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Chemically Amplified Imaging Materials Based on Electrophilic Aromatic Substitution: Poly[4-(acetoxymethyl)styrene-*co*-4-hydroxystyrene]

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ABSTRACT: A new family of versatile negative resist materials based on phenolic resins has been prepared. The resist design is based on radiation-induced cross-linking via an electrophilic aromatic substitution process in a series of copolymers consisting of vinylphenol and vinylbenzyl acetate units. Copolymers of varying compositions are prepared by random copolymerization of 4-(acetoxymethyl)styrene with 4-(*tert*-butyloxycarbonyloxy)styrene, a monomer pair with suitable reactivity ratios, followed by removal of the *t*-BOC protecting groups using hot acetic acid. Compositions rich in hydroxystyrene have high T_g values and are suitable for imaging experiments. When mixed with 5–10% of a compound such as a triarylsulfonium salt that generates acid upon radiolysis, the copolymers can be used as resist materials for microlithography. Exposure results in the generation of a latent image of acid dispersed into the copolymer; a postexposure heating step provides the activation energy necessary for the generation of benzylic carbocationic species that react in an electrophilic aromatic substitution process. Since the initiating proton is regenerated at each step, the process is catalytic or "chemically amplified". The new resists have been patterned by exposure to deep-UV, electron beam, or synchrotron X-ray radiation and show extremely high sensitivies and resolutions.

Introduction

The incorporation of chemical amplification into polymeric imaging systems has allowed a marked increase in resist sensitivity to be attained over previous systems. The application of radiation-sensitive onium salts[1,2] that efficiently generate strong acids on irradiation has been exploited in the design of a number of new, chemically amplified systems that exhibit a change in solubility upon irradiation. Several interesting approaches to radiation-sensitive resist systems that incorporate chemical amplification have been explored, some of which are outlined below.

For example, systems have been based on polymers such as poly[4-(*tert*-butyloxycarbonyloxy)styrene] that have side groups susceptible to acid-catalyzed thermolysis,[3-8] a process that yields a polar phenolic material having solubility properties markedly different from the starting material.[7,8] Another approach involves the use of polymers that undergo acid-catalyzed depolymerization. If the resulting monomeric species are sufficiently volatile, the use of solvents in the development step may be avoided.[8-10] Other systems are based upon free radical and cationic cross-linking processes involving either multifunctional monomers or polymers with reactive pendant groups. Examples include the acid-initiated ring-opening polymerization of epoxy resins[11,12] and the cross-linking of polymers via pendant oxirane rings.[13] Other systems that display chemical amplification but do not employ onium salts include electron beam irradiation of polymers bearing pendant oxirane rings, which appears to initiate an ionic chain cross-linking polymerization even though no initiator is added.[14] Free radical polymerization, unlike cationic processes, suffers the drawback of oxygen inhibition. Yet, such systems continue to receive attention and a recent approach involves the cross-linking polymerization of acrylated diols using an amine scavenger, which becomes bound into the network, to remove oxygen.[15] Cross-linking negative resist systems have the potential for greater sensitivity than systems that rely on a change in the nature of a pendant group, since fewer chemical events are needed per polymer chain to produce a change in solubility. However, as the requirements for resolution have increased a problem that has plagued negative cross-linking resists is the occurrence of image distortion due to swelling by organic based developing media.[1,16] Recent studies have shown that negative systems based on the cross-linking of phenolic or novolak resins show no deformation of the image when developed in aqueous base.[17-19] The explanation for this effect probably lies in the fact that the development step is an etching process, requiring formation of the phenolate anion rather than a "normal" Fickian-type dissolution.[20] Therefore, negative cross-linking resist systems exhibiting both chemical amplification and base solubility ought to be both highly sensitive and capable of producing distortion-free images.

As was shown in the preceding paper in this issue, negative-tone resists fulfilling the prerequisites mentioned above can be realized by designing a system comprising a latent electrophile, an aromatic nucleus activated toward electrophilic aromatic substitution, and a photoacid generator. As shown in Scheme I the electrophilic group that is freed by the photogenerated acid substitutes the activated aromatic nucleus, forming a new bond and regenerating the proton. Aromatic phenolic compounds are activated toward electrophilic aromatic substitution and therefore systems based on the cross-linking of phenolic polymers or novolak resins will exhibit the desired base solubility along with good plasma etch resistance.

In view of our model work with this bond-forming process, two approaches to cross-linking phenolic polymers were considered. One involved a polymer containing the phenolic moiety and a small molecule with two or more latent electrophiles as shown in Scheme II. The cross-

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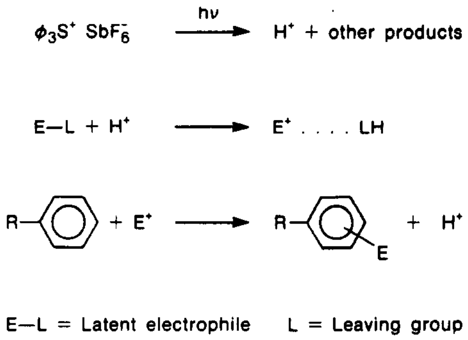
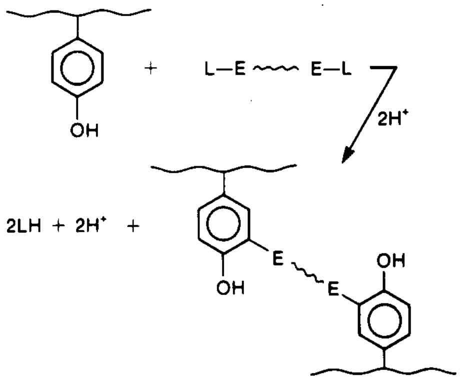
Scheme I



Scheme II



linking is shown as being via C-alkylation of the aromatic ring, but model studies have shown that O-alkylation is also a possibility. A number of resist systems based on this concept have been reported.[19,21-26] Typical latent carbocations include 1,4-bis(acetoxymethyl)benzene[25] and *N*-(methoxymethyl)melamine compounds.[21-24] The approach that we chose was to combine both the latent electrophile and the activated aromatic nucleus on the same polymer chain.[26-27] This affords a two-component system, consisting of the copolymer and a photoacid generator.

Experimental Section

Materials. (2-Bromoethyl)benzene was purchased from Aldrich. The monomer 4-(*tert*-butyloxycarbonyloxy)styrene (2) and the free radical initiator azobis(isobutyronitrile) (AIBN) were obtained from Kodak and used without further purification. The photoacid generator, triphenylsulfonium hexafluoroantimonate was prepared as described in the literature.[2] Propylene glycol monomethyl ether acetate was obtained from ARCO. The developer, MF 312, an aqueous solution of tetramethylammonium hydroxide, was obtained from Shipley Co.

Instrumentation. Infrared spectra were recorded on a Nicolet IR 44 (FTIR) spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with an IBM-Brucker AF-300 spectrometer operating at 75.4 MHz for ^{13}C nuclei. Shifts were measured relative to the residual proton signal of the deuterated solvent and are reported in parts per million from TMS. A Hewlett-Packard 8450 spectrometer was used to obtain ultraviolet spectra. Molecular weight determinations were carried out with a Waters 150C gel permeation chromatograph equipped with a differential refractometer detector and 4 PL Styragel columns of 10^6-, 10^5-, 10^4-, and 10^3-Å porosity; tetrahydrofuran was used as the mobile phase. Molecular weight data were obtained relative to polystyrene standards. Measurements of absolute molecular weight were obtained from a light-scattering equipment[28] that consisted of a DAWN F laser photometer (Wyatt Technology Corp.) connected to the eluent outlet of a Waters GPC chromatograph. Data analysis was carried out by using software provided by Wyatt Technology Corp. Thermal analyses were performed by using Du Pont 910 DSC or Mettler DSC 20 and DSC 30 differential scanning calorimeters (10 °C min^{-1} heating rate, N$_2$ atmosphere) and a Perkin-Elmer TGS-2 or Mettler thermogravimetric analysis instrument (5 °C min^{-1} heating rate, N$_2$ atmosphere).

Preparation of 4-(Acetoxymethyl)styrene (1). 4-(Acetoxymethyl)styrene (1) was prepared via 4-(chloromethyl)styrene, itself obtained from 4-(2-bromoethyl)benzyl chloride. This latter compound was obtained by the chloromethylation of (2-bromoethyl)benzene in 33% yield using the method of Kondo et al.[29] This material was then converted[29] to 4-(chloromethyl)styrene in 67% yield after distillation by treatment with sodium *tert*-butoxide. ^{1}H and ^{13}C NMR spectra were consistent with the desired product. Finally 4-(acetoxymethyl)styrene was obtained from 4-(chloromethyl)styrene by treatment with potassium acetate in DMF following the procedure given by Beihoffer and Glass.[30] The yield of the product was 80% after distillation. IR: aromatic and alkenic C—H stretch (3090–3009 cm^{-1}), aliphatic C—H stretch (2982–2891 cm^{-1}), C=O stretch (1741 cm^{-1}), aromatic and alkenic C=C stretch (1630 cm). The ^{1}H and ^{13}C NMR spectra are in agreement with the proposed structure.

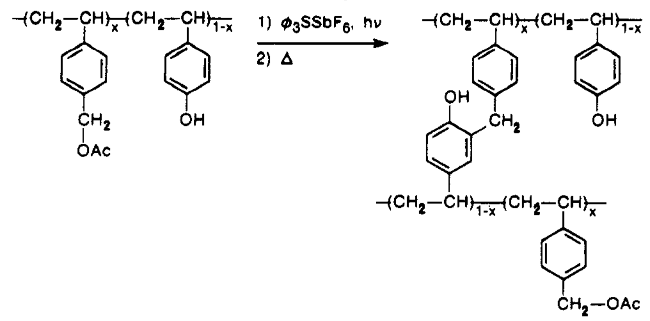
Copolymerization of 1 with 2. Copolymerizations were carried out in 50-mL, round-bottom, three-neck flasks equipped with a condenser, a nitrogen gas inlet, and a magnetic stirrer. After the required amounts of the two monomers (50 wt % in toluene) and AIBN had been added, the mixture was left stirring for 1 h prior to being heated to 75–77 °C for 19 h. The polymerization mixture was allowed to cool, diluted with toluene, and then poured dropwise into an excess of hexane to precipitate the copolymer 3. The polymer was dried for 24 h in vacuo. The copolymerization data used for the reactivity ratio study were obtained in the manner described above except that the reaction time at 73–76 °C was adjusted such that the conversion did not exceed 7%. Purification of the resulting copolymer was accomplished by two reprecipitations from toluene using hexane as the nonsolvent. The copolymer was then dried in vacuo for 48 h. All of the polymers (3–8) were fully characterized as described elsewhere in this paper.

Removal of the *t*-BOC Protecting Groups of Copolymer 5 and Conversion to Copolymer 11. In a typical procedure, copolymer 5 (80 mol % of 2) (2.57 g) was placed in a 50-mL, round-bottom, three-neck flask equipped with a condenser, a nitrogen gas inlet, and a magnetic stirrer. Glacial acetic acid (35 mL) was added to the flask and the solution left stirring under nitrogen for 1 h prior to being heated to reflux for 3 h. The solution was cooled, concentrated, and added dropwise to water to precipitate the polymer. After filtration and washing with water and hexane the slightly off-white precipitate was dried in vacuo for 48 h to give 1.6 g (97%) of the desired copolymer 11. Analytical data for the deprotected copolymers are in agreement with the proposed structure.

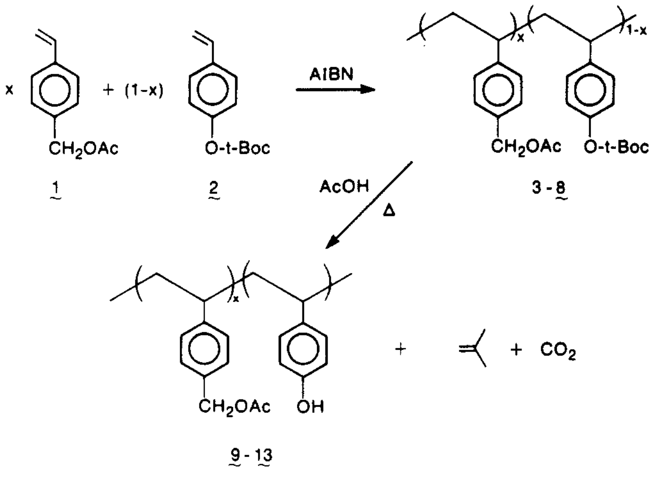
Sensitivity Measurements and Imaging Experiments. All the films were prepared by spin coating the appropriate substrate using a solution of the photoacid generator and copolymer in propylene glycol monomethyl ether acetate. The solutions were filtered through a 0.2-μm Teflon filter prior to use. Film thicknesses were measured by using a Tencor Alphastep 200. Films of the various copolymers were irradiated by an Optical Associates Inc. exposure system comprising a low-pressure mercury lamp with a shutter system, an intensity controller, and an exposure timer. Photon flux was measured with an Optical Associates Inc. 354 exposure monitor equipped with a thermopile detector. The output of the mercury lamp was filtered by using a 254-nm narrow-bandwidth filter from Oriel Corp. To produce a range of doses impinging on the resist film the light was passed through a multidensity resolution filter (Ditrich Optics Inc.).

Quartz or silicon wafers were coated with a 1.0 ± 0.05 μm film of the copolymer containing the photoacid generator. The films were prebaked at 120 °C for 15 min, irradiated, postbaked at 120 °C for 3 min, and then developed. For aqueous base development the films were dipped in a stirred solution of the developer, washed with distilled water, and air dried. For organic solvent development, the film was dipped in a stirred solution of the developer and then air dried. The thickness of the film remaining was measured as a function of the dose received. Some shrinkage of the film occurred on irradiation and postbaking amounting to ca. 5%. Thus the film thicknesses were normalized to the film thickness obtained that did not change with increasing dose.

Scheme III



Scheme IV



Further details of imaging experiments are found in the Results and Discussion section.

Results and Discussion

Copolymers containing varying proportions of 4-vinylbenzyl acetate units, as latent electrophilic moieties, and 4-hydroxystyrene units, as activated aromatic moieties, were synthesized. The incorporation of 4-hydroxystyrene units in the copolymers also provides for aqueous, swell-free development and plasma etch resistance, while the acetoxymethyl functionality undergoes acidolysis to yield a reactive benzylic carbocationic moiety. Key to the process depicted in Scheme III is the presence of a compound that can produce strong acid upon irradiation. While numerous such compounds exist,[34] we selected triarylsulfonium salts[2] for this study as they provide a convenient source of protons, they can be used with a variety of radiation sources, and they are soluble in common solvents used in resist formulation while also possessing excellent thermal stability. While Scheme III shows the cross-linking process occurring through a C-alkylation, our model studies have shown that O-alkylation also occurs in the early stages of the reaction and may be responsible for some of the cross-linking that is observed in the solid state. Similarly, our model studies have indicated that while alkylation occurs preferentially at positions ortho to the phenolic group, some alkylation of the ring of the benzyl acetate moiety is also observed. Again this may contribute to the cross-linking process in the solid state. Scheme III only serves to convey a very simplified picture of the overall cross-linking process. The direct free radical copolymerization of 4-(acetoxymethyl)styrene with 4-hydroxystyrene is difficult to achieve due to the propensity of the phenolic group of the latter to interfere with the polymerization process, giving rise to relatively low molecular weight material.[35] An indirect route via a precursor polymer was used involving the copolymerization of 4-(*tert*-butyloxycarbonyloxy)styrene[3] (2) and 4-(acetoxymethyl)styrene (1) (Scheme IV). The *t*-BOC phenolic protecting groups of the resulting copolymer were then removed selectively to afford the desired poly[4-vinylphenol-*co*-(4-vinylbenzyl acetate)].

Table I
Copolymerization[a] of Monomers 1 and 2; Determination of Reactivity Ratio

mole fractn 1 in feed	% yield[b]	mole fractn 1 in copolym	$10^{-3}M_w$[c]	$10^{-3}M_n$[c]	M_w/M_n[c]
0.133	4.2	0.146 ± 0.005	155.0	83.0	1.9
0.201	2.3	0.217 ± 0.006	165.0	85.0	1.9
0.303	5.7	0.324 ± 0.007	111.0	59.0	1.9
0.405	6.9	0.421 ± 0.004	88.0	45.0	2.0
0.502	2.9	0.524 ± 0.004	124.0	63.0	2.0
0.648	3.0	0.657 ± 0.003	113.0	61.0	1.9
0.799	3.0	0.779 ± 0.002	103.0	54.0	1.9

[a] Approximately 37–45 mmol of monomers in 8 mL of toluene with 0.3 mmol of AIBN at 75 °C. [b] After one precipitation in hexane. [c] Measured by GPC.

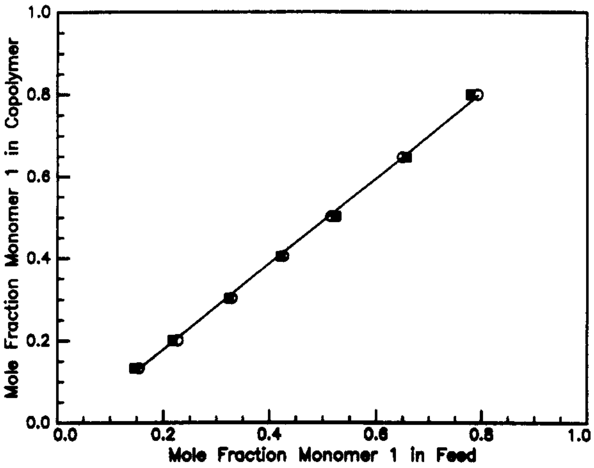


Figure 1. Copolymer composition as a function of feed ratio. (○) Calculated from reactivity ratios. (■) Determined experimentally by ^{1}H NMR.

Since the distribution of the various monomer units throughout the polymer chains may have a profound effect on the cross-linking of the copolymers as well as on their solubility, a study of the reactivity ratios of monomers 1 and 2 in their copolymerization was undertaken.

Table I gives the details of the copolymerizations that were carried out to less than 7% conversion and the molecular weight data obtained for this study. The composition of the copolymers was determined from their ^{1}H NMR spectra by comparing the ratio of benzylic methylene protons to the remainder of the aliphatic protons. These values were consistent with those obtained from the ratio of benzylic to aromatic protons.

The mole fractions M_1 and m_1 of monomer 1 in the feed and in the copolymer, respectively, are reported in Table I, while Figure 1 shows the copolymer composition as a function of the feed composition. By use of the Kelen–Tudos[36] method to calculate the reactivity ratios, the values of r_1 and r_2 were found to be 0.9 ± 0.1 and 0.8 ± 0.1, respectively. Thus the incorporation of monomer units into the copolymer chains is essentially random, with perhaps a slight tendency toward alternation. Figure 1 also compares the relationship between feed and copolymer composition as calculated from the reactivity ratios, with experimental compositions determined by ^{1}H NMR.

In order to determine the effect of copolymer composition on the resist sensitivity, a series of copolymers of similar degrees of polymerization were prepared. The

Table II
Preparation and Properties of Copolymers 3–8

co-polymer[a]	mole fractn 1 in feed	% yield	gel permeation chromatography			light scattering	
			$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	$M_w/10^{-3}$	DP_w
3	0.05	90	65.0	31.0	2.1	106.0	486
4	0.10	85	64.0	30.0	2.1	102.0	473
5	0.20	87	62.0	28.0	2.2	98.0	463
6	0.35	91	56.0	26.0	2.2	95.0	464
7	0.50	90	48.0	25.0	1.9	73.0	368
8	1.00	91	39.0	20.0	2.0		

[a] 32–40 mmol of monomers in 7 mL of toluene with 0.4–0.5 mmol of AIBN at 75 °C for 19 h.

Table III
Preparation of Copolymers 5 of Different Molecular Weight

co-polymer	mole ratio total monomers/AIBN	yield, %	$10^{-3}M_w$[a]	$10^{-3}M_n$[a]	M_w/M_n[a]
5	83	87	62.0	28.0	2.2
5a	42	95	38.0	17.0	2.2
5b	166	90	93.0	47.0	2.0
5c	239	81	165.0	76.0	2.2

[a] Measured by GPC.

conditions used in these copolymerizations as well as molecular weight data are summarized in Table II. As expected, the copolymer compositions matched those of the feed.

Absolute molecular weight measurements made by LALLS are shown in Table II. These absolute values of the weight-average molecular weight as determined by light scattering tend to exceed the GPC values by a factor of ≈1.6. This almost constant factor indicates that composition has little effect on hydrodynamic radius for this specific family of copolymers. As can be seen in Table II, the weight-average degrees of polymerization DP_w show a tendency to decrease slightly as the mole fraction of monomer 1 increases, while the polydispersity M_w/M_n remains essentially constant.

Similarly, a series of copolymers 5 of constant composition but of differing molecular weight were also prepared by using 20 mol % of monomer 1 in the feed to determine the influence of copolymer molecular weight on resist properties (Table III). As expected, NMR analysis confirms the mole fraction of 1 incorporated into copolymers **5a–c** with values of 0.20 ± 0.01, 0.19 ± 0.01, and 0.21 ± 0.01 obtained for samples **5a**, **5b**, and **5c**, respectively. As can be seen from Table III the number-average molecular weight can be increased from 17 000 to 76 000 by decreasing the amount of AIBN used from 2.4 to 0.4 mol %. The molecular weight data were obtained from GPC, but one would expect it to reflect the trend of the absolute molecular weight as was shown above. Copolymers having even higher molecular weights were not prepared, as their solutions would be too viscous for convenient spin coating at 1-μm thickness.

Removal of the *t*-BOC Protecting Groups of Polymers 3–7. The next step in the preparation of the desired copolymer was perceived as being the most difficult, that is, removal of the *t*-BOC protecting group to give the phenolic moiety while leaving the acetate group untouched. Two procedures reported in the literature[3] for deprotecting the homopolymer of 2 are thermolysis by heating the polymer to 200 °C and acidolysis using trifluoroacetic acid. The copolymer was thought to be too acid sensitive for the latter method and attempts to carry out the thermolysis by heating a copolymer containing 20 mol % of the monomer 1 dissolved in an inert solvent to 200 °C proved unattractive due to the occurrence of branching as evidenced by GPC. One of the methods favored in peptide synthesis for removal of the *t*-BOC group from amino groups involves treatment with acetic acid containing boron fluoride etherate.[37] However, it was decided to try acetic acid alone in an attempt to selectively remove the *t*-BOC groups since it was expected that acetic acid would not affect the acetate moieties of the vinylbenzyl acetate units in the copolymers, while the presence of BF_3 would likely prove deleterious.

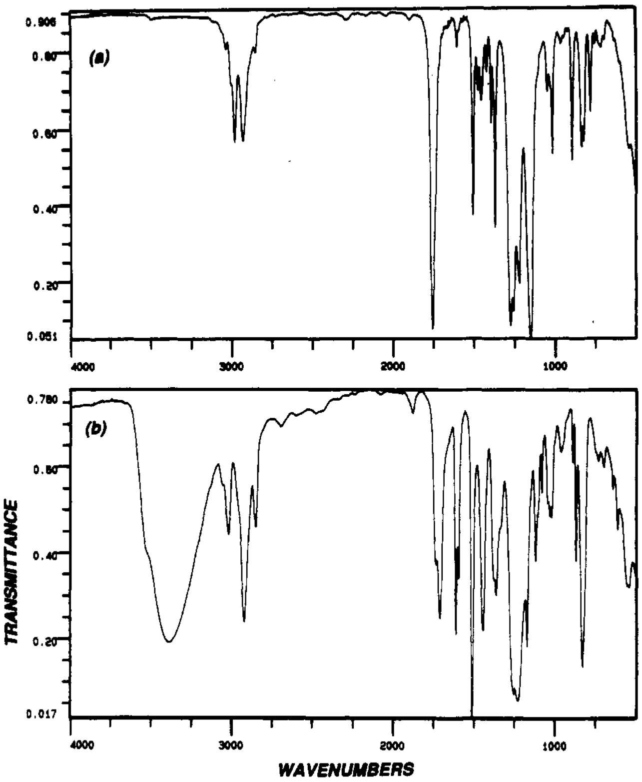


Figure 2. (a) IR spectrum of copolymer 5. (b) IR spectrum of copolymer 11 after removal of *t*-BOC groups.

Initial experiments were carried out using the homopolymer of 2. Treatment with glacial acetic acid while heating to 56 °C for 8 h resulted in little loss of the protecting group. However, treatment with refluxing acetic acid resulted in complete removal of the *t*-BOC group after 2–3 h with no apparent degradation of the polymer backbone. This method was then applied to copolymers 3–7. The deprotection proceeded cleanly, without the formation of any insoluble material.

The IR spectrum of copolymer 5 containing 20 mol % of monomer 1 is shown in Figure 2a. As expected, no hydroxyl functionalities are seen in this spectrum, while bands attributable to aromatic C—H stretch (3035 cm^{-1}), aliphatic C—H stretch (2982–2931 cm^{-1}), carbonate and ester C═O stretch (1757 cm^{-1}), and C—O stretching modes (1277–1151 cm^{-1}) are present. In contrast Figure 2b shows the IR spectrum of copolymer 11 obtained from 5 after removal of the *t*-BOC groups by refluxing in acetic acid. A very prominent OH band is seen and sharp decreases in the absorbances due to aliphatic C—H (2982–2931 cm^{-1}), C═O (1734 cm^{-1}), and C—O (1277–1151 cm^{-1}) stretching modes are apparent. The carbonyl absorption band remaining, attributable to the acetoxy group, has shifted frequency consistent with it being hydrogen bonded.

Similarly, Figure 3 shows the change in the ^{13}C NMR spectrum of 5 (curve a), as it is deprotected to afford 11. Most noticeable is the disappearance of the resonances at 27.7, 82.8, and 151.8 ppm due to the *t*-BOC methyl groups,

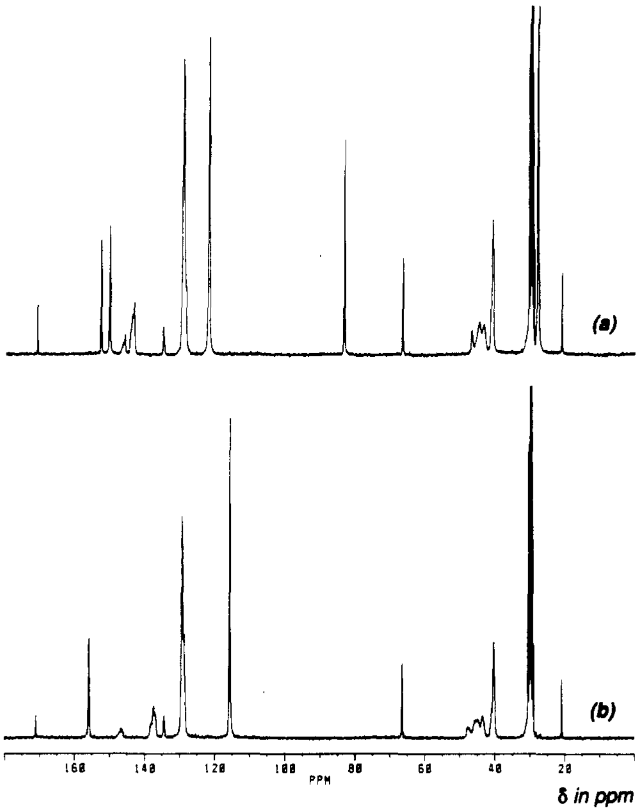


Figure 3. (a) ^{13}C NMR spectrum of copolymer 5. (b) ^{13}C NMR spectrum of copolymer 11 after removal of *t*-BOC groups.

quarternary carbons, and carbonyl carbons, respectively. Other changes observed in the resonances of the aromatic carbons are consistent with the freeing of the phenolic group. The signals for the acetoxymethyl group remain unchanged. The changes observed in the ^{1}H NMR spectra upon deprotection of **5** to **11** can be summarized as follows: the disappearance of the resonance at ca. 1.5 ppm associated with the methyl groups of the *t*-BOC moiety is readily seen; in addition, the resonances in the aromatic region change and a signal appears at 7.4 ppm attributable to the phenolic proton; finally, the resonances at 2.1 and 5.0 ppm due to the methyl and benzylic methylene protons of the acetoxymethyl group remain. Again the composition of the copolymers after deprotection can easily be confirmed from the ^{1}H NMR data by using the ratio of benzylic methylene protons to the aliphatic protons. Our measurements confirm that the deprotected copolymers contain the same mole fraction of **1** as their precursors.

The deprotection process can also be monitored by thermal analysis. A DSC study of copolymer **5** shows a glass transition temperature T_g of 115 °C, as well as a sharp endotherm at 195 °C corresponding to the loss of the *t*-BOC groups. The deprotected copolymer **11** shows a T_g of 157 °C. Thermogravimetric analysis also shows the loss of the *t*-BOC group of **5** upon heating between 190 and 220 °C. The observed weight loss of 37.7% is in good agreement with the calculated value of 37.9% for a copolymer containing 80% of **2**. In contrast, copolymer **11** shows no weight loss at these temperatures.

The above analytical data show that the *t*-BOC group is completely removed by treatment with refluxing acetic acid while the acetoxy group is left intact. A comparison of GPC data for copolymers **5** and **11** supports this as shown in Figure 4. The molecular weight decreases on deprotection as one would expect and so the curve shifts toward longer retention time. The shape of the curves before (a) and after (b) deprotection indicates that the molecular weight distribution remains constant; i.e., no chain scission or branching occurs during deprotection. Table IV gives the GPC molecular weight data obtained for the deprotected polymers. It must be noted that the decrease in GPC molecular weight upon deprotection appears to be less than expected from theory. This has been observed previously in the deprotection of homopolymers of **2** to poly(*p*-hydroxystyrene).[3] Of course the absolute values of DP_w remain identical for the protected and deprotected polymers.

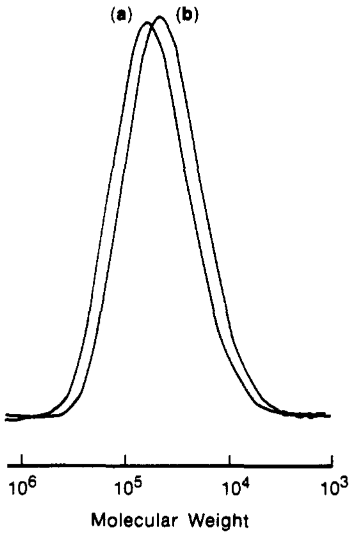


Figure 4. (a) GPC trace for copolymer 5. (b) GPC trace for copolymer 11 after removal of *t*-BOC groups.

Glass Transition Temperatures for Polymers 8–13. While the glass transition temperature of pure homopolymers of **2** is generally above 180 °C, that of homopolymer **8** is only 47 °C. As expected, the various copolymers **9–13** show intermediate glass transition temperatures that reflect their composition (Figure 5). Within the range of molecular weights prepared in this study, no significant change in T_g is seen for copolymers of constant composition. For example, copolymers **11a–c** that contain 20 mol % of monomer **1** have experimentally measured T_g values of 154, 153, and 154 °C, respectively.

Sensitivity Measurements. The advantage of using onium salt photoacid generators is that irradiation can be carried out using an electron beam or X-rays as well as deep-UV light, to initiate the proton formation. Thus the resist system should be sensitive to all three types of radiation.

UV spectra of the series of copolymers of varying composition were measured by coating quartz disks with 1.0-μm films containing 5–10% of the triphenylsulfonium salt. In all cases the absorbance of the films at 254 nm did not exceed 0.45 for all copolymers **9–13**. However, the absorbance at 278 nm does increase as the amount of **1** in the copolymer increases. After exposure, no change in the absorption spectra were observed; yet, on baking after exposure, the absorbances at both 254 and 278 nm were found to increase slightly.

The sensitivity of the resists formulated from polymers **8** to **13** was determined as described in the literature.[1] Figure 6 shows a typical sensitivity curve for copolymer **11** containing 5 wt % of triphenylsulfonium hexafluoroantimonate. The normalized film thickness is plotted versus log dose. The minimum dose required to give a totally insoluble film without loss of film thickness (D_i) is measured as shown. We use this value D_i as a figure of merit for sensitivity. The minimum dose required to leave

Table IV
Molecular Weight and Imaging Data for Deprotected Polymers 9–13

deprotected polymer	mole fractn 1	gel permeation chromatography $10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	D_i, mJ/cm^2	γ	development conditns
9	0.05	44.0	20.0	2.2	2.1	2.4	MF 312/H_2O (1/1); 1.0 min
10	0.10	45.0	21.0	2.1	2.1	2.4	MF 312/H_2O (1/1); 2.5 min
11	0.20	45.0	20.0	2.2	1.6	2.0	MF 312: 0.75 min
11a	0.20	29.0	14.0	2.1	1.8	1.9	MF 312: 0.75 min
11b	0.20	69.0	33.0	2.1	1.2	1.9	MF 312; 0.75 min
11c	0.20	125.0	59.0	2.1	0.8	1.9	MF 312; 0.75 min
12	0.35	46.0	22.0	2.1	1.2	2.4	MF 312: 3.5 min
13	0.50	41.0	21.0	2.0	1.4	3.2	MF 312/IPA[a] (9/1); 2.75 min
8	1.00	39.0	20.0	2.0	2.0	6.8	anisole/IPA[a] (3/4); 0.3 min

[a] IPA = isopropyl alcohol.

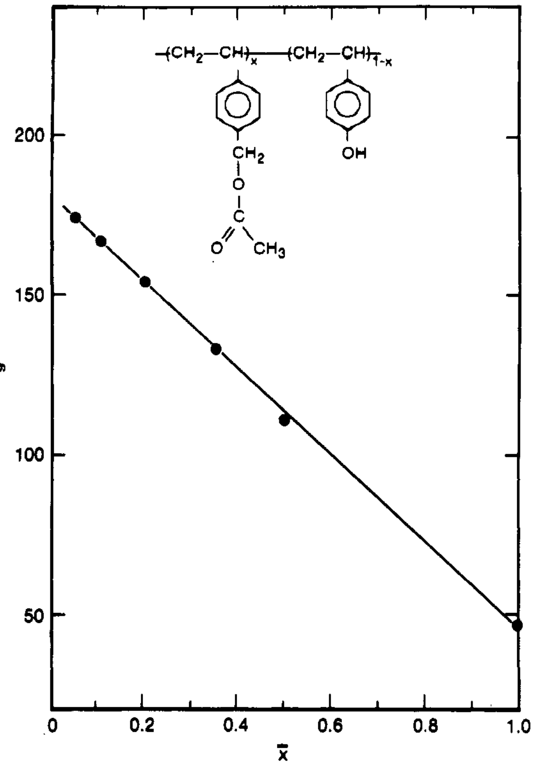


Figure 5. Glass transition temperatures of polymers 8–13.

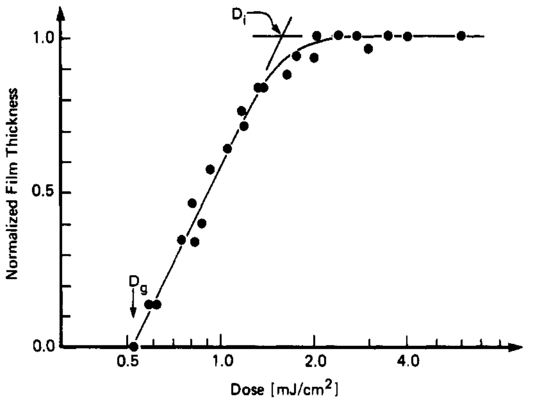


Figure 6. Sensitivity curve for copolymer 11 containing 5 wt % onium salt using 254-nm UV light.

an insoluble residue is the gel dose D_g. The slope of the line between D_g and D_i gives the contrast "γ", a relative measure of the difference in solubility between the exposed and unexposed regions.

The space of variables that must be studied for establishment of an optimum resist material and process is quite large. In order to choose a preliminary structure for imaging experiments, some parts of this variable space were explored. The effect on sensitivity of varying the mole fraction $\bar{x}$ of 1 in the copolymers is shown in Figure 7 and Table IV. Even at extremely low incorporation of the active acetate moieties, poly(vinylphenol) is rendered quite radiation sensitive in this application. The maximum sensitivity (lowest D_i) was measured for a mole fraction $\bar{x}$ = 0.35. However, at $\bar{x}$ = 0.35, the copolymer begins to suffer from poor aqueous base solubility, which may lead to some swelling, and the glass transition temperature of the copolymer is a bit low for convenient processing (Figure 5). Homopolymer 8 shows a very high sensitivity but cannot be developed in aqueous base and is therefore subject to swelling during development. Therefore, $\bar{x}$ = 0.2 (polymer 11) was chosen for further studies. This copolymer has slightly less than maximum sensitivity, but it is extremely soluble in dilute aqueous base, which is a prerequisite for development without resolution loss due to swelling. Figure 7 also shows that an increase in sensitivity can be obtained through an increase in the percentage of onium salt used in the resist formulation, though slightly different development conditions are required for the higher concentration of onium salt.

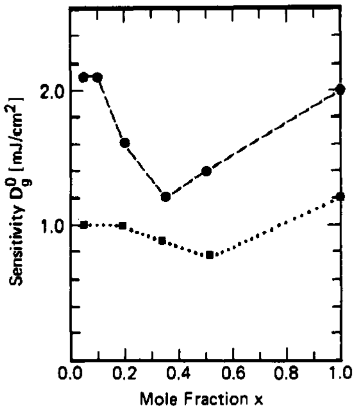


Figure 7. Sensitivity versus mole fraction of 1 in the polymer using 254-nm UV light. (●) 5 wt % onium salt; (■) 10 wt % onium salt.

The sensitivity of a series of copolymers of structure 11 for which $\bar{x}$ = 0.2 having varying M_n but constant polydispersity was measured. The sensitivity increases (D_i decreases) with increasing molecular weight, a phenomenon that is well-understood and has been observed in other systems.[38-40] A molecular weight of M_n = 40 000 was chosen for imaging studies since higher molecular weight samples provided solutions of too high viscosity for coating convenience. The relationship between D_i and M_n is provided in Figure 8.

It is of interest to know the extent of acetoxy group reaction at the exposure dose required for imaging. Following Flory,[41] an expression for the extent of reaction of acetoxymethyl groups at the gel point (corresponding

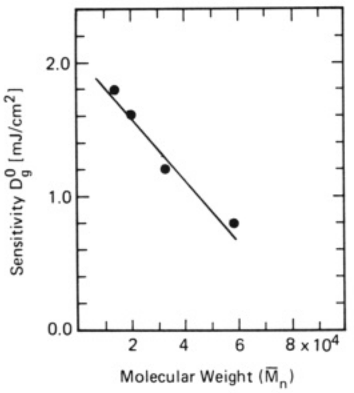


Figure 8. Sensitivity versus molecular weight for copolymers **11** and **11a–c** using 254-nm UV light.

Table V
Calculated Percentage of Acetoxymethyl Groups Having Reacted at the Gel Point

$\bar{x}$	0.05	0.10	0.20	0.35	0.50
DP_w	486	473	463	464	368
$n_a/N_a \times 100$	2.1	1.1	0.6	0.3	0.2

to D_g) can be determined. If it is assumed that there is equal reactivity of functional groups and that the distribution of monomer units is random, which in this system appears to be the case, the extent of reaction is then given by

$$n_a/N_a = 1/2DP_w\bar{x}$$

Where DP_w is the weight-average degree of polymerization prior to cross-linking, $\bar{x}$ is the mole fraction of acetoxy groups, n_a is the number of reacted acetoxymethyl groups, and N_a is the total number of such groups. We have a measure of the absolute value of the molecular weight M_w and $\bar{x}$, therefore DP_w is easily determined, as is n_a/N_a. Table V gives the theoretical percentages of acetoxy methyl groups reacted at the gel point for samples of varying molecular weights.

Lithographically, this extent of reaction corresponds to the point D_g where the first insoluble residue is formed. Since DP_w is reasonably constant the value of n_a is constant across the series; i.e., the same number of acetoxy groups need to react to produce gel. However as $\bar{x}$ increases the fraction n_a/N_a decreases. The values given in Table V illustrate why, by design, cross-linking systems are so sensitive, a small extent of reaction being required to generate a large change in solubility. The treatment neglects intramolecular reactions and so the actual values would be somewhat larger than those calculated above. It must be noted here that the polydispersity of the above copolymers was essentially constant. This is another factor that can affect the sensitivity and contrast of photoresist systems operating on the basis of cross-linking.[37,38] For polymers having the same DP_w but different polydispersities, fewer cross-links are required to produce gelation in the polymer with the broader molecular weight distribution. In lithographic terms, broadening of the molecular weight distribution should decrease the D_g value but increase the D_i value, the point corresponding to the incorporation of all the material into a network, since more molecules have to be incorporated. This will then result in a decrease in contrast. Consequently, we worked with samples of known and, as nearly as possible, constant polydispersity.

Based on the studies described above, imaging experiments were carried out with a standard formulation prepared from copolymer **11** ($\bar{x}$ = 0.2, M_w = 45 000, M_n = 20 000). The process described below is representative of that used in the actual imaging experiments, although some small variations in development time or other process conditions were made in some runs. The resist solution was prepared by dissolving the polymer in propylene glycol monomethyl ether acetate containing 5% by weight of triphenylsulfonium hexafluoroantimonate. Films were prepared by spin coating, baked at 120 °C for 10 min, exposed, baked for 3 min at 120 °C to complete the cross-linking reaction, then developed in Shipley MF-312 developer (an aqueous solution of a tetraalkylammonium hydroxide), and finally rinsed in deionized water. A typical development time is 45 s.

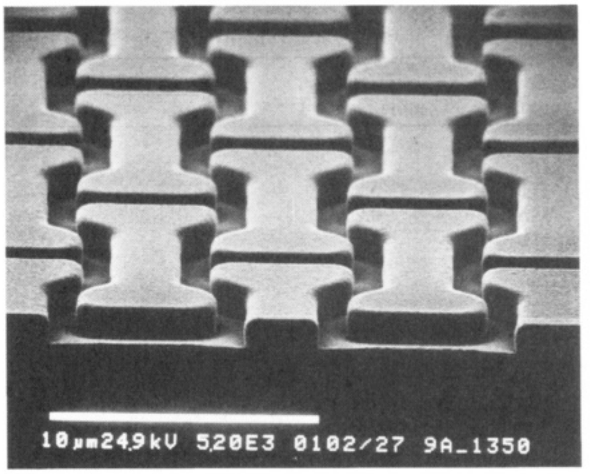


Figure 9. Scanning electron micrograph of a negative image obtained from copolymer **11** using exposure to 254-nm UV light.

A deep-UV sensitivity curve (Figure 6) was generated showing a sensitivity D_i = 1.6 mJ/cm^2 for narrow-bandwidth 254-nm radiation. Imaging studies were carried out on a Perkin-Elmer Micrascan 500 operating in the UV-2 mode (240–260 nm) with numerical aperture = 0.165. One to one projection printing of 1-μm features in 1-μm-thick coatings was achieved at a scan speed of 1350, corresponding to ca. 2 mJ/cm^2 exposure dose. A scanning electron micrograph of images printed in this experiment is provided as Figure 9.

Similar experiments with IR monitoring of the carbonyl band of 0.9-μm-thick films of copolymer **11** containing 5 wt % photoacid generator cast on NaCl plates were used to determine experimentally the extend of reaction of acetoxymethyl groups as a function of the exposure dose. Figure 10 shows an induction period for the loss of acetoxymethyl groups, followed by a more rapid increase. It is worthwhile noting that only 2–5% of the acetoxymethyl groups have reacted for exposure doses of 1–2 mJ/cm^2, a fact that illustrates again the high intrinsic sensitivity of negative cross-linking resists.

The electron beam sensitivity curve was generated with an IBM vector scan field emission lithography system operating at an accelerating potential of 25 kV.[31] Figure 11 shows a sensitivity D_i = 1.1 μC/cm^2 under these exposure conditions and a relatively high contrast. Figure 12 shows 0.25-μm images that were obtained at design dimension in 0.35-μm-thick films at a dose of 2.25 μC/cm^2.

Synchrotron X-ray exposures were carried out on the IBM beam line at the Brookhaven National Light Source. Sensitivity curves were generated for the standard formulation and for a second formulation containing 10% by weight to polymer of the sulfonium salt. Figure 13 shows the dramatic effect of increasing the loading of sulfonium salt. As the loading is increased from 5 to 10%, the sensitivity D_i changed from ca. 20 to ca. 10 mJ/cm^2. Figure

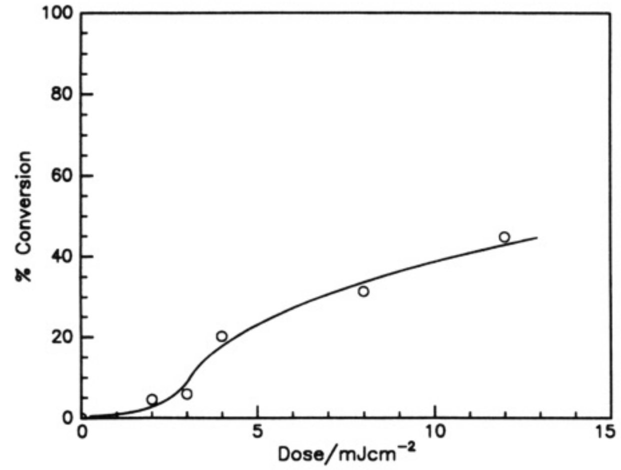


Figure 10. Loss of acetoxymethyl groups as a function of exposure dose (254-nm UV light) for copolymer **11** containing 5 wt % onium salt.

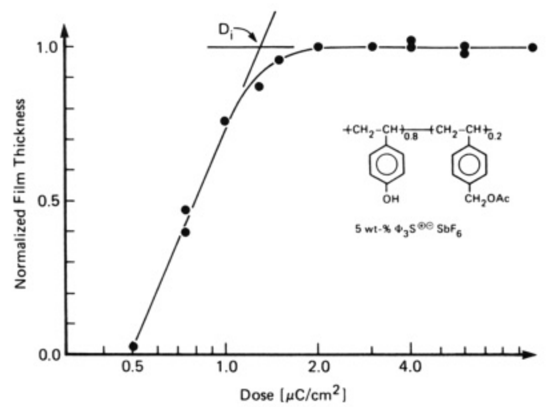


Figure 11. Sensitivity curve for copolymer **11** containing 5 wt % onium salt using E-beam radiation.

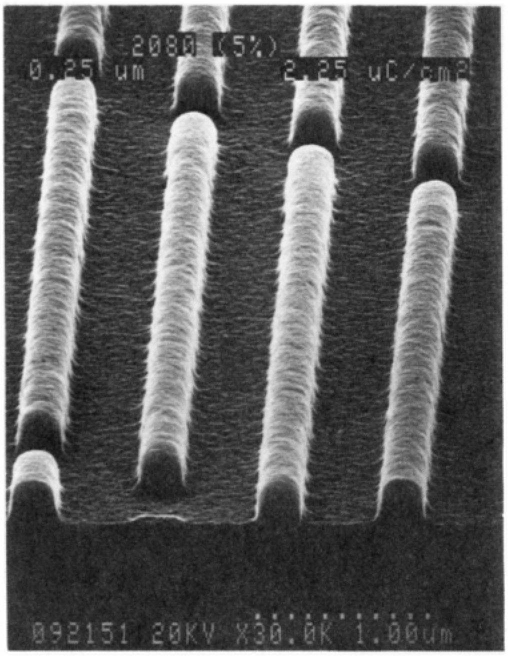


Figure 12. Scanning electron micrograph of a negative image obtained by E-beam exposure of copolymer **11** containing 5% onium salt.

14 shows a scanning electron micrograph of 0.5-μm lines printed in 1.5-μm-thick films of the 10% formulation using synchrotron X-ray radiation.

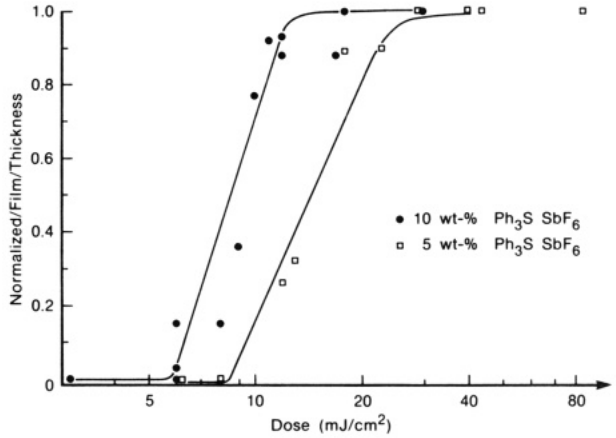


Figure 13. Sensitivity curve for copolymer **11** using synchrotron X-ray radiation. (□) 5 wt % onium salt; (●) 10 wt % onium salt.

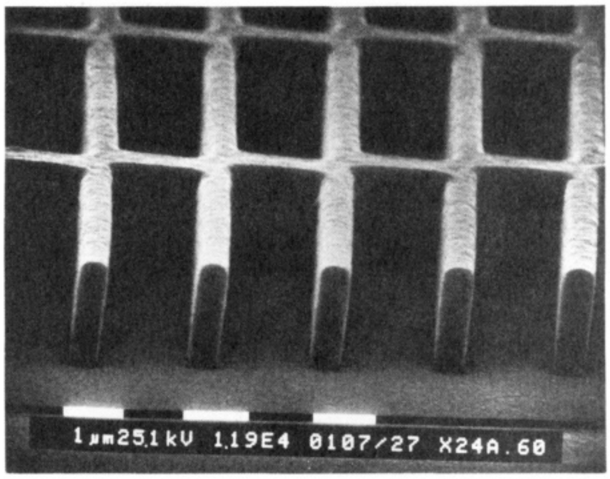


Figure 14. Scanning electron micrograph of 0.5-μm image obtained by exposure to synchrotron X-ray radiation.

Conclusions

Negative-tone resist systems based on acid-initiated cross-linking poly(1-*co*-4-hydroxystyrene) show excellent sensitivity to deep-UV, E-beam, and X-ray radiation and are aqueous base developable. The sensitivity of these systems results from chemical amplification and the use of cross-linking to obtain differential solubility. The copolymers are relatively easy to prepare via free radical, random, copolymerization of *t*-BOC protected 4-vinylphenol with 4-vinylbenzyl acetate followed by quantitative removal of the *t*-BOC group using refluxing acetic acid to generate the required copolymer. The sensitivity of the system may be varied by changing the composition and/or the molecular weight of the polymers, along with the loading of the photoacid compound. Preliminary imaging experiments using deep-UV, E-beam, and X-ray radiation illustrate the potential utility of this new resist system.

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Supplementary Material Available: Eight tables containing, Table 6, ^1H NMR analysis of 4-(acetoxymethyl)styrene (**1**);

Table 7, ^{13}C NMR analysis of 4-(acetoxymethyl)styrene (1); Table 8, composition of copolymer 5 and expected and observed values from ^{1}H NMR data; Table 9, copolymerization of 1 and 2, reactivity ratio study, and mole fraction of 1 in the feed (M_1) and in the copolymer (m_1); Table 10, ^{1}H NMR assignments for copolymer 5; Table 11, ^{13}C NMR resonances for copolymer 5; Table 12, ^{1}H NMR resonances for deprotected copolymer 11; and Table 13, ^{13}C NMR resonances for deprotected copolymer 11 and two figures of the ^{1}H NMR spectra of copolymers 5 and 11 and the TGA curve for copolymer 5 (6 pages). Ordering information is given on any current masthead page.

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