or transport different chemicals of interest. These can be inorganic metal ions and salts, organic nonlinear optical materials and other dyes, as well as complex biomolecules, oligomers or even other polymers. With a patterned and functionalized polymer film as product, the etching and stripping steps of the normal microlithographic process are now obviated, though certain areas may be selectively removed by liquid or plasma developers.

With their dramatic alterations in structure and reactivity upon small UV doses, deprotection-style CA systems are obviously the first choice for space-selective sorption. The *t*-butyl ester-based chemistry looks particularly attractive: along with its main function as an acid-labile moiety, this group is also the precursor of highly reactive carboxylic acid and, upon further heating, anhydride moieties. In previous reports we described the formulation of an onium salt with poly(di-*t*-butyl fumarate-*co*-styrene) (PDBFS) as a good resist for normal (relief-forming) lithography [3,4]. Its patterning with UV irradiation, followed by heating, produced contrasting areas of the initial poly(styrene-*co*-fumaryl) ester ("PSF-ester") and newly-formed poly(styrene-*co*-fumaryl) acid ("PSF-acid") or anhydride ("PSF-anh") polymers (**Figure D-1**). Preliminary experiments also showed that various fluorescent dyes could be made to bind into either the protected (PSF-ester) or deprotected (PSF-acid/anh) areas, according to the chosen solvent system, in patterns down to 5-10 μm resolution even with a rather rudimentary exposure tool, thus showing the applicability of such resists and processes to achieve space-resolved binding [3].

A number of articles have presented studies on the creation and application of patterned functionalization of resists. Some reported procedures for microlithography, such as DESIRE [5], CARL [6], and a surface (or near-surface) metallization [7-9], already depend on selective modifications of either irradiated or non-irradiated areas with plasma-resistant inorganic species. Photo-directed modifications of polystyrene and poly(3-octylthiophene) have been done with perfluorophenyl azides and fluorescent dyes [10]. Photo-induced grafting of unsaturated molecules to poly(organophosphazenes) have resulted in structures that were able to immobilize amines, some biomolecules, and metal ions [11]. In the last two examples, relatively large UV doses (in a range of 1000 mJ/cm^2) were needed, because the matrix was modified by direct photo-reaction, rather than by a catalytic process (chemical amplification). So far, patterning of organic dyes into CA resists has been briefly reported only from our lab [3,12], and from AT&T labs [13], where Schilling et al. used a polystyrene with capped phosphonic acid as a template.

Thus, the objective of our research was to explore a variety of ways and conditions to place species of different chemical nature into patterned polymer CA resist systems. This report concerns sorption of organic chemicals from solutions and vapors. A companion report on binding of several metal ions to the same templates of PDBFS:onium salt resist has been presented in the **Chapter C.**

A set of chemicals for binding was chosen among dyes and amines. Besides the products of dye patterning (e.g., non-linear optical materials), we were also interested in the process of dye sorption, as can easily be monitored at low concentrations by UV-VIS or fluorescence spectroscopies. Amino groups in particular can bind by H-bonding, or ionically, or covalently to acyl moieties. Synthetic dyes and alkylamines could also be models of biomolecules with amino groups, for techniques to place them into desired areas, which is of potential interest for ultra-microscale biochemical analysis or synthesis.

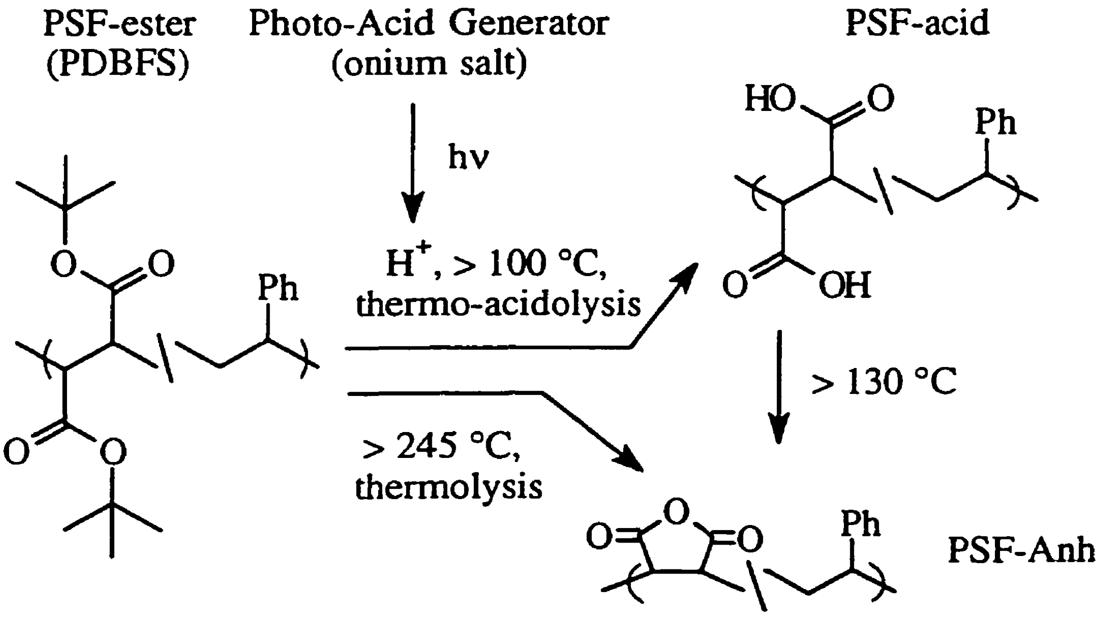


Figure D-1. Structures and transformations of the PDBFS resist.

D-2. EXPERIMENTAL SECTION

D-2.1. Chemicals

Hexane, toluene, methanol, *n*-, and *i*-propanol were all "glass distilled" grade from OmniSolv Inc., and *t*-butanol from Baker. Fluorescent dyes (see **Figure D-2**) Rhodamine-6G (R6G), 3-amino-9-fluorenone, 2-aminoanthracene, anthracene, fluorescein and Brilliant Sulphaflavine were purchased from Aldrich, and fluorescein dibutyrate from Nutritional Biochemicals. Preparations of strongly solvatochromic fluorescent dyes 2-[4-(N-methyl-N-octylamino)styryl)]pyridine (DAASP-8), its analog with a C_{18} alkyl tail (DAASP-18), and 4-(5-N,N-dimethylaminonaphthalenesulfonylamido)-1-methylpiperazine (DSMP), were all described previously [3]. Propylene glycol methyl ether acetate (PMA), aqueous ammonia solution (30% NH_3/H_2O diluted 1:5 with distilled water), and 1,10-diaminodecane, 2- and 4-aminopyridine, and 2,6-diaminopyridine amines were all from Aldrich, "analytical pure" pyridine from BDH, and poly(ethyleneimine) (M_w=10 Kg/mol, 30 wt % in water) from Polysciences.

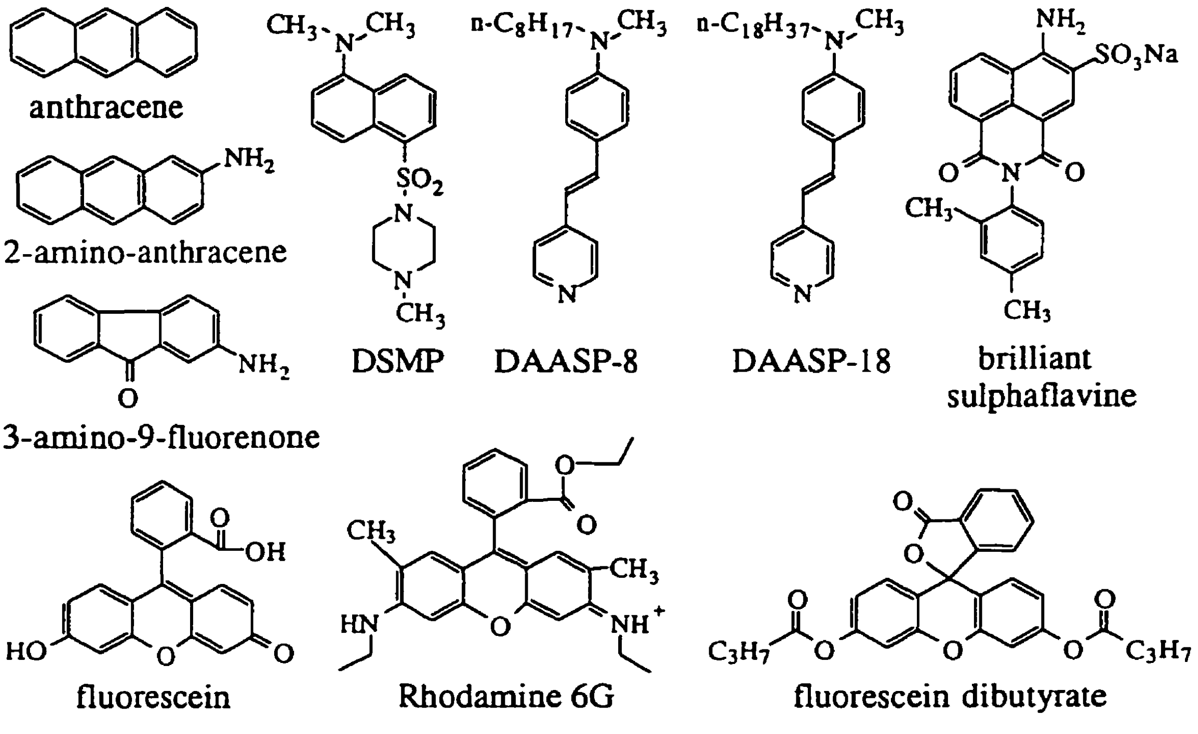

anthracene
2-amino-anthracene
3-amino-9-fluorenone
DSMP
DAASP-8
DAASP-18
brilliant sulphaflavine
fluorescein
Rhodamine 6G
fluorescein dibutyrate

Figure D-2. Structures and names of fluorescent dyes.

D-2.2. Photoresist Preparation and Exposure

Di-*t*-butyl fumarate was prepared from fumaryl chloride and potassium *t*-butoxide, and then polymerized with styrene in toluene by AIBN. The resulting PDBFS was mainly alternating with ca. 45 mol % of fumarate units, M_n = 12 Kg/mol, M_w = 20 Kg/mol, $[\eta]$ = 0.08 in chloroform (**Chapter B**). 4-(phenylthio)phenyldiphenylsulfonium hexafluoroantimonate (4TS-SbF_6) was synthesized by a known method [14].

Resist samples were prepared by dissolving 50 mg of PDBFS with 5 mg of 4TS-SbF_6 in 350 mg of redistilled PMA. These solutions were filtered through 0.2 µm inorganic membrane filters Anotop-10 (Phenomenex Inc.), and spin-coated onto a substrate at 1000 rpm for 40 s to give 0.8-0.9 µm optically clear films. After PAB for 60 s at 130-135 °C, the samples were irradiated at 254 nm to 100 mJ/cm^2, then PEB for 60 s at 130-135 °C. Although the resist can perform well at much smaller PAG loading and UV dose, these parameters were chosen on the basis of IR results, as discussed in the **Section B-3.2.**

D-2.3. Binding Experiments

Thirty millilitre portions of 0.1-0.2 wt % of dye or 1-2 wt % of colourless amine in an appropriate pure or mixed solvent were each placed in a 60 mL beaker. Polymer samples on pieces of Si wafer were immersed into these "functional developing" solutions for 15-30 s with gentle shaking. Samples were then quickly rinsed for 10 s in the same solvent(s) without additives, and air-dried before evaluation. To check stability of binding, the fluorescence of some samples was evaluated both before and after brief then prolonged continued similar rinsing. In most cases we irradiated only half the area of a coated wafer, then processed, treated, and analyzed both irradiated and non-irradiated areas in identical conditions. Thus, contrast (space-selectivity) between exposed and unexposed areas was determined in one run.

D-2.4. Instruments

Using a Headway Research spin-coater, films were applied onto either pieces of Unisil silicon test wafers 3" x 330-432 µm N/P <1-1-1>, or National Scientific GE 124 polished fused quartz plates 1" x 1" x 1/16" (for UV-VIS spectrophotometry). The UV source was a Cole-Palmer 9815 Series 100 W UV Hg lamp with a built-in 254 nm narrow-bandwidth filter. Exposures at 254 nm were measured using an Optical Associates OAI P306-001-002 powermeter, and controlled with a timer. PAB and PEB were done on a hot-plate with a surface thermocouple control.

Infra-red spectra of coated Si wafers were taken with the IR microscope accessory of a Bruker IF-48 FTIR spectrophotometer in transmission mode. Data were collected at 2 cm^{-1} resolution, and converted to graphics by SigmaPlot software from Jandel Scientific. UV-VIS spectra were taken on a Shimadzu Spectronic-210UV spectrophotometer. Fluorescence measurements were made with a Spex model F-112 spectrofluorometer with 450 W xenon lamp, with the sample surface perpendicular to the incident beam, and the emission detector at 90° for solutions in cuvettes, or at 22.5° for solid films. The concentrations of the dyes for the solution fluoroscopy were 1-2 g/L. The spectra were corrected and normalized for comparison. The qualitative evaluation of dye binding -- strong, moderate, weak, absent -- was estimated by visual inspection of the samples inside a Spectroline C-4 UV cabinet (Spectronics Corp.) under 365 nm illumination. Solubility of each dye in different solvents -- soluble, partially soluble, insoluble --was checked by the apparent fluorescence, color, and turbidity of the solution.

D-3. RESULTS AND DISCUSSION

D-3.1. Modes for Selective Binding

In CA resists in general, irradiation then heating creates a latent image (**Figure A-1**) of altered and unaltered areas. With the PDBFS resist, these areas consist of the non-polar PSF-ester and the highly reactive polar PSF-acid/anh materials (**Figure D-1**). We thus considered the following possible mechanisms of selective sorption:

- for the PSF-ester: treatment with moderately apolar solvents that swell and transport solutes into this non-polar matrix, to be non-specifically trapped on drying,
- for the PSF-acid/anh: similar non-specific trapping from more polar solvents, along with either ionic interaction or covalent binding of reactive solutes to acid groups, and or their covalent binding to anhydride groups.

Moreover, sorption can be made to occur from vapours and non-swelling solvents as well, and either into the bulk or merely onto the surface of a resist area.

D-3.2. Patterning of Dyes

Tables D-1 and **D-2** presents a summary of the binding experiments with different dyes from various solvent systems; the results are grouped to highlight effects of template, dye and solvent nature.

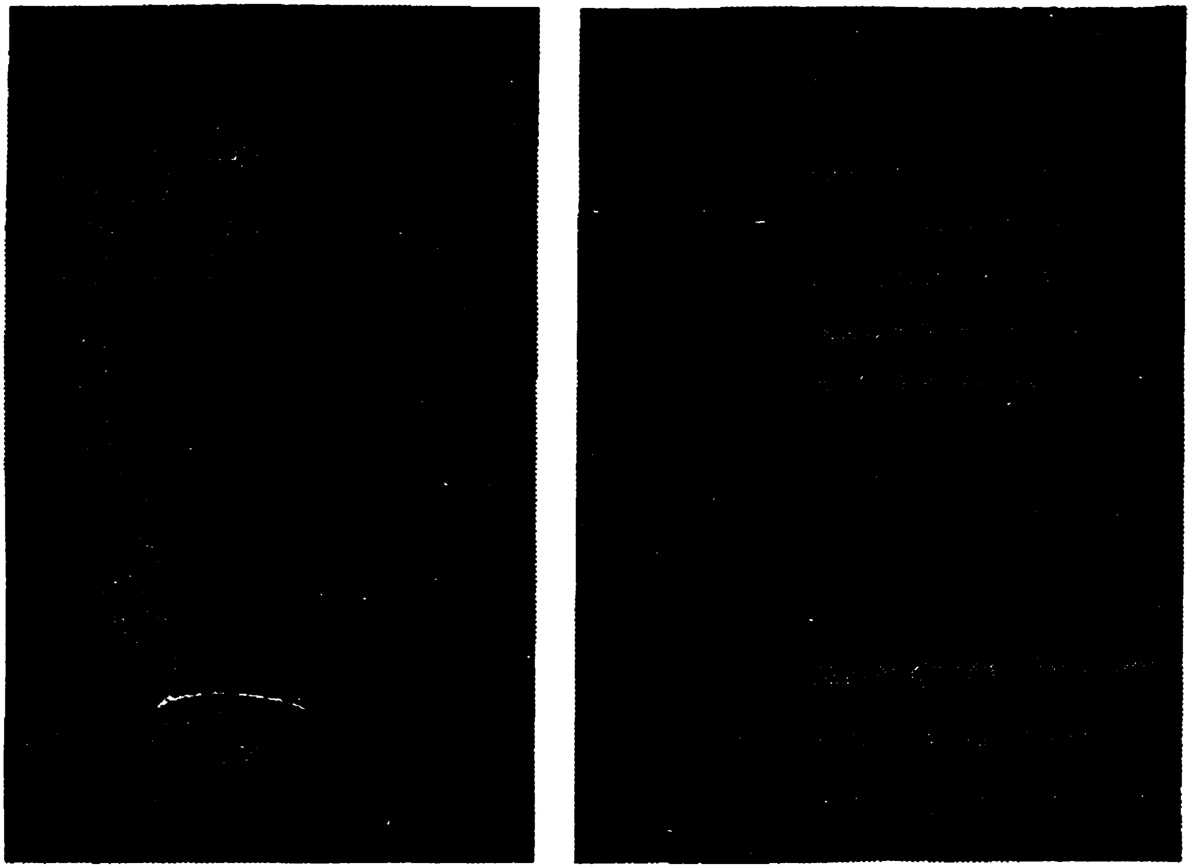
Table D-1. Binding of fluorescent dyes in the PSF-acid.

effect of..	dye	solvent(s)	v:v	binding, and comments
solvent's nature	rhodamine-6G	H_2O		no wetting of the film
		H_2O:methanol	10:5	weak, no film swelling
		H_2O:methanol	10:10	strong, partial swelling
		H_2O:methanol	10:20	film dissolved
		H_2O:*t*-butanol	10:5	strong, no swelling
dye's nature	DSMP	H_2O:methanol	10:10	strong
	DAASP-8	H_2O:*n*-propanol	10:7	strong
	DAASP-18	H_2O:*t*-butanol	10:10	strong
	fluorescein	H_2O:*t*-butanol	10:5	strong
	3-amino-9-fluorenone	H_2O:*t*-butanol	10:5	strong
	2-amino-anthracene	H_2O:*t*-butanol	10:5	strong
	brilliant sulphaflavine	H_2O:*t*-butanol	10:5	strong
	anthracene	H_2O:*n*-propanol	10:7	no binding

Table D-2. Binding of fluorescent dyes in the PSF-ester.

effect of..	dye	solvent(s)	v:v	binding, and comments
solvent's nature	DSMP	toluene		film dissolved
		hexane:toluene	10:1	strong
		hexane$^{(a)}$		weak, no swelling
dye's nature	R6G	hexane:toluene	10:1	dye insoluble in solvent
	DAASP-18	hexane$^{(a)}$		weak
	dibutyrate fluoresceine	hexane:toluene	10:1	no binding
	anthracene	hexane:toluene	10:1	no binding
stability of structures	DAASP-8	hexane		moderate, unstable in hexane rinsing
		hexane:toluene	10:1	strong, stable in hexane rinsing

(a) low solubility of the dye in the solvent



DAASP-8 binds only to exposed areas (PSF-acid) from *n*-propanol:water (1:3 v:v).

DAASP-8 binds only to unexposed areas (PSF-ester) from toluene:hexane (1:9 v:v).

1 µm film of PSF-ester:4TS-SbF$_6$ (9:1 w:w), PAB 30 s at 130 °C, 40 mJ/cm^2 of deep-UV, PEB 180 s at 135 °C. Excitation at 400 nm. Picturing with a >510 nm filter.

Figure D-3. 5 µm line/space fluorescent pattern

Having amino or quaternary ammonium groups, some dyes were soluble in pure water, but no sorption was detected from that solvent even into PSF-acid, which was not even wetted. The addition of different C1-C4 alcohols to water dramatically increased both the solubility of other dyes, and its wetting of the PSF-acid surface. Most alcohols improved this wettability after 10-15 vol % alcohol content but above 30-60 vol % of methanol, ethanol, *i*-propanol, and *n*-butanol, the PSF-acid dissolved away. From solutions of intermediate concentrations of these alcohols, we observed strong binding of dyes, but often accompanied by an undesirable swelling of the matrix. An exception was the water:*t*-butanol combination, which wetted but did not swell the PSF-acid at almost all solvent ratios. The alcohol t-butyl group appears to be sufficiently non-polar, and its hydroxyl sufficiently hindered, to prevent dissolution of the PSF-acid. From the 2:1 v:v water:*t*-butanol solution, almost all tested dyes were successfully placed into PSF-acid without any detectable adhesion to PSF-ester (**Table D-1**). Penetrability of the matrix by water:alcohol mixtures was also easily estimated by IR measurements from treated and semi-dried samples: additional strong bands at 3000-3500 cm^{-1} appeared from H-bonded hydroxyls of sorbed water and alcohol molecules.

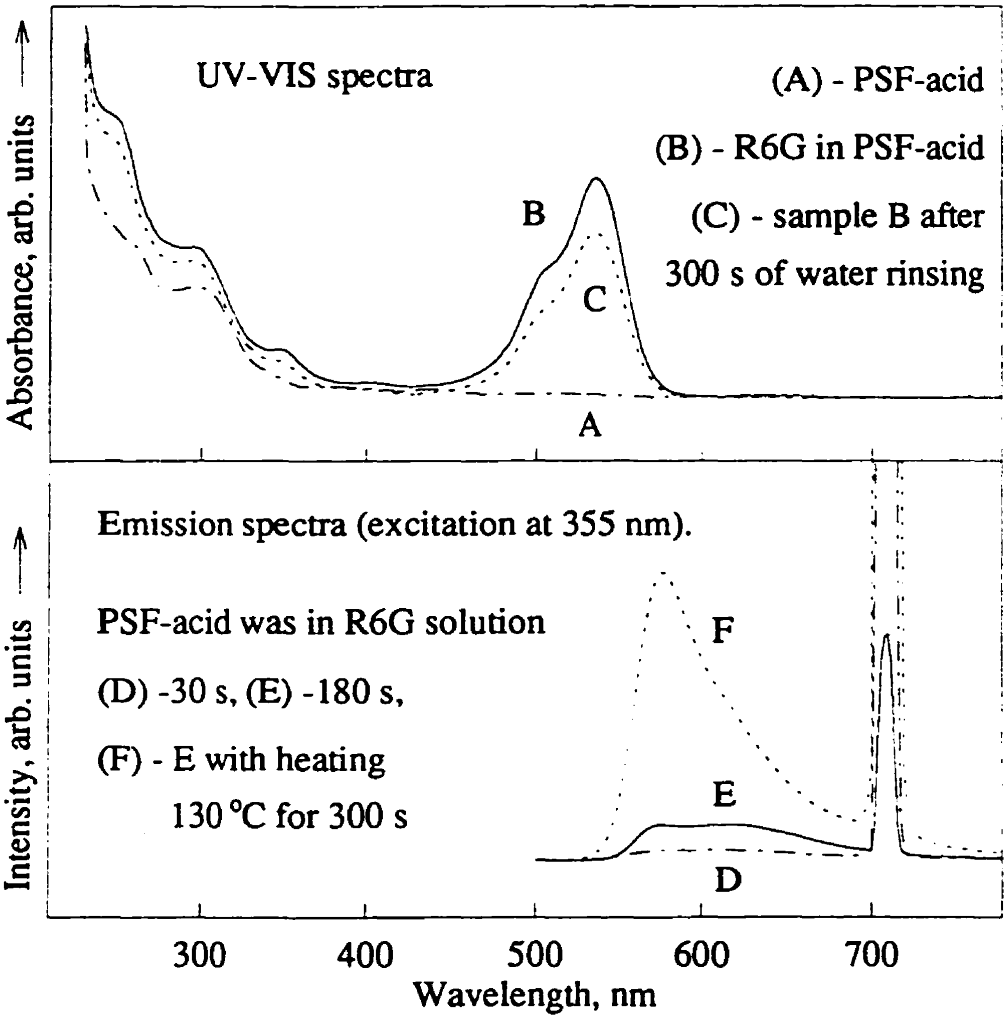
A somewhat similar picture was seen with selective binding into PSF-ester. Hexane wetted the PSF-ester matrix, but didn't swell it; however, hexane couldn't dissolve many dyes with polar groups. Toluene was a good solvent for these dyes, but dissolved the PSF-ester polymer completely. While a 3:1 v:v mixture of hexane and toluene was still a good solvent for PSF-ester, the 10:1 v:v mixture only slightly swelled the PSF-ester, trapping any solute there after its evaporation. Though many of the dyes were thus placed selectively in the PSF-ester, some, despite being soluble in the solvent mixture, could still not be made to adhere (**Table D-2**).

The nature of the dyes also played an important role here. Most of the dyes employed worked well in both water:alcohol or hexane:toluene mixtures. These dyes possessed amino, pyridinium, ammonium and carboxy groups (**Figure D-2**), that provided possibilities of ionic or covalent binding, along with dipole-dipole or other weaker interactions. Some non-polar dyes, such as anthracene and Fluorescein dibutyrate, could not be bound by these methods into either polar PSF-acid or non-polar PSF-ester matrices (**Tables D-1** and **D-2**).

We also checked the stabilities of dye-resist solid solutions created in both PSF-acid and PSF-ester. When binding was done from hexane dye solutions, reimmersion for a few seconds into pure hexane dramatically decreased the intensity of the fluorescence in PSF-ester; after a few minutes in hexane, pictures were no longer seen. As hexane doesn't swell the polymer, dye molecules had probably been only deposited *onto* the surface, and could thus be easily removed afterwards. The stability of binding from hexane:toluene solutions was much better: hexane alone could not then remove easily such dye molecules after they had been transported deeply *into* the film.

A prolonged (hours) water rinsing slightly decreased or did not change fluorescence from dyed PSF-acid (by visual inspection and UV-VIS spectroscopy). Even water:alcohol rinsing couldn't remove all dye, indicating the existence of both weak reversible trapping and strong ionic and/or covalent binding. **Figure D-4** illustrates this observation for the R6G binding. Non-normalized UV-VIS and fluorescence spectra clearly report the exent of this dye's uptake and the stability of its binding.

Figure D-4. UV-VIS and fluoroscopy of R6G dye in the resist

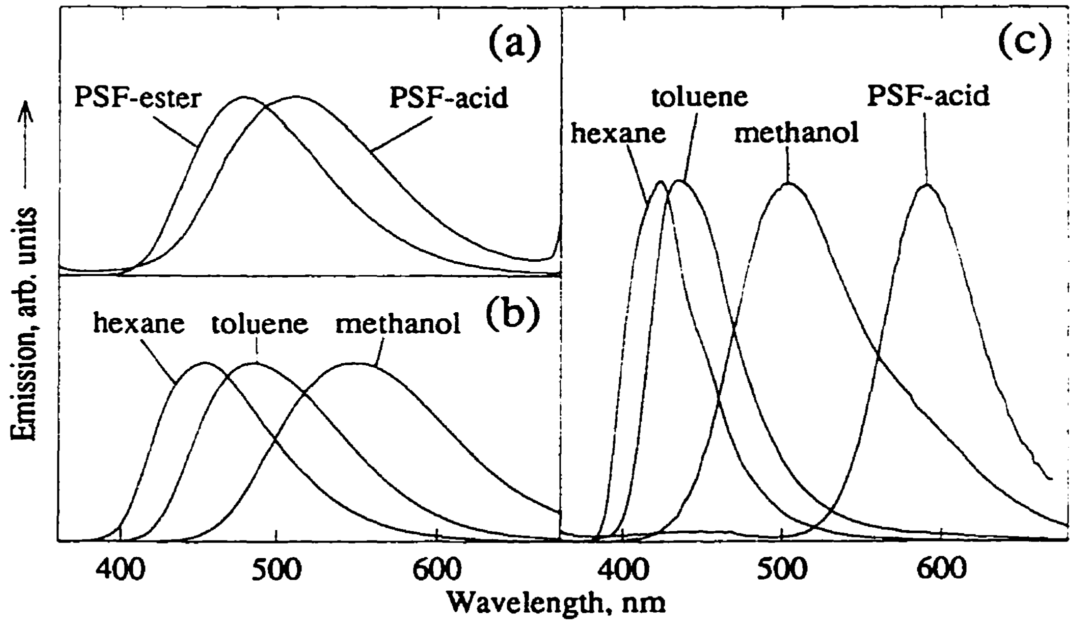


D-3.3. Spectrofluorometry of Dyes in the Resist

In addition to straightforward visualization of functional images from binding experiments, some dyes can supply interesting microenvironment information by their fluorescence and UV-VIS spectra. In particular, the position and intensity of their fluorescence emission peaks depend on a combination of factors: covalent, ionic or hydrogen bonding with a matrix, as well as polarity and viscosity of the medium [15]. For example, dansyl dye has been used to monitor solvent amount and interaction in the crosslinked polystyrene matrix [16]. By placing different dyes in either PSF-acid or PSF-ester, we hoped to understand more about the specific interactions of these polymer matrices with different functional groups on guest molecules. Thus, these fluorescent dyes served as binding species and "reporters" about binding interactions.

The dyes DAASP-18 and DSMP were chosen for a detailed study as each possess several basic functionalities (**Figure D-2**). The literature [17] reports the following pK_a values for somewhat similar protonated compounds in water: pyridine 5.25, 4-aminopyridine 9.11, 4-(methylamino)pyridine 9.65, piperazine 9.83, N,N-dimethylaniline 5.15. Effective acidity of the same compounds inside a polymer matrix may deviate from these values. Compared to ion solvation in polar and protic solvents, there is less (if any) stabilization of charged protonated forms in the largely non-polar polymeric matrix. Thus, some dye "basic" groups may not be fully protonated by polymeric carboxylic acid (pK_a = 2-5).

Figure D-5. Fluorescence emission spectra of DSMP (a, b) and DAASP-18 (c) in different solvents and resist areas. Excitation at 355 nm.



First, fluorescent spectra were taken from solutions of these two dyes in hexane, toluene and methanol, respectively representing non-polar, intermediate and polar environments. Both dyes showed strong solvatofluorochromism, with emission peaks shifted to longer wavelengths in the more polar solvents. Comparison with spectra from dyes in PSF-acid (loaded from water:*t*-butanol) and in PSF-ester (loaded from hexane or hexane:toluene) showed some interesting results. By emission wavelength, DSMP dye "reported" the following order of polarities: hexane 455 nm, PSF-ester 478 nm, toluene 485 nm, PSF-acid 510 nm, and methanol 550 nm (**Figure D-5a,b**). Protonation of the strongly basic piperazine amino nitrogen by polymer's carboxylic acid was expected from the pK_a values, but this probably did not affect fluorescence of the remote dansyl fluorophore. Thus, this dye directly reports polarity alteration of a resist matrix. In this particular matrix, even in such great excess, carboxylic acid appeared unable to protonate the N,N-dialkylarylamino group (pK_a ca. 5) that is conjugated to the dansyl's electron system, which would have caused complete quenching of the dansyl fluorescense [16].

Inside the various media, the DAASP-18 dye showed fluorescence emission peaks at the following positions: hexane 420 nm, toluene 435 nm, methanol 505 nm, and in PSF-acid 590 nm (**Figure D-5c**). The relatively large value of this last was probably due to additional hydrogen bonding or even complete protonation of this dye's pyridyl ring nitrogen by the acidic matrix. This site is basic enough for such proton transfer because the resulting positive charge is stabilized by the lone electron pair on substituent N via extended conjugation, as happens in 4-N,N-dialkylaminopyridines (pK_a ca. 9-10). Unlike the piperazine amine nitrogen in DSMP, this basic pyridine nitrogen is part of the fluorophore's conjugation system, and its protonation directly affects the fluorescence peak position. The emission spectrum of DAASP-18 dye in methanol also displayed a shoulder at the same 590-600 nm region, which may be due to hydrogen bonding between the alcohol and the same ring nitrogen.

D-3.4. Binding of Amines

Many biomolecules contain alkyl, aryl or heterocyclic amino or ammonium group(s), which can be used to immobilize them in an acid- or anhydride-containing matrix. Binding of some model non-dye amines was monitored by IR spectroscopy (**Figure D-6** and **D-7**). Some of the proposed resist-amine structures are summarized in **Figure D-7**.

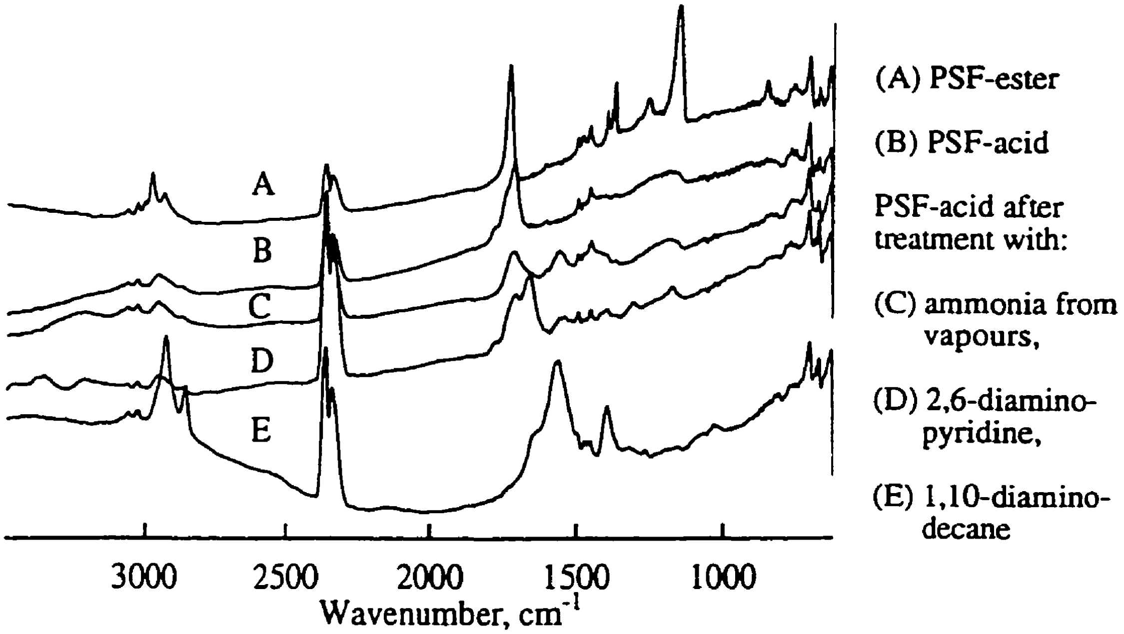


Figure D-6. FTIR spectra of the resist before and after functionalization.

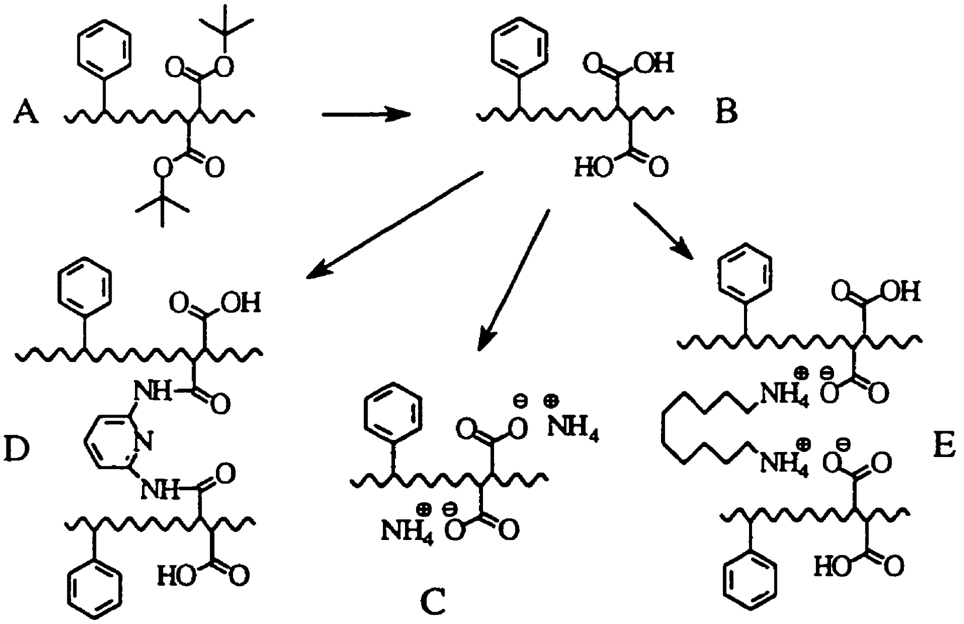


Figure D-7. Structures (simplyfied) of compounds in Figure D-6.

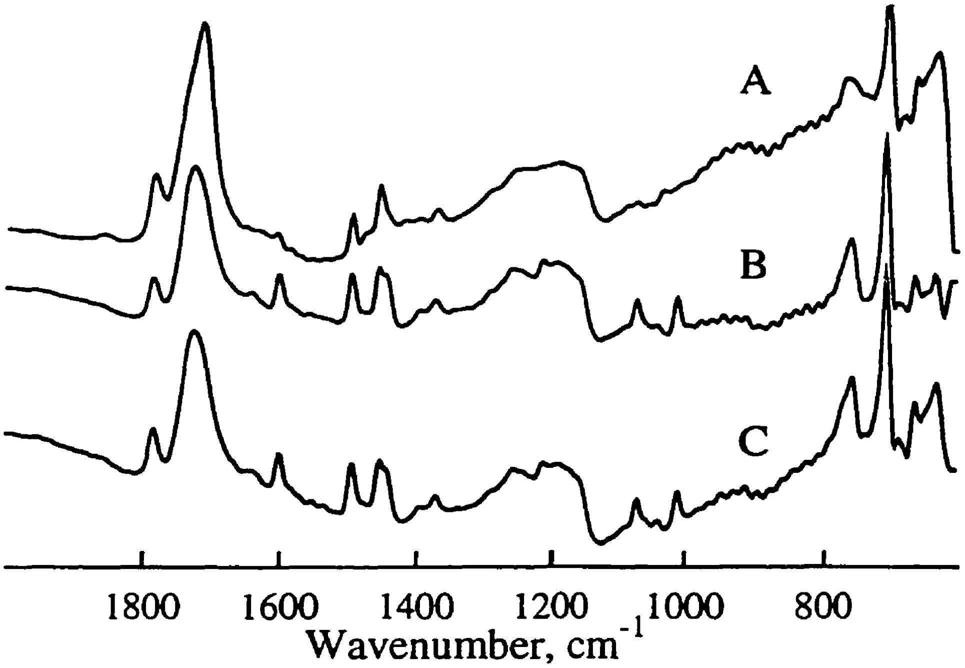


Figure D-8. FTIR spectra of PSF-acid before (A) and after 1 h (B) and 3 h (C) of pyridine vapour treatment.

Functional development was first accomplished with volatile amines from the gas phase. An irradiated and baked PDBFS sample was placed above 5 wt % aqueous ammonia solution for 120 s. The ammonia vapour was able to deprotonate carboxylic acid groups of the PSF-acid, resulting in a decrease of the 1708 cm^{-1} peak and appearance of peaks at 1450 cm^{-1}, 1560 cm^{-1} and a broad peak at ca. 3200 cm^{-1} (**Figure D-6**, spectrum C) that perfectly matched carboxylate anion and ammonium cation peaks. Further exposure to ammonia vapour rapidly led to complete transformation of acid to salt. Though IR showed some deterioration of PSF-ester after more than 600 s of this ammonia vapour treatment, there was a broad time range for transforming only the PSF-acid into a water-soluble salt form. By then immersing *in pure water*, ammonia-treated samples of patterned PSF-acid and PSF-ester gave clean positive-tone relief images, providing an alternative to conventional [3] aqueous base for such development.

Pyridine vapours were also taken up in PSF-acid, to a maximum at 1 hour, with no further change at 3 hours (**Figure D-8**, spectra B and C, by new IR peaks at 1596 cm^{-1}, 1435 cm^{-1}, 1010 cm^{-1}, 750 cm^{-1} and 700 cm^{-1}). However, the polymeric carboxylic acid was not detectably deprotonated by this weaker base (see pK$_a$ values above). Here, a limited uptake was still provided by hydrogen bonding interactions alone, even when complete proton transfer with ionization seemed to be thermodynamically unfavourable in this polymer matrix.

IR showed PSF-ester to be unaffected by aqueous monoamine solutions. Dilute solutions of monoamines in water did not wet or otherwise affect PSF-acid either, while higher concentrations dissolved these areas completely. The critical concentration for such dissolution proved to be ca. 0.5 wt % for ammonium hydroxide, 2- and 4-aminopyridines, which are monobasic compounds towards carboxylic acids. However, diaminopyridine, as well as 1,10-diaminodecane and polyethyleneimine, were all able to form multiple ammonium salts to crosslink carboxylate-bearing polymer without dissolving it (**Figure D-6**, spectra D and E). Along with the salt formation, the presence of amide groups here was also often evident by amide-I and amide-II IR peaks at ca. 1640-1660 cm^{-1} and 3100 cm^{-1}, even without further heating. That PSF-ester was not detectably affected by alkylamines implies good contrast for this kind of functional development.

D-4. CONCLUSIONS

In planning a patterned modification of polymer film (functional development), one must consider the species to bind, the template resist and its photospeed, along with resolution, contrast, and amount and stability of uptake. The present report creates a basis for a systematic approach to binding a variety of organic species into microscale resist templates. The report's main conclusions are:

- For small irradiation doses, the CA chemistry offers the best scope for massive material alteration particulary with (sub)micron resolution. As shown with a CA resist based on PDBFS, transformation of ester to acid groups led to great changes in properties, and, thus, to selectivity and contrast in uptake of sorbates between PSF-ester and PSF-acid. UV dose and PEB temperature were found to be the main factors controlling the ester:acid:anhydride ratio.

- Fast and massive uptake occurs when strong covalent and/or ionic bonds are formed between a solute and a matrix. Various amines were well immobilized selectively within PSF-acid areas of pattern-wise irradiated and heated PDBFS resist. Weaker interactions, e.g., hyrogen bonding, can also be used for a limited sorption of less basic compounds.

- For stable binding from solution, the solvent must be: (i) able to dissolve a compound to be sorbed; (ii) able to wet and penetrate only one of contrasting areas of a resist;

(iii) unable to dissolve either of these resist areas. For the carboxylic acid matrix, we found the appropriate solvent to be a water:alcohol mixture, while for non-irradiated PSF-ester it was a hexane:toluene combination. Yet another way to control wettability is by adjusting pH, as described in **Chapter C.**

- Instant crosslinking by polybasic species (e.g., polyamines or polyvalent ions [12]) is obligatory if the polymer films are not to dissolve as they ionize. On the other hand, pre-treatment with gaseous monobasic species, like ammonia, allows positive-tone relief developing of PDBFS-based resists in *pure water*.

Further experiments will explore the image resolutions of the various types of functional development we have here discussed. As in the CARL and other chemical treatments and processes [6], with careful control of uptake and swelling, one could expect these to be limited only by the UV exposure technology itself (less than 0.15 μm with modern vacuum-UV tools).

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Chapter E

Completely Water-Processable and Other Chemically Amplified Resists from Maleic Anhydride Copolymers

E-0. ABSTRACT

A new family of chemically amplified resists is presented for an *all-water* microlithography process. Polymeric vicinal carboxylic acid moieties undergo dehydration to cyclic anhydride at a lower temperature in the presence of an acid catalyst, than upon uncatalyzed thermolysis. For example, a mixture of hydrolyzed ethylene- or methyl vinyl ether-*alt*-maleic anhydride copolymer with a photo-acid generator can be spin-coated from water to form a clear film. Exposing areas to ca. 25 mJ/cm^2 of UV irradiation, followed by mild heating, selectively transforms the hydrophilic diacid matrix there into a hydrophobic anhydride form ("dehydration" design). This latent image is developable in pure water to the negative-tone relief image, or in acetone to the positive-tone one. Alternatively, acid-catalyzable insertion of water vapors into UV-exposed anhydride matrix areas (an innovative "hydration" design) allows positive-tone developing *also in pure water*. Yet another new family of microlithographic resists uses acid-catalyzable alcohol elimination from polymers of maleic acid monoesters, e.g., poly(styrene-*alt*-maleic acid monoethyl ester). The difference in reactivity and hydrophobicity between exposed and non-exposed areas in these resists also allows their functional developing, e.g., by introducing multivalent amines or metal ions selectively into diacid resist areas.

Keywords: microlithography, chemically amplified resists, maleic anhydride copolymers, water-processable resists, relief and functional imaging.

E-1. INTRODUCTION

As described in **Chapter A**, chemically amplified resists are an important and expensive part of electronic production. To the best of our knowledge, all CA resists have been based on specially designed and synthesized (and thus expensive) specialty polymers. Moreover, some also require organic solvents to cast their films, and often to develop and strip them off, creating hazards of health and fire, and thus problems in handling and costs. New formulations and processes using only inexpensive and easy-to-handle components would therefore be of great practical importance.

Several resist systems are known [4-7] that are castable and/or developable with pure water or simple alcohols. They are all based on crosslinking chemistry, and so are typically limited to 1-2 μm resolution due to swelling problems. Also, final stripping of their crosslinked residues still requires somewhat harsh solvents.

Our previous research [8-10] showed that poly(di-*t*-butyl fumarate-*alt*-styrene) (PTBFS) easily undergoes thermo-acidolysis at 100-130 °C towards poly(fumaric acid-*alt*-styrene), which is rapidly soluble in an aqueous base to form positive-tone relief images. But above 130 °C, a detectable dehydration reaction to cyclic anhydride groups again increases the hydrophobicity of the matrix and depresses such dissolution [9]. An ester→acid→anhydride sequence has also been involved [11] in another design that uses "polarity reversal", but that requires aqueous base for developing. Since a strong acid catalyzes a variety of rearrangements, we presumed that a photo-produced acid may promote dehydration at moderate temperatures, so that exposed and baked areas would be dissolved more slowly or not at all by polar solvents. Thus, the idea was to start from a hydrophilic polymer with carboxylic acid moieties, and to use acid-catalyzed dehydration towards hydrophobic anhydride (**Figure E-1**, R = H). This concept can also be extended to some partially esterified copolymers (containing groups that are half-ester or semi-ester derivatives of cyclic anhydride groups) capable of similar acid-catalyzed cyclo-dealcoholation (**Figure E-1**, R = alkyl). Ito et al. [11] and Uchino et al. [12] have developed CA resists working by other hydrophilic→hydrophobic transformations involving acid-catalyzed dehydrations (e.g. pinacol rearrangement), but these aren't water-soluble in any processing step.

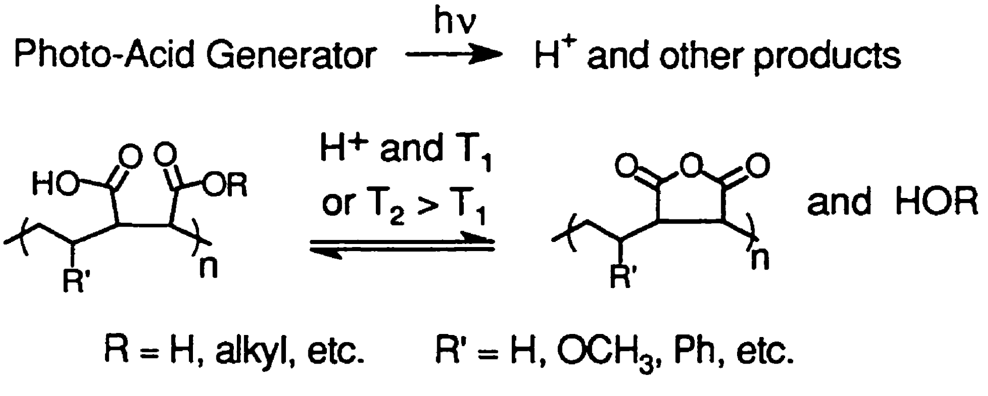


Figure E-1. Design for resists based on copolymers of maleic anhydride.

Yet another idea was to check an acid-catalyzed "insertion" reaction for polymer modification. Alternatively to the "extrusion" of small molecules such as isobutylene or carbon dioxide, a new one employs *acid-catalyzable insertion* of some volatile compound from its vapors. In fact, vapor treatment is known for CA resist processes, but only to help cleave some protective groups by hydrolysis or alcoholysis, and so promote release of other small molecules, or to introduce plasma-resistant groups after acid-catalyzable transformations [13,14].

Among water-soluble polymers, maleic anhydride (MAn) and maleic acid (MAc) copolymers with ethylene and methyl vinyl ether are mass-produced items (for example, from ISP Inc. [15]). Poly(MAn-*alt*-styrene) is another well-known copolymer, although it is not water-soluble at neutral pH. Along with good mechanical, optical and film-forming properties, such copolymers possess a highly reactive anhydride moiety, that is easily transformable into acid, ester, salt, amide, etc. by appropriate reagents [16,17]. Particularly in microlithography, several MAn copolymers have been used as the inert matrix in a mixture with photosensitive dissolution inhibitors [18,19]; as a protection layer against basic contaminants [20]; in crosslinking chemistry designs [21,22]; or as E-beam positive-tone resists [23,24]. Siemens AG uses MAn copolymers in the "CARL" advanced process [25]: after having been photoimaged through *t*-BOC-protected comonomer, anhydride moieties bind Si-containing oligomers for oxygen-plasma developing. Nevertheless, to the best of our knowledge, no anhydride, monoester, or carboxylic acid moieties have ever been used in microlithography as the principal sites for polarity-alteration rearrangements.

Onium salts are standard Photo-Acid Generators (PAG) in microlithography [1,2,26], but the existence and applicability of their solubility in water has been ignored till very recently [27]. Some onium salts are in fact fairly soluble in alcohols and alcohol:water mixtures, and thus might (as we thought) be soluble in aqueous solutions of hydrophilic polymers, and dispersible in films of such polymers.

This **Chapter E** presents the design, study, and microlithographic evaluation of new families of CA resists, including all-water processable formulations. We also studied the irradiation-directed introduction of metal ions and polyamino compounds into a latent resist pattern, as further examples of "functional developing" for non-standard lithographic applications [9,10].

E-2. EXPERIMENTAL SECTION

E-2.1. Instruments

Resist solutions were filtered throughout 0.8 µm Acrodisc-13 filter (Gelman Science) or 0.2 µm inorganic membrane filter Anotop-10 (Phenomenex). Using a Headway Research spin-coater, films were applied onto either pieces of Unisil silicon test wafers 3" x 330-432 µm N/P <1-1-1>, or National Scientific GE 124 polished fused quartz plates 1" x 1" x 1/16" (for UV-vis spectrophotometry). Post-Applied Baking (PAB) and Post-Exposure Baking (PEB) were performed on a hot plate with a thermocouple control. Film thickness was measured using a Sloan Dektak profilometer. UV sources consisted of a Cole-Palmer 9815 Series 100 W Hg lamp with build-in 254 nm narrowband filter; a home-made system with 1 kW Xe-Hg lamp in an ORIEL housing, condensing lenses, circulating water to filter IR radiation, but without any UV filter; and an open 150 W Hg lamp without any filter. Exposure doses were measured by Optical Associates powermeters OAI P306-001 and -008 at 254 and 313-365 nm, respectively. Irradiation of samples was performed at 20-30 cm from lamps and controlled by a timer. An REK/73 step tablet (from Optoline-Fluroware) was used, containing several windows of 0-100% transparency with down to 1 µm line/space test patterns. For evaluation of samples, the following apparatus and techniques were used: UV-vis Shimadzu 210-UV spectrophotometer with sample films on quartz windows; Brooker IF-48 FTIR spectrophotometer in transmittance IR-microscope mode with sample films on IR-transparent silicon wafers; Gemini 200 MHz ^{1}H-NMR tool with samples dissolved in acetone-d6; 200-400X optical microscope with attached 35-mm camera; and Seiko TGA-7 station with nitrogen gas bypass at 100 mL/min and with heating rate 10 °C/min, data are presented as TG curves (mass vs. temperature, M vs. T), and their derivatives DTG curves (dM/dT vs. T).

E-2.2. Chemicals

Table E-1 presents the names, abbreviations, sources and supplementary information for the polymers and some of the chemicals used in this study. Diphenyl iodonium triflate (DPI-OTf), diphenyl iodonium hexafluoroantimonate (DPI-SbF_6), and triphenyl sulfonium hexafluoroantimonate (TPS-SbF_6) were synthesized by reported methods [26]. Propylene glycol methyl ether acetate (PMA), malic, glycolic, tartronic, and lactic acids were from Aldrich. Acetone, diglyme, methanol, ethanol, were all of analytical grade from BDH.

Table E-1. List of chemicals

chemicals	abbreviation	source[a] and CAS #	specifications
poly(methyl vinyl ether-*alt*-maleic anhydride)	PMVEMAn1	SP2, cat# 317, [9011-16-9]	M_w = "medium"
poly(methyl vinyl ether-*alt*-maleic anhydride)	PMVEMAn2	ISP, Gantrez AN-119, [9011-16-9]	M_w = 50 K
poly(methyl vinyl ether-*alt*-maleic acid)	PMVEMAc	SP2, cat# 374, [25153-40-6]	M_w = "low"
poly(acrylic acid)	PAAc	SP2, cat# 026, [9003-01-4]	M_w = 250 K
poly(ethylene-*alt*-maleic anhydride)	PEMAn	Ald., cat# 18,805-0, [9006-26-2]	M_w = 100-500 K
poly(maleic anhydride)	PMAn	POLY, cat# 02348, [24937-72-2]	-
poly(itaconic acid)	PIAc	POLY, cat# 09534, [25119-64-6]	-
PMVEMAc monoethyl ester	MEE	Ald., cat# 41,629-0, [25087-06-3]	50 wt % in ethanol
PMVEMAc mono-*i*-propyl ester	MIPE	Ald., cat# 41,639-8, [31307-95-6]	50 wt % in *i*-propanol
PMVEMAc mono-*n*-butyl ester	MNBE	Ald., cat# 41,630-4, [25119-68-0]	50 wt % in ethanol
poly(styrene-*alt*-maleic anhydride)	PSMAn	SP2, cat# 456, [9011-13-6]	M_w = 100-500 K
2,6-diaminopyridine	DAP	Ald., cat# D2,440-4, [141-86-6]	-
1,10-diaminodecane	DAD	Ald., cat# D1,420-4, [646 -25-3]	-
silver triflate	Ag-OTf	Ald., cat# 17,643-5, [2923-28-6]	99+% purity

(a) SP2 = SP2 Scientific Polymer Inc.; ISP = International Specialty Products (known also as GAF); Ald. = Aldrich Chemical Corporation; POLY = Polyscience, Inc.

E-2.3. Synthesis of MAc Monoesters Copolymers

The general procedure for preparation of PSMAc monoesters is shown for the ethyl derivative. PSMAn (2.0 g, 9.9 mmol) was added to 99% ethanol (10 mL, 170 mmol) in a 100 mL flask. The initially insoluble copolymer dissolved slowly upon stirring at room temperature overnight. The resulting viscous solution was poured into 20X excess of diethyl ether or water. After several cycles of dissolution and precipitation, a white product was isolated by filtration (>90% yield), and dried 6 h in air and 2 h under mild vacuum. The IR spectrum of the product showed strong carbonyl peaks at 1710 cm^{-1} (RCOOH) and 1735 cm^{-1} (RCOOR'); peaks at 1850 and 1780 cm^{-1} (5-member anhydride cycle) were much weaker than in the starting material. For modification with other hydroxy compounds, 1 g of PSMAn and 2 g of glycolic, lactic, tartronic, or malic acids were placed in 5 mL of acetone or diglyme. After refluxing for several days at 60 °C under nitrogen, products were isolated as described above. Esterification conversion was monitored by IR and ^1H-NMR measurements.

E-3. RESULTS AND DISCUSSION

E-3.1. Solubility of some Onium Salts in Water

To check solubility of several commonly used onium salts in pure water, about 25 mg of fine crystals of each were shaken overnight in 5 mL of water. Of these, DPI-OTf dissolved completely to give a transparent solution. Only a small number of crystals were left in the clear solution of DPI-SbF_6, while many remained in the cloudy TPS-SbF_6 solution. After filtration (0.8 μm then 0.2 μm), all three solutions showed very strong peaks (>3 absorption units/cm) in the deep-UV region that were typical of aryl moieties of onium salts. Thus, even the TPS-SbF_6 salt had some solubility in water. The addition into the same vials (without filtration) of ca. 5 wt % of PMVEMAn1, and shaking a further 0.5 h, gave clear solutions with both DPI salts, and a still slightly cloudy solution with TPS-SbF_6, but now without big crystals. This polymer of medium polarity, containing both hydrophilic (acidic) and hydrophobic (hydrocarbon backbone) portions, thus can act as a dissolution promoter of rather hydrophobic onium salts into water.

E-3.2. Water-Soluble Resists from PMVEMAn and PEMAn

Solutions were obtained by shaking a polymer and a PAG in water for 0.5 h at room temperature, or for 2-3 min at 80-90 °C. After 0.2 μm filtration, the solutions were spin-coated onto silicon wafers at 600-2000 rpm to form optically clear smooth films of 0.3-2 µm thickness without visible phase separation. Such ca. 1 µm films, cast from water:PMVEMAn1:DPI-OTf (100:10:1 w:w), were subjected to brief evaluation using various deep-UV doses and temperatures of PAB and PEB. After cooling, the samples were then developed in distilled water for 30 s, spin-dried, and their sensitivities were estimated by identifying the lowest UV-dose to produce the apparently water-insoluble area (see **Table E-2**). The only acceptable baking conditions for producing negative-tone relief images were PAB 100-130 °C, and PEB around 130 °C. Both irradiated and non-irradiated areas appeared to be water-insoluble after any baking at 160 °C. Lower temperatures of PAB <100 °C or PEB <130 °C left all areas water-soluble, again regardless of exposure. The simplest explanation is that insufficient PAB leaves some volatile contaminants to severely inhibit acid-catalyzed reactions [28,29].

Table E-2. Sensitivity of the PMVEMAn1:DPI-OTf resist (a)

PAB 120 s at ↓	PEB 120 s at →	100 °C	130 °C	160 °C
60 °C		soluble	soluble	n/a
100 °C		soluble	25 mJ/cm^2	insoluble
130 °C		soluble	25 mJ/cm^2	insoluble
160 °C		insoluble	n/a	n/a

(a) "soluble" and "insoluble" refer to solubility at any UV-dose, n/a - was not tested

Under fixed processing conditions of PAB 10 s at 130 °C and PEB 40 s at 130 °C, compositions PMVEMAn1:DPI-OTf of weight ratios 100:10, 100:5, and 100:2.5, showed sensitivities of 25, 42 and ca. 100 mJ/cm^2, respectively. A similar 100:1 composition failed to produce any image with less than 300 mJ/cm^2. Thus, ca. 2-5 parts of the PAG per 100 parts of the polymer were needed to absorb enough UV energy and to produce enough strong acid to alter the matrix.

The resulting relief patterns were not affected by water at room temperature within several minutes. However, a few minutes in hot water, or hours in room-temperature water, were enough to dissolve all these patterns completely. These results and the IR study (see below) preclude any possible crosslinking by esterification between methoxy and acidic or anhydride moieties. Thus, all steps -- casting, developing, and stripping, -- were accomplished with pure water.

Even with a home-made illumination system (contact printing with unfiltered light from the 1 kW Xe-Hg lamp), we succeeded in obtaining a resolution of 1 µm (the limit of our mask) with the PMVEMAn1:DPI-OTf resist. Relief images were clean without any residue in unexposed areas, and without any detectable swelling of exposed areas. Thus, such resists may have much better submicron resolution than other water-processable or MAn-containing swellable crosslinking compositions known from the literature [4-7,21,22]. The presented water-processable resists showed good adhesion to the substrate, definitely due to their high COOH content; calculated shrinkage due to mass loss during the PEB step was less than 2.5% in any direction (<10 vol% from calculations and TGA).

Although it does not fit to the objective of all-water processing, it was possible to develop a positive relief image by treatment with organic solvent(s). Since the exposed areas here turn from polar diacid into less polar anhydride, a developer must be nonionic and of medium polarity. The PMVEMAn1:DPI-OTf (20:1 w:w) composition showed photospeed ca. 50 mJ/cm^2 with gamma value γ>7 after 10 s of acetone developing (PAB 10 s at 130 °C, PEB 45 s at 130 °C).

Compositions DPI-OTf with PMVEMAn2, PEMAn or PMAn showed the same excellent all-water processability as PMVEMAn1 under similar conditions (PAB and PEB 20-60 s at 120-140 °C, DUV doses 25-35 mJ/cm^2). Lower molecular mass PMVEMAc behaved much worse than PMVEMAn1: its catalytically dehydrated areas were rather quickly eroded by water. We were unable to cast good films from 10-25 wt % water solution of the purchased PIAc, apparently due to its low molecular mass. Unlike DPI-OTf, the other onium salts DPI-SbF$_6$ and TPS-SbF$_6$ failed to produce any developable image with PMVEMAn1 and PEMAn under various conditions. Either hydrolysis of these PAGs, or photo-produced acid, or the phase separation from the copolymers, or lesser catalytic activity of hexafluoroantimonic vs. triflic acids, can account for the inefficiency of these salts. While studying PTBFS:onium salt resists, we already noted [9] that under similar conditions, more anhydride was formed with DPI-OTf salt than with DPI-SbF$_6$ or TPS-SbF$_6$. Thus, for capped carboxylic acid deprotection CA processes, choosing SbF$_6$ anion would prevent undesirable acid-catalyzable anhydride formation, because the first portion of water would deactivate the corresponding HSbF$_6$ acid.

Various inorganic compounds are known [30] to produce strong acid upon irradiation. One of them, silver triflate, was successfully tried as a PAG for our resists. Images were obtained with irradiation from an open 150 W Hg lamp for several minutes. Using similar processing conditions as for DPI-OTf systems, resists with 100 parts of PEMAn and 10, 5 and 3 parts of Ag-OTf become water-insoluble after irradiation for ca. 90, 140 and 200 s respectively. No pictures were seen after 300 s irradiation when light was filtered by a polyester film (UV cut-off ca. 340 nm).

E-3.3. IR and UV Study

IR techniques are widely used in qualitative and quantitative studies of resist transformations. Superposition of plots of characteristic peak intensities and normalized film thickness vs. UV-dose gives valuable solubility vs. composition information [10]. **Figure E-2** features such plots, along with an FTIR spectra set, for the water-soluble PMVEMAn1:DPI-OTf resist (10:1 w:w, PAB 30 s at 110 °C, PEB 30 s at 130 °C, development in room-temperature water for 20 s). The spectra show that increasing UV dose caused a steady decrease of IR signal from COOH groups at 1710-1725 cm^{-1} and 3000-3500 cm^{-1}, with an increase of peaks at 1780 and 1850 cm^{-1}. The latter doublet exactly matches peaks of starting maleic anhydride copolymer, whose 5-membered rings are much more sterically favorable than possible intermolecular or alternative 7-membered intramolecular ring anhydrides. Other characteristic anhydride peaks also appeared at ca. 920 and 970 cm^{-1}. The peak at 1120 cm^{-1} from methyl ether remained stable under such conditions. Thus, the main process here is acid-promoted dehydration, from the almost completely hydrolyzed diacid form of the copolymer into cyclic anhydride. Semi-quantitative evaluation of the curves shows that the matrix is soluble in water at a diacid:anhydride ratio of ca. 2:1, but is insoluble (within minutes) at ca. 1:1. Similar IR evaluation is shown in **Figure E-3** for a PEMAn based resist.

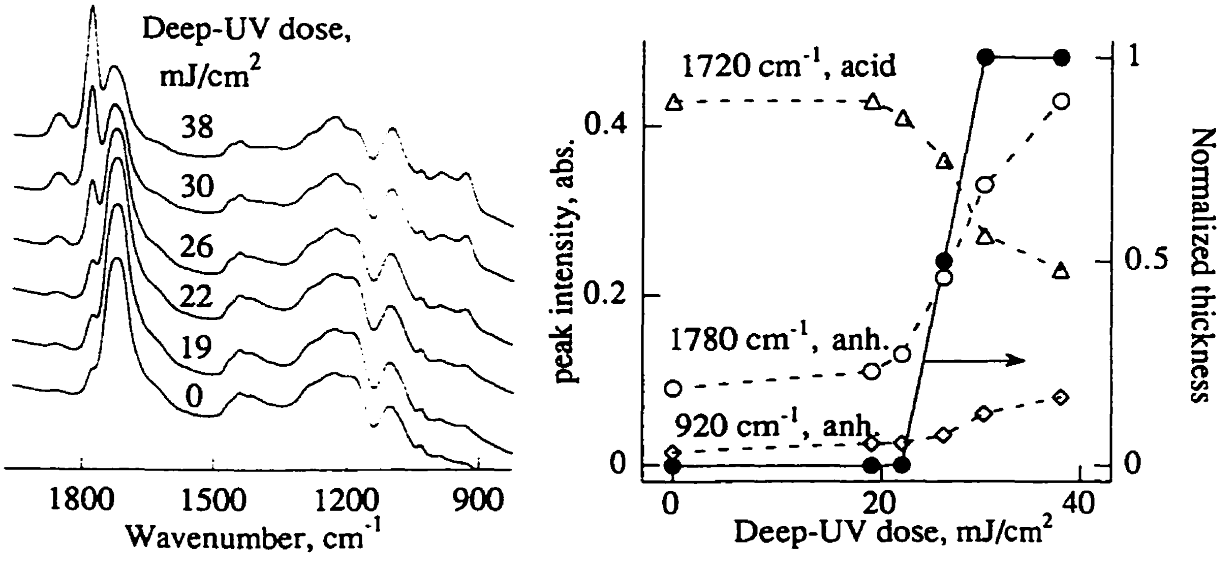


Figure E-2. IR study of PVMEMAn1:DPI-OTf (10:1 w:w).
PAB 30 s at 110 °C; PEB 30 s at 130 °C; development in RT water for 20 s

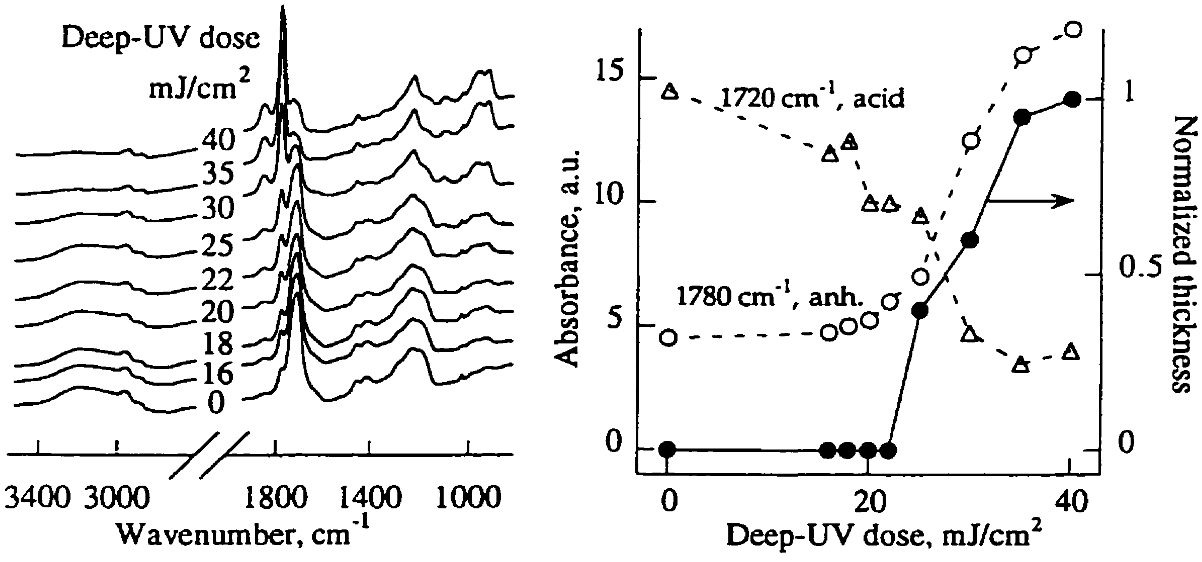


Figure E-3. IR study of PEMAn:DPI-OTf (10:1 w:w). Conditions are in Figure E-2.

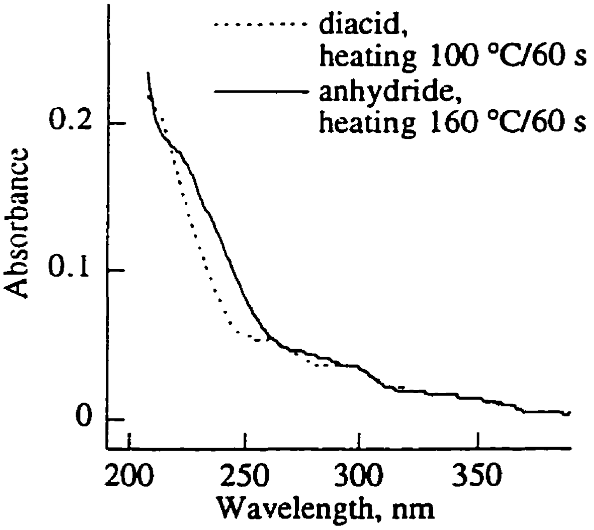


Figure E-4. UV spectra of diacid and anhydride matrix of PMVEMAn1.

Optical transparency of a resist matrix is important for in-depth uniformity of the exposure. Figure 3 presents UV spectra of pure PMVEMAn1 in diacid and anhydride forms (obtained by heating spin-coated films for 60 s at 100 °C and 160 °C, respectively). Excellent transparency suggests a potential of such materials for deep- and vacuum-UV lithography.

E-3.4. TGA Study

Temperature control is of critical importance for all processing steps of CA resists. PAB temperature is responsible for eliminating volatile contaminants, appropriate drying and annealing of films, while PEB temperature controls the rate and extent of catalyzed reactions. Additional attention must be paid to volatility of PAG photolysis products, side-reactions in exposed areas, and uncatalyzed reactions in unexposed areas. TGA is an excellent tool for choosing a suitable temperature range (so-called "processing window") for thermal processing steps.

Figure E-5 shows TGA curves taken from pure copolymer PMVEMAn1 (curve A, 1.5 mg sample), and from resist formulation PMVEMAn1:DPI-OTf, 10:1 w:w (B, 1.1 mg, and C, 0.17 mg). Sample A was not baked; sample B was subjected to PAB 30 s at 110 °C; and sample C was subjected to similar PAB and deep-UV exposure of 50 mJ/cm^2. For the pure copolymer, TGA shows drying at 50-80 °C, which is essential for further image formation (see **Table E-2**). Next, a mass loss of ca. 10% occurred at 130-180 °C (with a maximum at 160 °C), evidently [31] corresponding to dehydration to cyclic anhydride (calculated as ca. 10 wt % for complete dehydration of the given formulation). Next, a ca. 30 wt % was lost at 210-300 °C, and only mild decomposition continued until 500 °C. Much the same thermal behavior has been reported [31] for pure PMVEMAn2 (Gantrez AN-119). Curve B (with the PAG, but unexposed) shows that after a given PAB, the resist was almost completely dry; and maximal dehydration occurred at 156 °C, only slightly less than for the pure copolymer. An important feature of curve C is a 35 °C decrease in the temperature of cyclo-dehydration in the presence of photo-generated acid.

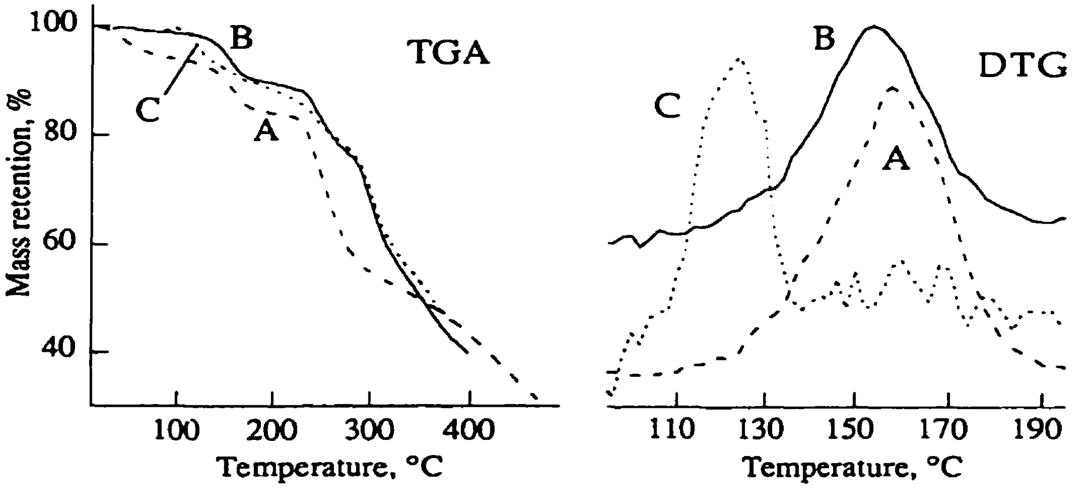


Figure E-5. TGA of the PMVEMAn1:DPI-OTf resist; details are in text.

Thus, according to TGA, the best contrast in composition between exposed and unexposed areas would be achieved by PAB in the 110-140 °C range. Since non-catalyzed thermolysis also starts in this range, PEB time must be rather short to avoid non-catalyzed reactions. Overall, the TGA results are in excellent agreement with the data in **Table E-2** and the IR study.

E-3.5. Poly(Acrylic Acid) Evaluation

PAAc was studied as another water-soluble resist candidate, since it also possesses many carboxylic acid groups per molecule. While a non-irradiated sample loses ca. 13 wt % (presumably water) at 205-215 °C, the irradiated system shows similar mass loss at 120-200 °C (**Figure E-6**). However, a brief test of several PAAc compositions with the onium salts failed to produce any image under processing conditions of PAB and PEB within 130-170 °C and deep-UV dose <100 mJ/cm^2. Both non-irradiated and irradiated areas became water-insoluble even upon 20-40 s of PEB at various temperatures. It is known [32], that PAAc is less prone to form intramolecular (e.g., 6-member) anhydride rings upon heating, so that even the very first anhydride groups are intermolecular to prevent matrix dissolution.

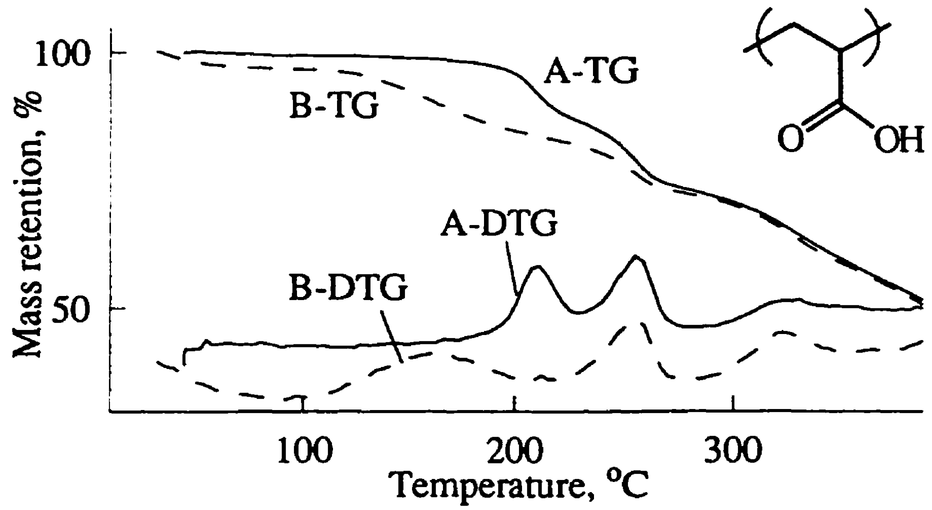


Figure E-6. TGA of PAAc:DPI-OTf (10:1 w:w).
A - unexposed sample; B - 60 mJ/cm^2 of DUV.

E-3.6. A New Reverse ("Insertion") Design

Many of the known CA resists are designed to perform the following "extrusion" reaction in areas with a photo-produced catalyst ("X" will denote any evolving product):

$$\text{polymer}\sim X_{(\text{solid})} \xrightarrow{\text{catalyst, heat}} \text{polymer}_{(\text{solid})} + X_{(\text{gas})}\uparrow$$

During PEB, a generally volatile small molecule X escapes the matrix. One of catalyst property is that it promotes the reaction in both directions. Thus, with increasing concentration of X (e.g., its pressure above a film) , it is possible to reverse such design:

$$\text{polymer}_{(\text{solid})} + X_{(\text{gas})} \xrightarrow{\text{catalyst, heat}} \text{polymer}\sim X_{(\text{solid})}$$

Theoretically, any known deprotection chemistry can be reversed. For example, acid catalyzes isobutylene elimination from polymers with the *t*-BOC protector [33]. It is therefore logical to suggest, that isobutylene can react with a carboxylic acid-containing matrix selectively in areas with photo-produced acid under certain condition. Indeed, the reaction was used to produce *tert*-butyl protected monomers: liquid phase synthesis, excess of *i*-butylene, very low temperature (e.g., -30 °C), triflic acid as a catalyst [34]. But we haven't found any reports of a solid phase (polymer matrix) analog of such reaction with a photo-produced acid.

A better system would involve an equilibrium more balanced between reagents and products (thus more reversible, unlike in known resist systems), and, of course, capable of large catalytic acceleration. In fact, a large negative $\Delta G°$ (more than ca. 40 kJ/mole) of any deprotection reaction prevents reverse reaction under practical vapor pressures of X. With smaller $\Delta G°$, a modest increase of P_X would drive reaction from right to left. The following set of equations (1)-(4) discribes our particular hydrolysis (bulk molar concentrations are in squared brackets; P_W = water vapor pressure; eq. = equilibrium):

$$\text{diacid} \rightleftharpoons \text{anhydride} + \text{water (vapors)} \tag{1}$$

$$\frac{[\text{anhydride}]_{\text{eq.}}}{[\text{diacid}]_{\text{eq.}}} = \frac{K_{\text{eq.}}}{P_{\text{w.eq.}}} \tag{2}$$

$$\Delta G = \Delta G° + RT \ln\left(\frac{[\text{anhydride}]*P_W}{[\text{diacid}]}\right) \tag{3}$$

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K_{\text{eq.}} \tag{4}$$

The possibility of the reverse reaction (1) is determined by the equation (3): a high enough water vapor concentration (P_W) can drive ΔG to some positive value. The anhydride:diacid ratio at equilibrium will be governed by P_W in the equation (2). To be exact, one must consider diffusion and activity of the reactants into a matrix's bulk; for example, increasing of the diacid content may increase "solubility" of water molecules in the matrix, but may also decrease their activity by hydrogen binding. Due to $T\Delta S°$ contribution in the equation (4), low temperature will favor diacid formation (or any protected polymer in general considerations), but kinetics of such reaction would be rather slow. Too high a temperature would eventually favor extrusion. Thus, for a reverse reaction some optimum temperature must be found that is suitable for both thermodynamic and kinetic reasons.

We have checked the reverse design in the following unoptimized experiments. Resist formulation water:PEMAn:DPI-Tf (100:10:1 w:w) was spin-coated onto a silicon wafer and heated 60 s at 160 °C, in order to obtain the mostly anhydride form. After 100 mJ/cm^2 of patterning deep-UV irradiation, the sample was placed (resist side up) onto the neck of a 200-mL Erlenmeyer flask with boiling water. This way, water vapors freely fly through the neck, without undesirable direct condensation onto the resist side. All this was covered with 1-L beaker upside-down, to retain the vapors and heat. After 180 s of such treatment, then air-cooling, the sample was developed in room-temperature water. Photo-exposed and subsequently catalytically hydrolyzed areas quickly disappeared leaving a positive-tone pattern. **Table E-3** presents IR and lithographic evaluations of the water:PMVEMAn2:DPI-OTf (1000:70:5 w:w) resist after similar treatment. Links between DUV-dose (amount of acid catalyst), final film composition (anhydride:diacid ratio) and water-solubility are well seen. Conditions were: PAB 120 s at 170 °C, water vapor treatment for 300 s, and developing 15 s in room-temperature water.

Table E-3. Acid-catalyzable anhydride hydrolysis and water-solubility.

DUV dose, mJ/cm^2	1780 cm^{-1} : 1725 cm^{-1} ratio (a)	stability in water
0	1.46	stable
18	1.17	stable
24	1.12	residues
32	0.93	residues
40	0.97	fast dissolution
48	0.90	fast dissolution

(a) ratio of anhydride:diacid IR peak intensities

E-3.7. Monoesters of MAn Copolymers as CA resists

Synthesis of a variety of PSMAc monoesters was accomplished by treatment of an anhydride precursor with simple alcohols and other hydroxy-containing compounds. According to NMR and IR, overnight stirring of PSMAn in methanol unexpectedly resulted in mostly complete double esterification. Lithographic evaluation of this diester (with DPI-OTf and DPI-SbF_6) failed to produce any image. However, stopping the methanol reaction after 3 h resulted in the desired methyl monoester product, with ca. 40% conversion of starting anhydride units. Overnight stirring in ethanol gave ca. 60 mol % conversion of groups to the PSMAc monoethyl ester.

Several hydroxy-carboxylic acids were used in attempts to confer water-solubility on the rather hydrophobic PSMAn copolymer. Detectable (by IR) conversion with tartronic, lactic, glycolic and malic acids was obtained only after days of heating at over 60 °C. Unfortunately, resulting conversion to monoesters were only 40-60 mol %, and none of the polymers were soluble in pure water. Nevertheless, all these PSMAc monoesters appeared to be good resists for use with other solvents. These polymers were completely miscible with all three PAGs, and soluble in simple alcohols and in such typical spin-coating solvents as PMA. Several lithographic experiments with commercially available PMVEMAc monoesters (MEE, MIPE, and MNBE) also were successful. **Tables E-4 and E-5**, and **Figures E-7,8,9**, present lithographic evaluation, IR and TGA analyses of several members of the MAc monoester family. Most of these promising results were obtained in the very first runs, and one can expect even better lithographic performance under optimized conditions. Casting solvents were either PMA or *i*-propanol. The negative-tone developer was 1.5 wt % aqueous K_2CO_3 solution; almost similar sensitivity was measured with *i*-propanol (Figure 8). Positive-tone developing with acetone failed, due to a smaller alteration of polarity, than for PMVEMAn and PEMAn.

Table E-4. TGA of several MAc monoesters (see structures in Figure E-1)

R'	ROH	temperature$^{(a)}$, °C (mass loss, wt %)		mass lost, wt % (calculated)
		thermolysis	thermo-acidolysis	
OMe	H	155 (10)	120 (11)	10
OMe	ethanol	190 (22)	125 (10), 190 (10)	23
OMe	*i*-propanol	235 (40)	140 (27)	26
Ph	glycolic acid	130 (4), 160 (6)	115 (10)	-

(a) maximum in a DTG curve

Table E-5. Evaluation of resists based on MAc monoesters (see structures in Figure E-1)

R'	ROH	polymer : PAG w:w	PAB, PEB (°C*seconds)	sensitivity
Ph	ethanol	100:5	130*30, 140*30	50
Ph	methanol	100:7[a]	130*30, 130*30	18
Ph	methanol	100:7	130*30, 130*30	22
Ph	malic acid	100:5	130*30, 140*30	35
Ph	lactic acid	100:7	120*20, 130*40	30-33 (**Fig.E-9**)
OMe	ethanol	100:5	130*30, 130*30	ca. 40
OMe	*i*-propanol	100:5	130*30, 150*30	ca. 35

(a) PAG is TPS-OTf

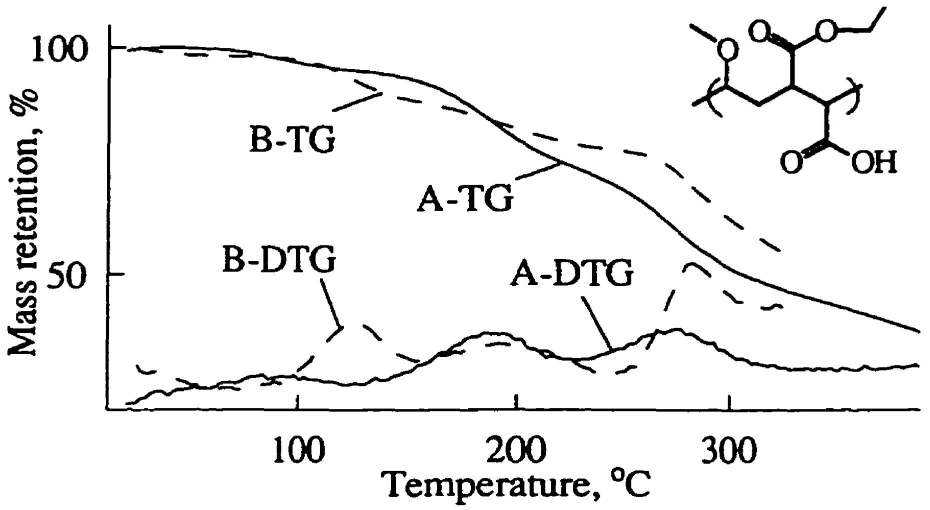


Figure E-7. TGA of MEE:DPI-OTf (20:1 w:w). A - unexposed sample, B - 60 mJ/cm² of DUV.

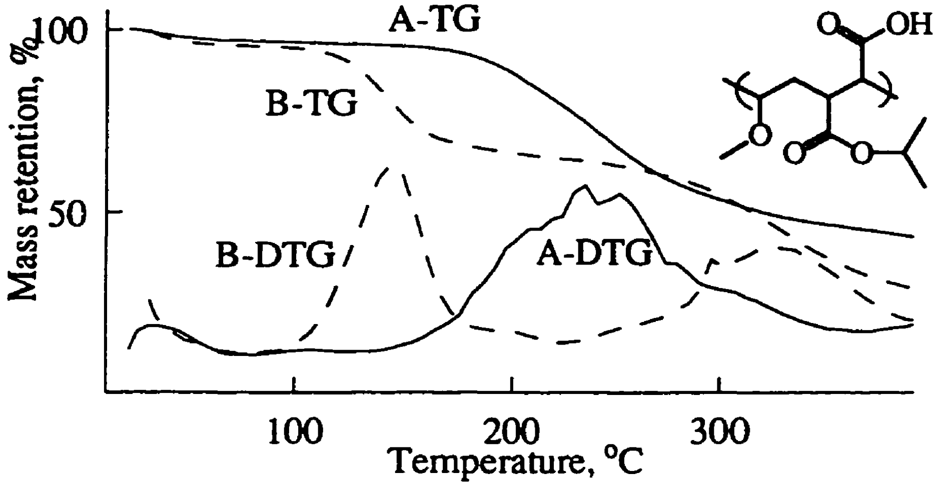


Figure E-8. TGA of MIPE:DPI-OTf (20:1 w:w). A - unexposed sample; B - 60 mJ/cm² of DUV.

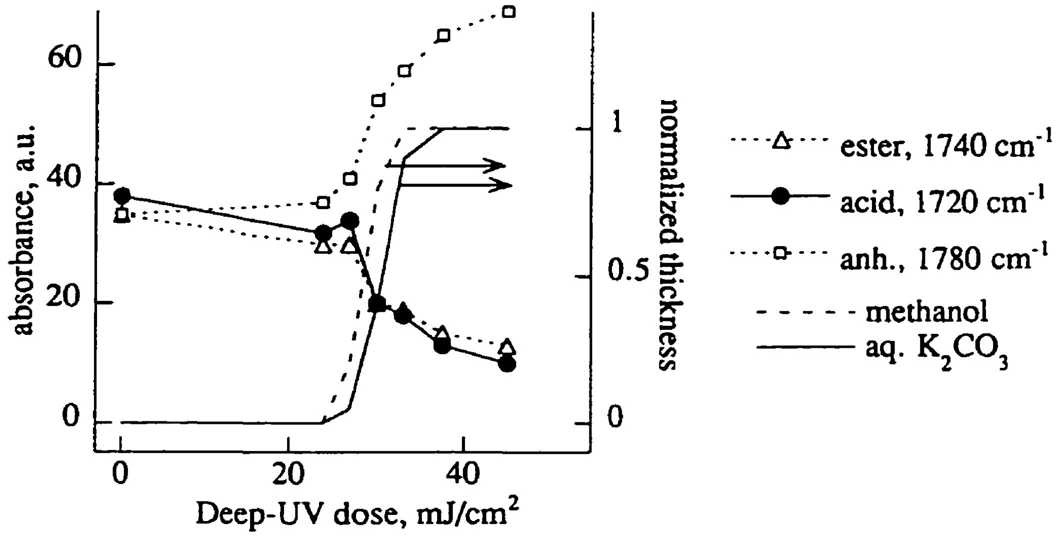


Figure E-9. IR evaluation of PSMAc lactic acid monoester with DPI-OTf (10:1 w:w). PAB 20 s at 120 °C, PEB 40 s at 130 °C.

E-3.8. Mechanism of Acid-Catalyzable Anhydride Formation

Figure E-10 presents the most probable pathway for an acid-catalyzable anhydride formation. This $A_{AC}2$-tetrahedral mechanism is adopted from an organic textbook [35]. The similar pathway in reverse order would be expected for acid-catalyzable hydrolysis/alcoholysis. In both cases formation of the tetrahedral intermediates are expected to be the rate determining steps [35]. Without strong acid and at higher temperatures, one can expect the similar mechanism with participation of polymer's own carboxylic acid, if not by direct proton transfer, then by hydrogen bonding. Having a more bulky R group, there is a remote theoretical possibility for the $A_{AC}1$-mechanism: initial protonation of ether oxygen, and departure of ROH before the intramolecular attack. With an R group able to form a stable carbocation (e.g., *t*-butyl), initial protonation of ether oxygen (**Figure E-10**) may also cause fast elimination of $R^{\oplus}$ and carboxylic acid formation. This $A_{AL}1$-mechanism corresponds to the well-known *t*-BOC-deprotection chemistry [36]. Such chemistry decreases hydrophobicity of the matrix, and contradicts our initial hydrophilic→hydrophobic design. But this would not be a problem, if immediately followed by dehydration to hydrophobic anhydride.

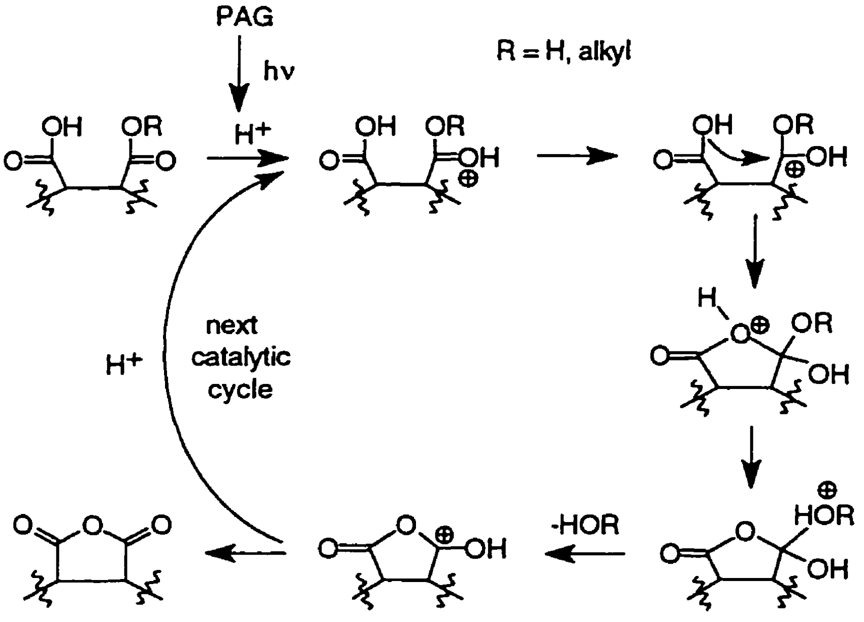


Figure E-10. Probable $A_{AC}2$-mechanism for acid-catalyzable ahhydride formation.

Some resist formulations gave step-wise mass loss (**Table E-5**), probably due to more complex (unidentified) chemistry. Higher temperatures of thermolysis for the *i*-propanol ester caused 40 % mass loss vs. calculated 26 %, likely due to additional decarbonylation or decarboxylation [37]. TGA results in **Table E-5** indicate that bulkiness of an ester alkyl only slightly raises the necessary temperature of acidolysis, but dramatically increases the temperature for uncatalyzed thermolysis (giving wider range for PEB). These observations suggest some difference between rate-determining steps of the catalyzed and uncatalyzed pathways, and more studies must be done to identify the exact mechanisms. In general, by varying the ester R group, one can adjust many properties at once: solubility, thermo- and etch stability, T_g, temperature of catalyzed and uncatalyzed rearrangements, and even reaction pathway.

E-3.9. Functional Development: Space-Selective Binding of Metals Ions

With the appearance of various microdevices for opto-electronic and biological applications, there is an increasing demand to place compounds of interest within submicron patterns. Recently, we showed how PTBFS works as an excellent template for irradiation-directed sorption of dyes, polyamines, polymers and metal ions with formation of covalent, ionic, or other bonds [9,10]. The nature of a metal, composition of a matrix (e.g., ester-acid-anhydride ratio in PTBFS system), and pH of a contacting solution, all affect uptake of metal ions into a polymer matrix. Similarly, with MAn copolymers, exposure and subsequent heating turned the hydrophilic and highly reactive acidic functions into rather hydrophobic and less reactive anhydride moieties. Although for the acidic form of PTBFS it was necessary to raise the pH of the solution above 7 to ensure its wetting, PEMAc and PMVEMAc were already hydrophilic enough at the outset. Thus, for any given metal, we expected the existence of a critical concentration, below which dissolution of the matrix would prevail over its ionic crosslinking.

A simple experiment was conducted to get an idea about water solubility of metal-polymer salts. 2 drops (ca 0.08 mL) of a polymer in water (10 wt %) were added with shaking into 2 mL of 1.0 to 0.004 M solutions of various metal salts. Except for the lowest salt concentrations, this corresponded to a huge excess of the salts in a vial. **Table E-6** reports the minimal salt concentrations that formed definite precipitates. pH values after mixing are reported here as well, since both hydrolysis of the salts and presence of acidic copolymers strongly affected pH.

Table E-6. Minimal concentrations of salts to form metal-polymer precipitates

salt	metal concentration, mole/L (final pH)		
	PEMAc	PMVEMAc2	PAAc
$CeCl_3$	0.1 (5.0)	>1.0 (5.0)	<0.004 (5.5)
$CuCl_2$	0.2 (4.0)	>1.0 (4.0)	0.01 (4.5)
$FeCl_3$	0.25 (1.0)	0.05 (1.5)	0.02 (2.0)
$ZnCl_2$	1.0 (6.0)	>1.0 (6.0)	0.1 (6.5)
$NiCl_2$	1.0 (6.0)	1.0 (6.0)	0.4 (6.5)
$CaCl_2$	>1.0 (7.5)	>1.0 (7.5)	0.4 (7.5)
$CoCl_2$	>1.0 (6.0)	>1.0 (6.0)	1.0 (6.0)

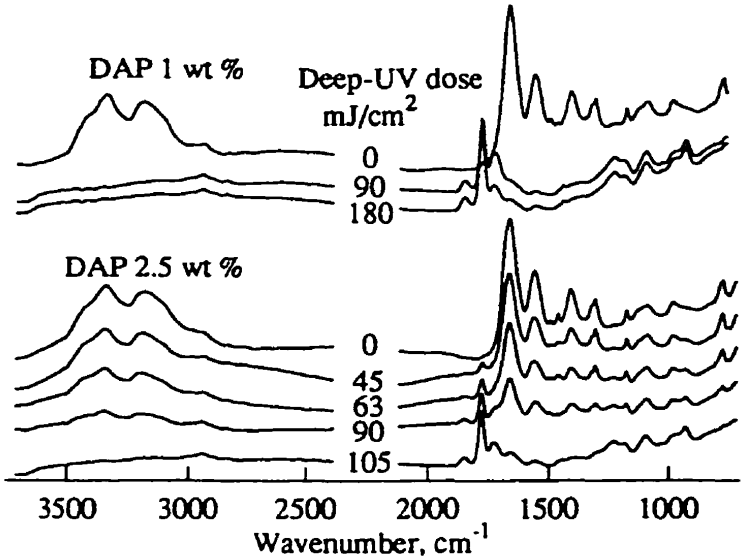
PAAc appeared to precipitate at much lower salt concentrations, compared to MAn copolymers. This is connected with its predominantly intermolecular complexation with polyvalent metal ions (in effect, crosslinking). But for hydrolyzed MAn copolymers, it is known [38] that vicinal carboxylic acid moieties often behave synergistically. Thus, a polyvalent metal ion would rather bind to two adjacent -COOH sites without inter-chain crosslinking. Moreover, MAc copolymers are known to be strong acids with pK_a of about 2, which increases the solubility of their salts. Except for that of Fe(III), PMVEMAn2 salts appeared to be quite water soluble, perhaps due to the additional methoxy groups. PEMAn formed precipitates with moderately concentrated solutions of several ions. Due to their different complexation abilities, various metals showed different critical concentrations: from 0.004 M for Ce(III)-PAAc to >=1 M for Ca and Co(II). All freshly formed precipitates with MAc copolymers could be redissolved by addition of several drops of aqueous concentrated HCl. Extending such experiments to involve more metals and polyacids, as well as careful adjustment of pH with non-interfering buffers, would be of great theoretical and practical interest.

The next experiment was conducted with ca. 1 μm polymer films on silicon wafers. 2 drops of $FeCl_3$ solutions of different concentration were placed on dried (20 s at 100 °C) films of PAAc, PMVEMAc2, and PEMAc. After 15 s these drops were rinsed out with water, and samples were air-dried. When these metal ions were able to penetrate and crosslink the matrix, the apparent color of the treated spots was very different from surrounding unmodified areas due to changes in thickness and a refractive index. When a drop dissolved the film, we observed a hole, with only traces of solid polymer remaining. The minimal $FeCl_3$ concentrations at which film integrity was apparently preserved, were 0.1, 0.05 and 0.05 M, for PEMAc, PMVEMAc2 and PAAc, respectively. This is in good agreement with the precipitation experiment described above ($FeCl_3$ line in **Table E-6**)). Thus, the possibility and minimum ion concentration for binding can be easily estimated by these screening tests. Another set of the three copolymers was heated at 160 °C for 180 s to transform them all to the mostly anhydride hydrophobic forms. There was no apparent effect on these films from drops of the $FeCl_3$ solutions: after water rinsing and air-drying, the interference color was the same in the test spots as in surrounding areas.

Thus, good selectivity (contrast) can be expected in metal binding with the described water-soluble resists. To be able to bind more metal, and use lower salt concentration without losing the film integrity, somewhat *less* hydrophilic resists would be better.

E-3.10. Functional Development: Space-Selective Binding of Aminocompounds

Amino groups are found in many compounds, including dyes, bioactive chemicals, polymers, etc. As was expected, from water solutions both DAP and DAP selectively entered only non-exposed areas containing mostly COOH groups (**Figure E-11**). Loading of these amino compounds was easily controlled by (i) UV dose, (ii) concentration of modifying solution and (iii) contact time. **Figure E-11** shows that from the more concentrated (2.5 wt %) solution, DAP penetrated the exposed areas faster, but less selectively, than from the less concentrated one (1 wt %). With acidic resist matrix, polyamines form multiple ammonium-carboxylate ionic linkages, and even covalent amide bonds [9,10], to heavily crosslink a matrix and prevent its dissolution.



Ca. 1 μm films of
Pol:PAG 20:1 w:w,
PAB 30 s at 110 °C,
DUV exposure,
PEB 30 s at 130 °C,
and 20 s treatment with
DAP aqueous solutions.

Figure E-11. Functional development with PVMEMAn2:DPI-OTf

E-4. CONCLUSIONS

For the first time, CA resists with micron-scale resolution have been demonstrated that are able to be spin-coated, developped in either positive or negative tones, and stripped, all in pure water. In the presence of a photo-produced acid, water-soluble polymers with vicinal carboxylic acid groups undergo cyclo-dehydration to water-insoluble products at 30-50 °C lower temperature than without the acid. This design lacks the swelling problems that have been found to limit some other environmentally-friendly designs with crosslinking chemistry. A careful choice of processing conditions (formulation, PAB, UV dose, and PEB) can enable the production of both negative- and positive tone images with 1 µm (or better) resolution. We also introduced an entirely new family of resists based on commercially available or easily synthesized monoesters of MAc copolymers. Alternative functional development with metal ions and some amino compounds led to a variety of patterned matrix modifications. Such structures could be used in space-directed biosynthesis, or to create micron-scale lines of organic-polymer or inorganic-polymer composites with various optical, thermal, electrical or other properties.

E-5. ACKNOWLEDGMENTS

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Chapter F
Contributions to Original Knowledge and Conclusions

F-1. CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

The following is the list of what can be considered as main contributions to scientific knowledge:

- Design and synthesis of new photoresists based on (i) maleic diacid copolymers, (ii) maleic diacid monoester copolymers and (iii) maleic diacid diester copolymers.
- Introduction of new environment-friendly water-processable photoresists.
- Study of acid-catalyzable and non-catalyzable thermolysis of said copolymers.
- Developing of new techniques for immobilization of various organic and inorganic species within micron-scale photo-defined polymeric templates.
- Application of IR, UV-Vis and fluorescent techniques for study of resist transformations and resist-sorbate interactions.

F-2. NEW PHOTORESISTS

An up-to-date review of Chemically Amplified resists was presented. Known relationships between lithographic performance and polymer structures, formulation, processing parameters were sorted out and critically discussed. A number of important requirements and tradeoffs of resist design were realized, and such understanding resulted in syntheses and optimization of several new families of photoresists.

The *t*-butyl oxycarbonyl moiety offers a clean, fast and effective acid-labile deprotection chemistry with large changes in polymer solubility and other properties. But simple *t*-butyl methacrylate copolymers are not resistant enough to plasma etch. The presence of aromatic groups (ie., polystyrene) improves such etch-stability. However, attachment of the *t*-butyl group as vinyl benzoate ester or in (vinyl)phenyl carbonate ester increases aromatic conjugation and DUV absorbance to inappropriate values (>1.5 abs.unit/μm).

An approach to structure/properties tailoring by copolymerization was successfully applied for syntheses of new photoresists. Styrene-*co*-*t*-butyl fumarate copolymer was designed to balance etch-resistance of the aromatic moiety with double-deprotectable fumaric unit. Several obstacles were overcome in synthesis, purification and characterization of this copolymer. Optimization of compositions and numerous processing parameters resulted in a robust method to obtain relief patterns with 1 micron resolution (**Table F-1**) and templates for innovative functional developing.

Evaluation of such photoresists with the vicinal diester moiety gave in-depth understanding of the processes: (i) diester-to-diacid deprotection and further (ii) diacid-to-anhydride dehydration. The polarity changes from non-polar diester to very polar diacid in the step (i), and to intermediate polarity of anhydride in step (ii). Thus, detection of the processes (i) and (ii) by TGA and FTIR allowed better optimization of several thermotreatments to give clean deesterification but without massive dehydration.

New families of photoresists with unique water-processability were developed. Two generic reactions (diacid dehydration and monoester dealcoholation) were applied for the first time for acid-catalyzable photoresist chemistry. In exposed areas, acid-catalyzable dehydration changes water-soluble diacid polymeric matrix to water-insoluble anhydride. Similarly, several polar maleic acid monoester copolymers can be converted to the less polar anhydride forms by acid-catalyzable dealcoholation.

In contrast with known resist formulations, photoresists presented here are made from inexpensive starting materials, and all processing steps -- film casting, developing and stripping -- require only water. Thus, such photoresists offer great advantage in terms of reduced cost and elimination of environmental, health and fire hazards of organic solvents.

To explore water-processable resists, a variety of commercially available or easily prepared polymers and several photo-acid generators were tried under various processing conditions. An all-water process is summarized in the **Table F-2**.

The type of alkyl group in polymeric monoester was found to affect several properties, like solubility, temperature of thermodeprotection, but not temperature of acid-catalyzable thermodeprotection. This knowledge offers control over processing windows and processing latitude by choice of appropriate alcohol for monoester polymer.

Another so-called "insertion" lithographical process with acid-catalyzable addition of small molecules was given preliminary development. The chemistry is the thermodynamical reverse of the preceding Chemically Amplified designs. A set of equations was presented to discuss driving forces and equilibria for the "insertion" lithography.

Table F-1. Diester and monoester type resist lithography.

	acceptable	preferred (PDBFS)
polymers	PDBFS, copolymers of maleic acid monoesters with styrene or vinyl methyl ether	
PAG	aryl sulfonium or iodonium salts	
formulation	90-80 wt % of PMA, chlorobenzol, etc., 20-10 wt % of a polymer and 10-3 wt % (to all solid) of a PAG	PMA:PDBFS:PAG 1000:100:7
film casting	30-60 s at 700-2000 rpm, 0.3-2.0 μm films	1200 rpm, 0.8 μm
PAB	30-300 s at 100-150 °C	60 s, 130-135 °C
exposure	15-100 mJ/cm^2 at deep- or mid-UV	60 mJ/cm^2
PEB	30-300 s at 100-150 °C	60 s, 130-135 °C
positive-tone developing	aqueous base (e.g., TMAH, KOH, >0.5 wt%), with optional 10-20 vol % of *i*-propanol	3 wt % TMAH
positive-tone developing	ammonia vapor treatment, 20-200 s, followed by developing in pure water	
negative-tone dev.	toluene, CCl_4, etc. (PDBFS only)	toluene:hexane 1:3
stripping	acetone, *i*-propanol	

Table F-2. Water-processable lithography.

	acceptable	preferred (PMVEMAn)
polymers	copolymers of maleic anhydride, e.g., with ethylene or vinyl methyl ether	
PAG	DPI-OTf or AgOTf	
formulation	10-20 wt % of a polymer in water; 3-10 wt % (to all solid) of a PAG	PMA:PMVEMAn: DPI-OTf 1000:100:7
film casting	30-60 s at 700-2000 rpm to obtain 0.3-2.0 μm films	1500 rpm, 0.8 μm
PAB	30-300 s at 100-150 °C	30 s, 130-135 °C
exposure	15-100 mJ/cm^2 at deep-UV	60 mJ/cm^2
PEB	30-300 s at 100-150 °C	20-40 s, 130-135 °C
positive-tone dev.	water, 20-40 s	30 s
negative-tone dev.	acetone, 10-30 s	20 s
stripping	hot water, >100 s	

F-3. INNOVATIVE FUNCTIONAL DEVELOPING

As electrical, optical, bio- or chemo- devices and their features continue to shrink, demand will continue to grow for micron-scale patternable systems. One way to create such structures is to make a relief image, then to fill back holes with inert or contrasting material. Another way is to modify a resist-like system with spatial selectivity by multiple transformation and by further sorption of active materials with desired properties.

In standard lithography, resists play only the brief role of pattern translator. Alternatively, resist layers can be used as a carriers of patterned chemical, physico-chemical or physical properties. **Table F-3** summarizes the functional development approach by listing altered properties, modes of such modification, and possible applications. The table covers all possible ways to design and use microresist templates.

Table F-3. Functional Imaging.

Resists	chemically amplified resists, DQN-Novolac, etc.	
Altered properties	chemical	structure, reactivity, binding ability
	physico-chemical	wettability, swellability, solubility, gas and liquid penetration and transmittance, miscibility, thermostability, etc.
	physical	thermal, electrical and thermo-dynamically, refractive index, dimension, density
Property vs. composition		linear or non-linear smooth or abrupt
Sorption modes	source	from vapors or solution
	destination	surface, near-surface layer, bulk
	tone	positive or negative-tone
	nature of sorption	covalent, ionic, ion-dipole, dipole-dipole, weak interactions, trapping
Modification by	inorganic and organic compounds, oligomers and polymers, bio-organic compounds	
Applications	lithography	liquid and plasma developing
	micro-optics	passive and active optical components
	bio	array biosynthesis and array biosensors
	etc	data-recording media, holography, displays micro-pipes and micro-reactors............

This thesis has provided insight into pattern-wise binding as a complex chemical and physico-chemical process. It was estimated by FTIR, that gradually increasing the UV dose results in smooth chemical transformation within a polymer matrix. Subsequently, many chemical, physico-chemical and physical properties were found to have sigma-type or step-wise dependency on exposure dose. It was thus understood, that space-selective deposition and/or immobilization of a sorbate is controlled by following factors:

(i) preferential interface accessibility (wettability),

(ii) preferential transportation into exposure-selected areas,

(iii) preferential ionic and/or covalent binding into exposure-altered resist matrix,

(iv) combinations of these factors.

It was shown that space-selective surface deposition can be provided solely by changing wettability of a polymer/solvent interface. This type of uptake is rather non-specific to sorbate/matrix interactions and, thus, is universal for various sorbates. Solvent diffusion into a polymer matrix is important for massive bulk uptake of solutes.

Polymer molecules act collectively in physico-chemical phenomena of wettability and diffusion. But after a sorbate is transported into the bulk, then molecular-scale phenomena, such as ionic or covalent binding of a sorbate molecule to an individual unit of a polymer matrix dominate. This type of design is more specific in terms of sorbate choice. For example, to have massive uptake and to preserve the integrity of a resist pattern, only multi-basic species like amines or metal cations can be used.

In planning a functional imaging process (**Table F-3**), after choosing the species to bind, one must consider a template resist and its photospeed, resolution and space-selectivity, uptake amount and stability of structure, etc.. The main considerations are:

- ***A resist template:*** CA resists with "polarity alteration" design are an excellent choice for space-selective sorption. Both ester-to-acid and acid-to-anhydride reactions in a polymer resist provide massive properties alteration. In turn, the resulting chemical contrast provides excellent space-selectivity during any following functionalization.

- ***Sorption uptake***: Fast and massive uptake occurs when strong covalent and/or ionic bonds are formed between a sorbate and a matrix. Various amines were well immobilized selectively within areas with predominant carboxylic acid content. Weaker interactions, ex. hydrogen bonding, can also be used for limited sorption of less basic compounds.

- ***Solvent(s)***: For stable binding from solution, the solvent must have the following properties: (i) ability to dissolve a compound to be sorbed; (ii) ability to wet and penetrate only one of the contrasting areas of a resist; (iii) no ability to dissolve these resist areas. For a carboxylic acid matrix (deprotected PDBFS), the appropriate solvent is a water:alcohol mixture, while for non-irradiated PDBFS-ester it is a hexane:toluene combination. Yet another way to control wettability is by adjusting pH.
- ***Template stability:*** Instant crosslinking by multi-basic species (e.g., polyamines or polyvalent ions) is obligatory if the films are not to dissolve as they ionize. On the other hand, pretreatment with gaseous monobasic species, like ammonia, allows positive-tone relief developing of PDBFS-like resists in pure water.

The following **Table F-4** summarize a process of space-selective binding for several organic and inorganic species.

Table F-4. Process of the functional development

resist template	film cast, PAB, exposure and PEB, as in **Tables F-1 or F-2**
metal ions (for PDBFS)	ca. 0.1 M aqueous salts of Ni, Co(II), Cu(II), etc., add ammonia hydroxide to pH 8-9, or saturated $Ca(OH)_2$, 10-40 s
metal ions (for PMVEMAn)	0.1-1.0 M aqueous salts of Ni, Co(II), Fe(III), etc., 10-40 s
dyes	ca. 0.1-0.2 wt % solutions in water:*t*-butanol 2:1 for positive-tone; or in toluene:hexane 1:9 for negative-tone modification
amines from solutions	ca. 1-2 wt % aqueous solutions of multi-basic amines, 10-60 s
amines from vapors	10-300 s above aqueous ammonia (5 wt %) or up to 1 hour above pure pyridine
to finish up	rinse in the same solvent without additive and air-dry

F-4. SUGGESTIONS FOR FUTURE RESEARCH

The following are several potential areas for development of the ideas discussed in the thesis:

- better understanding of structure/properties relationships and industrial requirements for polymeric microresists, for example trade-off between deep-UV transparency and plasma-etch stability;
- design of new chemistry for acid-(or base)-catalyzable transformations;
- structure and properties tailoring by copolymerization and formulation to balance photospeed, UV transparency, thermostability, substrate adhesion, extent of polarity alteration, shrinkage control, etc.;
- comparison of a structure alteration (chemical contrast) with properties alteration (e.g., solubility contrast) for in-depth understanding of resists physico-chemical behavior. Ranking a number of polarity alteration reactions by extent of their hydrophobic->hydrophilic transformation;
- Optimization of the resist processing: film cast, PAB, exposure, PEB, developing, and stripping to meet requirement of modern <0.25 μm patterning;
- exploring all possible variations for pattern-wise immobilization in microresist template;
- using such micron-scale structures for various (even still unknown) applications in optics (e.g., active and passive wave-guiding), bio-chemistry (array bio-synthesis and array bio-analysis), or micro-mechanics.

Appendix

Details on experimental techniques.

THERMAL ANALYSIS

Thermal Gravimetric Analysis (TGA) was used to monitor thermo-induced mass losses associated with polymer drying, deprotection and thermodecomposition. Samples were used directly as obtained from sources, or scratched from silicon wafer after several processing steps.

For example, 0.15-3.0 mg of a sample was placed in pre-weighed aluminium pan and then into the TG section of a Seiko TG/DTA 220 station. The following conditions were used: heating rate of 10 °C/min, and under 50 cc/min nitrogen flow. Mass retention vs. temperature data were transferred as a Macintosh X-Y ASCII file and further into SigmaPlot (TM) software (Jandel Scientific). In most cases, data were presented as mass vs. temperature plots (TG curve) and as the derivative plot (DTG curve). A maximum in the DTG curve is reported as the temperature for the corresponding mass reduction. Mass losses were determined from normalized TG curves.

Differential scanning calorimetry (DSC) was done using the DSC section of the Seiko TG/DTA 220 station at a heating rate of 10 °C/min (no nitrogen flow). The glass transition temperature (T_g) was taken as the midpoint of a trace inflection.

FOURIER-TRANSFORM INFRARED ANALYSIS (FTIR)

0.5-1.0 μm films for FTIR measurement were prepared by spin-coating onto IR-transparent silicon wafers. After desired treatment (baking, exposure or any chemical modification), the samples were analyzed in a Bruker IFS-48 FTIR spectrophotometer with IR-microscope accessory in transmission mode.

Then data from polymer samples were collected at 2 cm^{-1} resolution, in 32 scans in absorption mode. In some cases, the quality of the spectra were improved by interactive subtraction of a water vapour spectrum. The results were converted to graphics by SigmaPlot (TM) (Jandel Scientific).

Quantitative information about polymer composition was obtained by assuming direct correlation between height of an IR absorption peak and amount of the related functional group. Each height value was obtained as a vertical distance from a peak maximum to a spectrum baseline. A baseline was obtained by hand-drawing as a smooth line connected areas of a spectrum where any peaks were obviously absent.

The main peaks being monitored were from (i) C-O-C of esters in the 1100 cm^{-1} region, (ii) C=O of anhydrides, esters, acids and carboxylic salts in the 1880-1400 cm^{-1} region, and (iii) C-H of the *t*-butyl group in the 3000 cm^{-1} region. The unchanging peak at 740 cm^{-1} from styrene C-H was used as a reference for normalization. Thus, data for IR-absorption vs. UV dose were directly transformed to plots of composition vs. UV dose. Overall error can be roughly estimated as 5-10 % for isolated peaks, and to 20 % for some overlapped C=O peaks.

UV-VISIBLE SPECTROMETRY

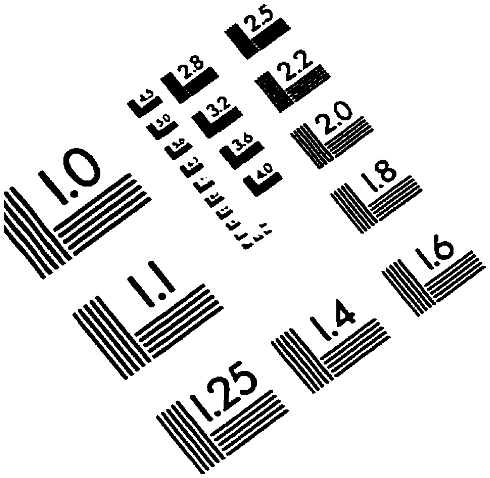
UV-visible spectra were recorded on a Shimadzu/Bausch & Lomb Spectronic 210UV spectrophotometer. 0.5-1.0 µm films were coated on fused silica windows, and thickness was obtained by DEKTAK profilometer. Spectra were obtained by a two-beam experiment against similar clean window as a reference. Scanning speed was 4 nm/s with the slit at 2 nm. The spectra were normalized to 1.0 µm thickness and combined for presentation by SigmaPlot (TM) software.

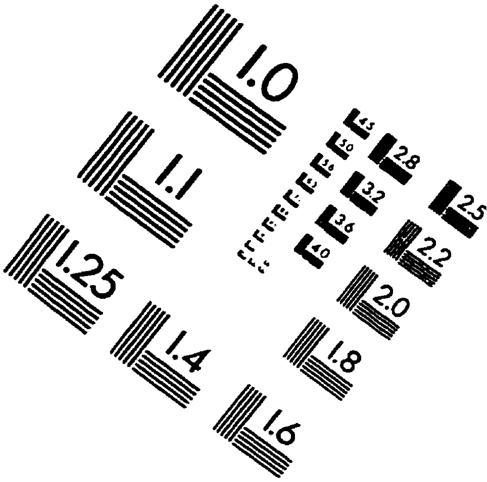
FLUOROSCOPY

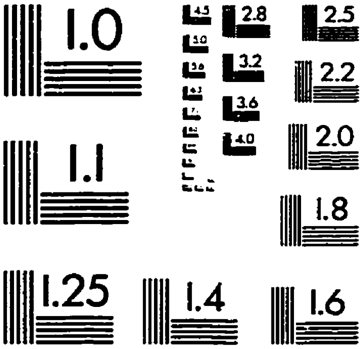
Fluorescence measurements were made with a Spex model F-112 spectrofluorometer with 450 W xenon lamp. Resist samples were prepared as films on silicon wafers, as for FTIR measurements. These samples were placed perpendicular to the incident beam. The emission detector was positioned at 22.5° for solid films. The spectra were corrected and normalized for comparison. The rough evaluation of relative dye binding -- strong, average, absent -- was estimated by visual inspection of the samples inside a Spectroline C-4 UV cabinet (Spectronics Corp.) under 365 nm illumination.

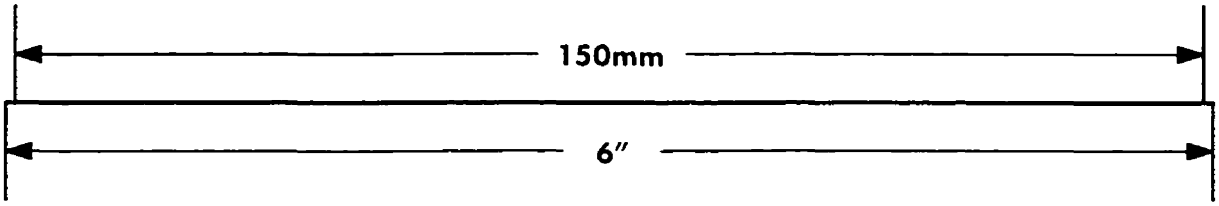
Solubility of each dye in different solvents -- soluble, partially soluble, insoluble --was checked by the apparent fluorescence, color, and turbidity of the solution. Fluorescence spectra of solutions were taken in the same Spex model F-112 spectrofluorometer. Incident beam and a detector were at 90° to each other. Concentrations of the dyes were 1-2 g/L.

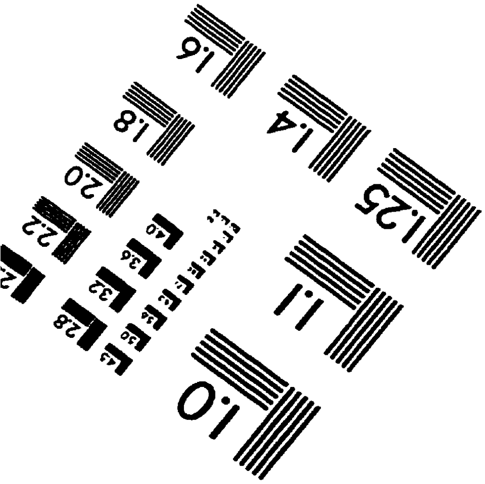
IMAGE EVALUATION TEST TARGET (QA-3)

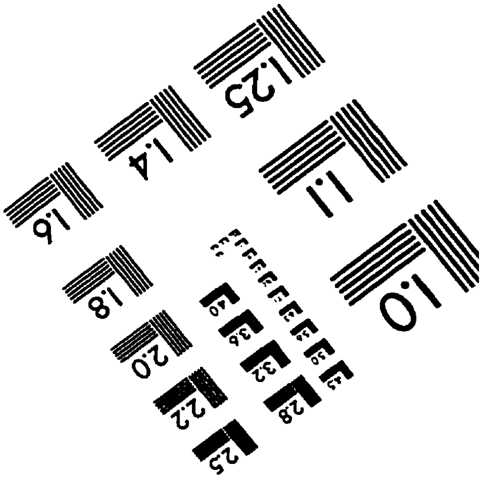












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