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Relief and Functional Photoimaging with Chemically Amplified Resists Based on Di-*tert*-Butyl Butenedioate-*co*-Styrene

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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 or negative 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} at 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). The transformation of carboxylic ester to acid or anhydride functional groups also facilitated an alternative method of development, in which various chemical species were selectively bound out of contacting solution to further alter the properties of photoselected areas of polymer film. Production of micron-scale functional images, including dual-tone developability with amphiphilic molecules, was demonstrated using fluorescent dyes.

Introduction

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 even higher resolution, sensitivity, and endurance. So far, relief images for microlithography with submicron resolution and excellent process latitude have been achieved[1−3] by combining advanced technology with new chemistry. Particularly fruitful has been the strategy of chemical amplification,[4] in which a primary photochemical event produces a reactive species that goes on to catalyze extensive transformation of the resist material. Thus, in combination with onium salts or other acid photogenerators, certain functionalized novolak or styrene polymers have shown promising lithographic properties, poly(*p*-((*tert*-butyloxy)carbonyloxy)styrene) or P(*p*-TBOCST) being the best-known example.[2−5]

Recent similarly acidolizable 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;[6] their physical and chemical properties could be fine-tuned by manipulating ratios of the several comonomers.[7] The further incorporation of styrene or other vinylarene monomer into such acid-sensitive polymethacrylate 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).[7] 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)[8] so that latent or developed images would be even less prone to soften or melt during processing.

Regular microlithography relies on radiation-induced changes of solubility or etch resistance in a polymer coating, so that selected areas can eventually be removed to form a relief image. Alternatively, both

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photoexposed and -unexposed polymer can be retained, with perhaps further modification of one or the other, to produce a functional image of contrasting materials. Physical or chemical properties that can be so altered include the following: adhesion or molecular affinity; gas or liquid permeability; refractive index or nonlinear optical susceptibility; conductivity or other electrical attributes. Possible applications of such functional images include the following: electronic or photonic devices or circuits; supports for programmed solid-phase syntheses or separations; printing or other further image transfers.[9−13] A simple and general way to alter the properties of exposed or unexposed polymer would be to have it bind various chemical species out of a surrounding medium through ionic, covalent, capillary, or other forces or processes. The sorbed substances could be organic, inorganic, or biochemical in nature, with such properties as to make the eventual materials refracting, refractory, colored, fluorescent, hyperpolarizable, bioactive, photoconducting, superconducting, catalytic, etc. Among the sensitive imaging materials employing chemical amplification that have been investigated for photolithography, those that involve transformation of pendant functional groups, rather than photopolymerization, cross-linking, or scission of polymer chains, would appear to be the most suitable for such development to functional images. Butenedioate copolymers, generally able to form smooth clear films, would contain or produce a particularly high density of carboxylic acid and/or anhydride groups. That such groups can go on to bind a wide variety of basic or nucleophilic species (they are probably better and more versatile at this than phenolic −OH such as from P(*p*-TBOCST) and others)[13] should make these polymers particularly appropriate to prepare functional images, besides relief images as well.[14]

Experimental Section

Materials and Instrumentation. Unless otherwise noted, all chemicals were purchased in reagent grade from Aldrich Chemical Inc. and used as received. Styrene was distilled before use under reduced pressure. Toluene for polymerization 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 (DPI), triphenylsulfonium (TPS), and 4-(phenylthio)phenyldiphenylsulfonium (4PS) hexafluoroantimonates were prepared according to reported procedures.[15] 2-[4-(*N*-Methyl-*N*-octylamino)styryl]pyridine (ASP) was prepared as previously described.[13]

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 ^{1}H 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 in. × 330−432 μm N/P/⟨1−1−1⟩, or National Scientific GE 124 polished fused quartz plates 1 in. × 1 in. × $^1/_{16}$ in. 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 the sample or an Oriel 87100 exposure system in mid-UV mode; corresponding exposure doses were measured at 254 nm and "mid-UV" (90% 365 nm, 10% 313 nm) using Optical Associates OAI P306-001-002 and -008-002 power meters, 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. Fluorescent photographs were taken using a Nikon-based Photon Technologies Scan-1 fluorescence microscopy system with tunable excitation wavelength and emission filtered to above 510 nm.

Synthesis of Di-*tert*-butyl *cis*-Butenedioate (Di-*tert*-butyl Maleate) (1).[16] Maleic aicd (20 g, 172 mmol), concentrated sulfuric acid (2 mL, 40 mmol), *tert*-butyl alcohol (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 colorless crystals of **1** (31 g, 79%): mp 65−66 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.0 (s, 2H, $=CHCOO-$), 1.5 (s, 18H, $-COOC(CH_3)_3$).

Synthesis of Di-*tert*-butyl *trans*-Butenedioate (Di-*tert*-butyl Fumarate) (2).[17] 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; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.6 (s, 2H, $=CHCOO-$), 1.4 (s, 18H, $-COOC(CH_3)_3$).

Synthesis of Poly(di-*tert*-butyl *trans*-butenedioate-*co*-styrene) (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 and thrice degassed under vacuum and then refilled with nitrogen; then the tube was sealed, heated at 60−70 °C for 24 h, and then cooled to room temperature, and its contents were 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

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3a (13.5 g, 36%): GPC ($CHCl_3$, polystyrene standard) M_n 1.2 × 10^4, M_w/M_n 1.7; viscometry ($CHCl_3$, 25 °C) [η] 0.10; ^1H NMR (200 MHz, $CDCl_3$) δ 7.5–6.2 ($C_6\mathbf{H}_5$), 2.8–2.2 ($>C\mathbf{H}CO_2-$), 1.9–0.5 ($-COOC(C\mathbf{H}_3)_3$), 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 ($\mathbf{C}=O$), 142.2, 140.0, 128.2, 126.2 ($\mathbf{C}_6H_5$), 81.1, 80.3 ($-COO\mathbf{C}(CH_3)_3$), 54.8, 42.9, 40.2 ($-\mathbf{C}HPh-\mathbf{C}H_2-$, $>\mathbf{C}HCOO-$), 27.9 ($-COO(\mathbf{C}H_3)_3$).

Synthesis of 4-[5-(Dimethylamino)-1-naphthalenesulfonyl]-1-methylpiperazine (DSMP). Dansyl chloride (0.29 g, 1.1 mmol) was added to 1-methylpiperazine (0.24 g, 2.4 mmol) and triethylamine (0.5 mL, 4 mmol) in methylene chloride (10 mL) at 0 °C, and the mixture was stirred at room temperature for 5 h. After extracting with 1 N NaOH and water, then drying over CaO, solvents were evaporated to give yellow solid residue DSMP (0.36 g, 97%): mp 112–113 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.57 (d, J = 9.7 Hz, 1 H), 8.44 (d, J = 9.4 Hz, 1H), 8.19 (d, J = 9.4 Hz), 7.53 (t, J = 4.1 Hz, 2H), 7.17 (d, J = 9.4 Hz), 3.21 (t, J = 5.2 Hz, 4H), 2.87 (s, 6H); 2.41 (t, J = 5.0 Hz), 2.21 (s, 3H).

Preparation of 3a-Based Photosensitive Coatings. Polymer **3a** was dissolved, together with 5–10% of its weight of DPI, TPS, or 4PS hexafluoroantimonates, 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 and then spin-coated onto silicon or quartz substrates at 1200 rpm for 1 min followed by postapply baking (PAB) on a hot plate at 100–135 °C for 1–5 min to form a ca. 1 μm thick film. FTIR (IR-transparent silicon substrate) and UV (fused quartz substrate) spectra were obtained therefrom by transmittance spectrophotometries.

Development into Relief Images. **3a**-based photosensitive coatings on silicon substrate were exposed to UV radiation as described, generally through the step tablet, then treated by postexposure baking (PEB) on a hot plate at 110–150 °C for 2–7 min, and 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% K_2CO_3 (with or without added isopropanol) or 1–5% 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.[3] Appropriate portions of the images were then inspected and photographed through optical or scanning electronic microscopes.

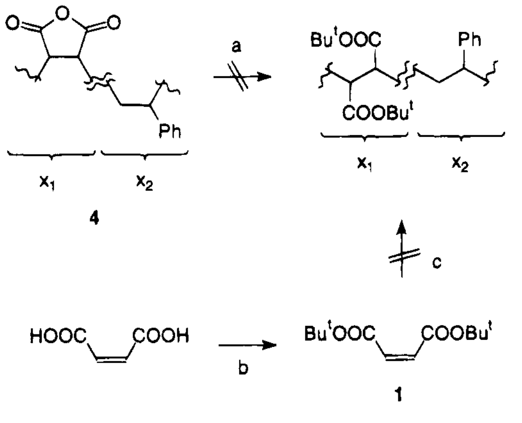
Development into Fluorescent Functional Images: Rhodamine 6G (R6G). **3a**-based photosensitive coatings ca. 1 μm thick were exposed (20–100 mJ/cm^2 at 254 nm) through the step tablet, then subjected to PEB at 135–140 °C for 30 s, and developed either as positive or negative relief images as above or not developed at all, before a few drops of 0.01 wt % R6G in methanol:water 1:1 v:v were spread overtop. After 30 s soaking the samples were then spin-dried, rinsed with water, and spin-dried again. Fluorescent images were observed and photographed with the fluorescence microscopy system, using 490 nm excitation wavelength.

Development into Fluorescent Functional Images: DSMP and ASP. **3a**-based photosensitive coatings ca. 1 μm thick were exposed and subjected to PEB as described above. A few drops of 0.01 wt % DSMP or ASP in water:*n*-propanol 3:2 v:v (for positive images) or toluene:hexanes 1:10 v:v (for negative images) were then spread over the samples for 30 s, followed by spin-drying, rinsing with hexanes, and spin-drying again. Fluorescent images were observed and photographed with the fluorescence microscopy system, using 380 and 400 nm excitation wavelengths for DSMP and ASP, respectively.

Results and Discussion

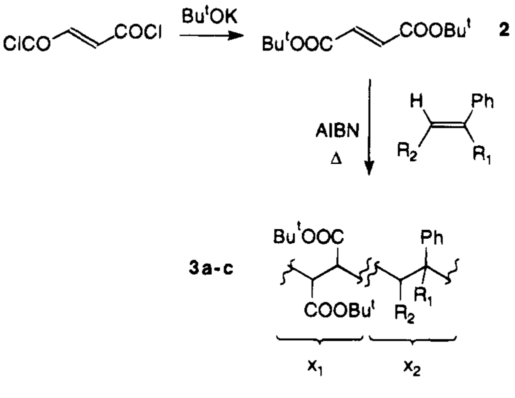
Possible synthetic routes to a dialkyl butenedioate–vinylarene copolymer include (i) esterification of preformed (even commercial) maleic acid or anhydride copolymer (**4**), (ii) copolymerization of dialkyl maleate with appropriate comonomer, and (iii) copolymerization of dialkyl fumarate with appropriate comonomer. Although many procedures[18] for esterification of carboxyl-containing polymers are available, our attempts toward synthesis of acidolizable poly(di-*tert*-butyl maleate-*co*-styrene) via route (i) were complicated by incomplete reactions and cross-linking or other side reactions. The potential maleate monomer **1** was then synthesized, but its attempted copolymerization with styrene failed to give any copolymer product (Scheme 1).

Scheme 1. Attempted Synthesis of Poly(di-*tert*-butyl maleate-*co*-styrene) through Copolymerization and Esterification[a]



[a] (a) $(Bu^tO)_2CHNMe_2$/toluene, or other reagents. (b) 2-Methylpropene/*tert*-butyl alcohol/acid catalyst. (c) Styrene/AIBN catalyst/Δ.

Scheme 2. Synthesis of Di-*tert*-butyl Fumarate and Copolymerizations with Vinylarenes



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

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.[19] The much more polymerizable monomer **2** was prepared by modifying a reported method[17] reacting fumaryl chloride with potassium *tert*-butoxide (Scheme 2): substituting THF for benzene, and distillation for crystallization, gave a

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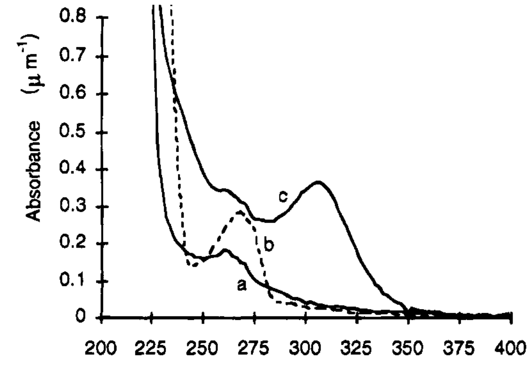
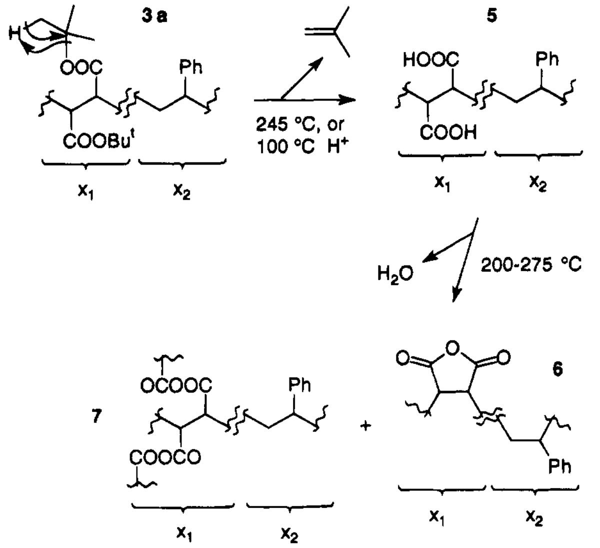


Figure 1. UV spectra of 1 μm thick films of (a) **3a** alone, (b) P(*p*-TBOCST) alone, for comparison, and (c) **3a** with 10% of 4PS hexafluoroantimonate.

Scheme 3. Reactions of Di-*tert*-butyl Fumarate Copolymer



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.[19,20] This suggested a somewhat random distribution of styrene and butenedioate units in our copolymer rather than the pure alternation that might be expected of these electron-rich and -poor monomers. 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 1). DSC showed its T_g to be 139 °C, a good compromise between requirements for mild post-apply baking (PAB) conditions and for stability of images against thermal distortion during postexposure baking (PEB) and some dry etching procedures. A characteristic reaction of *tert*-butyl ester compounds, including di-*tert*-butyl butenedioate homopolymer,[20] is cleavage to isobutylene gas and free carboxylic acid. With **3a** (Scheme 3), results from DSC, TGA (Figure 2b–e) and FTIR (Figure 3a–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 3c) and TGA (Figure 2d) showed only 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.

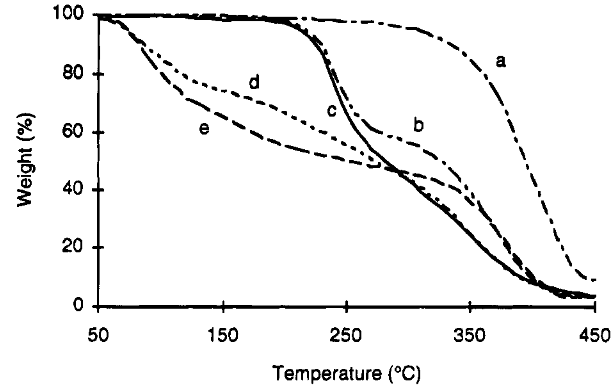


Figure 2. TGA curves from (a) styrene–maleic anhydride copolymer **4**, (b) copolymer **3a** alone, (c) **3a** with 10% of 4PS salt, (d) as previous, but exposed to 254 nm at 100 mJ/cm^2, and (e) **3a** with 10% toluenesulfonic acid.

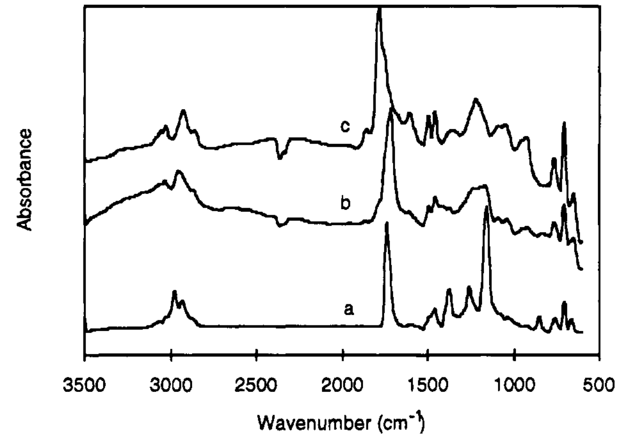


Figure 3. IR spectra of (a) **3a** (–COOBu^t) containing 10% of 4PS hexafluoroantimonate, after exposure to 254 nm light (100 mJ/cm^2), (b) the same after subsequent heating at 135 °C for 10 min (–COOH), and (c) the same after further heating at 250 °C for 10 min (–CO–O–CO–). Note the distinctive C=O peaks at 1700–1800 cm^{-1} in each.

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

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Table 1. Development of 3a-Based Resist into Positive or Negative Relief Images[a]

acid photogenerator	light source	PEB (°C/min)	developing solvent[b]	sensitivity (mJ/cm^2)	contrast[c] (±1.0)
5% 4PS	254 nm	135/5	2.5% TMAH/H_2O	42	7.6
5% 4PS	mid-UV	135/5	1.5% K_2CO_3/H_2O	40	4.5
5% 4PS	mid-UV	135/5	1.5% K_2CO_3/H_2O: *i*PrOH 3:1	30	7.0
10% 4PS	mid-UV	135/5	1.0% TMAH:H_2O	36	6.1
10% 4PS	mid-UV	135/5	5.0% TMAH:H_2O	27	6.0
10% 4PS	mid-UV	135/5	1.5% K_2CO_3:H_2O	38	4.0
10% 4PS	mid-UV	135/5	1.5% K_2CO_3/H_2O: *i*PrOH 3:1	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% 4PS	254 nm	135/5	toluene:hexanes 1:3	24	4.6
5% 4PS	mid-UV	150/5	toluene:hexanes 1:1	20	5.0
10% 4PS	mid-UV	135/5	toluene:hexanes 1:1	14	7.1
10% 4PS	mid-UV	135/5	*n*-butyl acetate	22	5.1

[a] 1.0 ± 0.1 μm films of **3a** plus onium salt on silicon wafers. [b] Development times 10–30 s. [c] Absolute value of slope of contrast curve between normalized thicknesses of 0 and 0.7.[3]

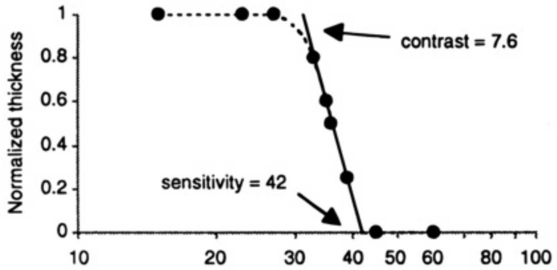

Figure 4. Deep-UV (254 nm) contrast curve of **3a** with 5% of 4PS hexafluoroantimonate, developed using 2.5 wt % TMAH/H_2O.

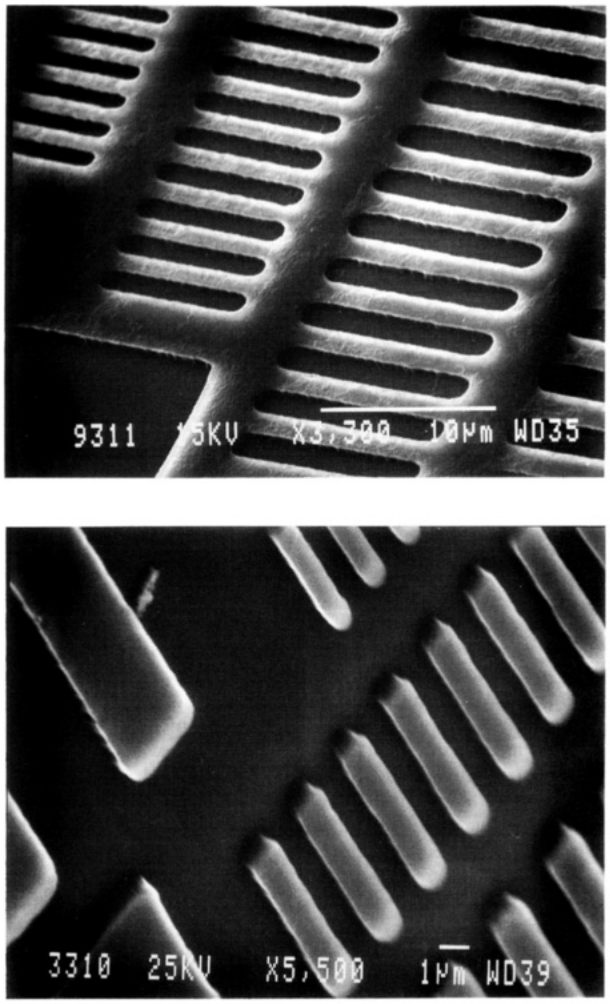

Figure 5. Scanning electron micrographs of relief images from **3a** and 10% 4PS hexafluoroantimonate resist: (top) exposed 40 mJ/cm^2 mid-UV, postbaked 135 °C 5 min, developed in 1.0 wt % TMAH/H_2O to give a positive relief image; (bottom) exposed 25 mJ/cm^2 mid-UV, postbaked 135 °C 5 min, developed in toluene:hexanes 1:1 v:v to give a negative relief image.

(DPI or TPS for deep-UV, and 4PS for mid-UV exposures) could be dissolved in organic solvents, and the solutions spin-coated onto flat substrates (e.g., silicon wafers), followed by PAB near the T_g of the polymer to dry and anneal it,[21] to give films that were smooth and clear. Contrast curves (Figure 4) showed how the 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 isopropyl alcohol (*i*PrOH) improved contrast with the inorganic base (Table 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 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 (γ = 4–7). With even very modest optic systems, relief images to 1 μm resolution (the mask limit) could be produced (Figure 5), providing at least 5 wt % onium salt had been employed, and PEB done promptly after exposure (to avoid the surface "skin" known[22] to complicate positive-tone development by aqueous base).

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 30 min 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

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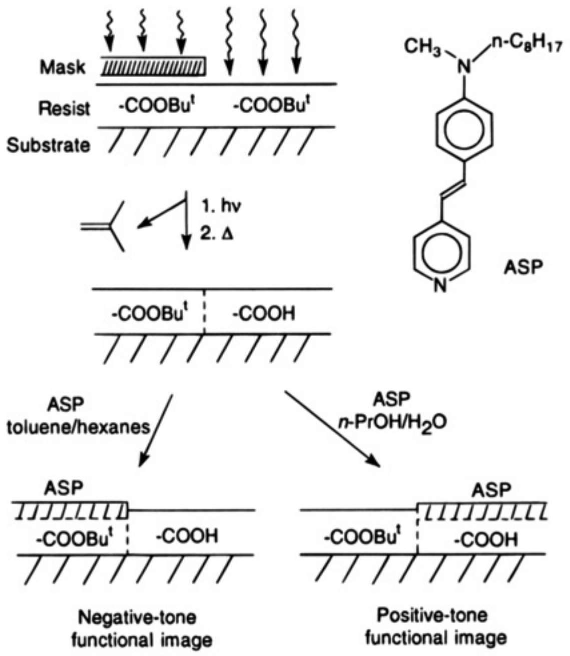
(21) Paniez, P. J.; Rosilio, C.; Mouanda, B.; Vinet, F. In *Advances in Resist Technology and Processing XI*; Nalamasu, O., Ed.; SPIE Proceedings 2195; SPIE: Bellingham, WA, 1994; pp 14–27.

(22) MacDonald, S. A.; Hinsberg, W. D.; Wendt, H. R.; Clecak, N. J.; Willson, C. G. *Chem. Mater.* **1993**, *5*, 348–356. Hinsberg, W. D.; MacDonald, S. A.; Clecak, N. J. *Chem. Mater.* **1994**, *6*, 481–488.

Scheme 4. Dual-Tone Fluorescent Functional Images with ASP



by further flood-exposure before baking to 135 °C or higher.

Formation of a functional image was demonstrated using the cationic fluorescent dye rhodamine 6G (R6G). The dye was dissolved in methanol−water, a solvent system that was repelled by **3a** but was able to wet (yet not dissolve) deprotected polymer **5**. Patterned exposure and PEB were performed on a 1 μm thick film of **3a**-based resist, but then, instead of dipping into an organic solvent or aqueous base, a few drops of fluorescent dye solution were spread onto the film, followed by rinsing with water. Subsequent fluorescence microscopy clearly showed a positive fluorescent image, presumably formed by the cationic solute becoming bound only to regions or film where photoexposure and PEB had generated polar and acidic −COOH functionalities (**5**). It was particularly obvious that unexposed resist (based on **3a**) was not stained under these conditions in samples from which exposed resist (containing **5**) had been removed by aqueous base before dye treatment: these samples appeared uniformly dark under UV illumination. Very interestingly, dual-tone functional development could be achieved with amphiphilic fluorescent compounds 2-[4-(*N*-methyl-*N*-octylamino)styryl]pyridine (ASP) and 4-[5-(dimethylamino)-1-naphthalenesulfonyl]-1-methylpiperazine (DSMP), according to the solvents in which they were dissolved. Thus, ASP or DSMP in water−alcohol only wetted and penetrated "acidic" (**5**-containing), exposed areas to form positive functional images, while the same dyes in hexanes−toluene could enter only unexposed "ester" (**3a**) areas to form negative functional images (Scheme 4, Figure 6). Further manipulation of development conditions could place dyes either at the surface (as previously described[13] for other maleic anhydride copolymers) and/or into the bulk of exposed or unexposed polymer films.

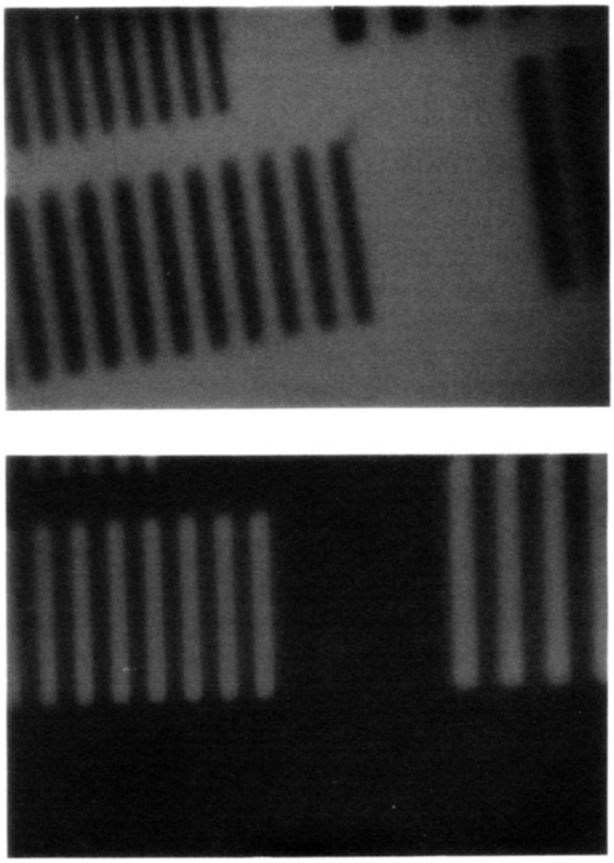


Figure 6. Fluorescence micrographs (excitation 400 nm; photographed through a >510 nm filter) showing 10 μm patterns from binding of ASP on an exposed (254 nm, 40 mJ/cm^2) and postbaked (135 °C, 3 min) film of **3a** with 10% 4PS hexafluoroantimonate: (top) treatment with ASP in *n*-PrOH:H_2O 1:3 v:v gives a positive-tone fluorescent functional image; (bottom) a negative-tone image results from application of ASP in toluene:hexanes 1:10 v:v.

Further investigations on development of these polymer materials into both relief and functional images, with particular attention to process latitude, and to application as patterned organic nonlinear optical materials,[13] are in progress.

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