Photo-Cross-Linking of Poly(4-hydroxystyrene) via Electrophilic Aromatic Substitution: Use of Polyfunctional Benzylic Alcohols in the Design of Chemically Amplified Resist Materials with Tunable Sensitivities

S. Ming Lee and Jean M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

C. Grant Willson[†]

IBM Almaden Research Center, San Jose, California 95120-6099

Received April 4, 1994[®]

ABSTRACT: The use of polyfunctional benzylic alcohols as latent cationic cross-linkers for polymers such as poly(4-hydroxystyrene) has been explored. Photogeneration of acid within thin films of the phenolic resin containing the latent cross-linker results in their thermal cross-linking via electrophilic aromatic substitution in a self-perpetuating process. This cationic photo-cross-linking reaction has been used to design resist materials that show remarkably high sensitivities in the three common modes of lithography: deep-UV (0.2 mJ/cm^2), E-beam (0.1 μC/cm^2), and X-ray (<10 mJ/cm^2). A comparative study involving numerous cross-linkers with related structures demonstrates a direct correlation between the resist sensitivity, or the initial rate of cross-linking, and the stability of the carbocationic intermediate that is formed in the rate-determining step. In some cases, the sensitivities of these chemically amplified materials are so high that they have surpassed the capabilities of many existing exposure tools. To make the resists more versatile, tuning of sensitivity can be achieved through the addition of an electron-rich species to the resist to partially capture the acid photogenerated within the polymer thin film.

Introduction

The development of efficient methods for the cross-linking of polymers is of great importance to the polymer field since polymers frequently need to be insolubilized or cured to achieve their targeted properties. For example, the curing of elastomers is key to their application in the tire industry. Thin film coatings, paints, foams, and structural materials all have properties that are intimately related to their extent of cross-linking. Radiation curing is a particularly efficient process for the cross-linking of thin film coatings. In particular, radiation curing is used extensively in the insolubilization of polymer films known as resists that are used in imaging applications for the lithographic manufacturing of circuit boards or advanced microelectronic devices. In microlithography, the demand for ever-decreasing feature size (<0.5 μm) in transistor elements is pushing "conventional photolithography", defined as photolithography employing 350–450-nm light, to its limit in terms of attainable resolution. The primary technological alternatives to conventional photolithography are deep-UV (<280 nm) photolithography, scanning or projection electron-beam, X-ray, and scanning ion-beam lithography,[1] or the use of phase-shifting masks.[2] However, conventional photoresists may not be ideally suited for use with these new lithographic technologies. Possible shortcomings of the conventional novolak–diazonaphthoquinone resists are their relatively low sensitivities and the absorption properties of the materials.[3] The new lithographic tools, having lower brightness sources, require higher sensitivity resists. Sensitivity can be improved through the use of chemical amplification, a concept pioneered by researchers from IBM and this laboratory.[4] In chemical amplification, species that catalyze many subsequent chemical events are generated photochemically. The overall quantum efficiency of such reactions is effectively much higher than that for initial catalyst formation. The radiation power is essentially amplified by the catalytic nature of the chemistry involved.

One class of such chemically amplified resist utilizes electrophilic aromatic substitution for cross-linking.[5–9] Typically, such a resist will contain the following three components: a photo-acid generator such as onium salts or certain sulfonate esters,[10] a latent or masked electrophile that is transformed into an electrophile upon reaction with acid, and a polymer containing an aromatic moiety that is susceptible to electrophilic aromatic substitution; this polymer provides for cross-linking in the radiation-exposed regions, and aqueous base development in the unexposed regions.

When the mixture is irradiated, a strong protonic acid is generated in the exposed areas as a result of the photochemistry of the onium salt. Subsequent heating results in the formation of electrophilic species that cross-link the neighboring polymer chains by electrophilic aromatic substitution. This leads to a drastic increase in the molecular weight of the polymer. As a result, the solubility of the exposed areas of the resist in the developer is decreased and a negative tone image is obtained.

Poly(4-hydroxystyrene) is frequently used as the polymer matrix due to its good coating properties and solubility in high-pH aqueous medium. Nonogaki et al.[11] have shown its usefulness even in the negative tone mode as it does not swell appreciably in the aqueous base used in the development step, in sharp contrast with classical negative tone resists that are plagued by swelling and image distortion problems.

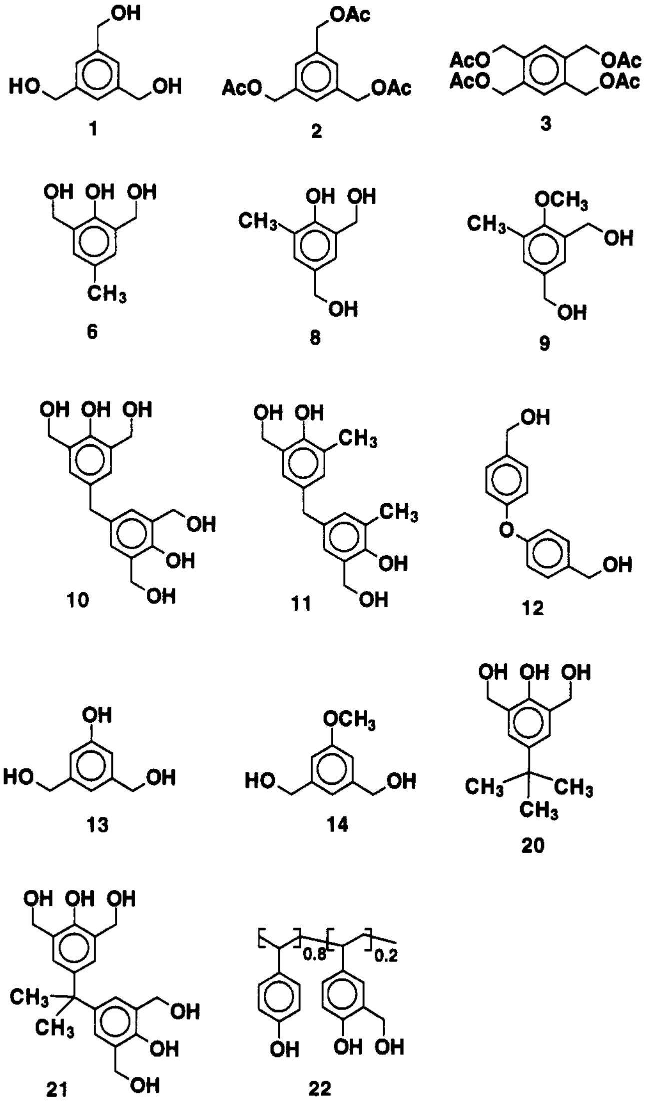
Recently, our laboratory has studied several three-component resist systems in which the latent electrophile, instead of being part of the polymer chain, is a separate small molecule capable of cross-linking several polymer

---

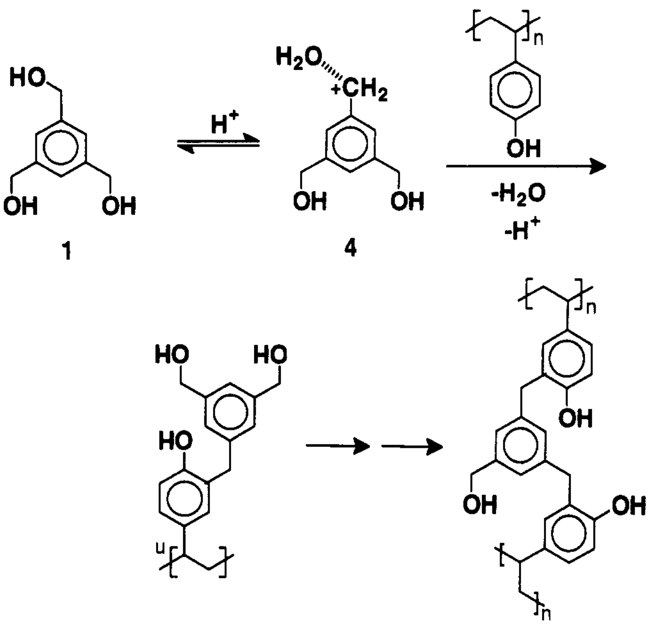
[†] Present address: Dept. of Chemistry, University of Texas, Austin, TX 78712-1062.

[®] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

Scheme 1



Scheme 2



chains.[12,13] Examples of previously used cross-linker molecules include benzylic alcohol **1**, and benzylic acetates **2** and **3** (Scheme 1). These compounds, used in three-component resists with poly(4-hydroxystyrene) and a photoacid generator, show high lithographic sensitivities and are considered to be more flexible than copolymers containing the electrophile[7] because the proportion of the various components can be adjusted very easily. The key intermediate in the cross-linking process is believed to be a highly reactive carbocationic moiety, such as **4** (Scheme 2). In this paper, the use of new cross-linkers, with designs that optimize sensitivity through higher carbocation stability, are tested with poly(4-hydroxystyrene) that contains phenolic groups susceptible to electrophilic alkylation processes.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker WM-300 300-MHz spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer at 75 MHz with the solvent carbon signal as standard. Infrared spectra were obtained on a Nicolet FTIR/44 spectrometer. A Nicolet 9430 UV-visible spectrophotometer was used to obtain ultraviolet spectra. Differential scanning calorimetry was done on a Mettler DSC 30 instrument. Size-Exclusion chromatography was carried out on a Nicolet 9560 liquid chromatograph using THF at 30 °C as the mobile phase at a flow rate of 1.0 mL/min. Molecular weights were measured using universal calibration (in line viscosity detector from Viscotek and refractive index detector) based on polystyrene standards.

Resist film thickness was measured with a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed either by contact printing using a Canon HTG Systems III Contact Aligner or 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 using an Optical Associates Inc. 354 exposure monitor. The output of the mercury lamp was filtered through a 254-nm narrow-bandwidth interference filter from Oriel Corp. Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 Multidensity resolution target (Ditric Optics Inc.). Sensitivities reported are accurate to ±0.05 mJ/cm^2. Electron beam exposures of the resist films were conducted with a Cambridge Instruments Electron Beam Microfabricator 10.5/CS. Scanning electron micrographs were recorded on a Cambridge Instruments Stereoscan 200 microscope.

Materials. Poly(4-hydroxystyrene) was obtained from IBM Corp. GPC analysis: M_w = 31 000; M_n = 12 100. AZ312MIF developer (0.54 N aqueous tetramethylammonium hydroxide solution) was obtained from Hoechst Celanese. The onium salt **5**, triphenylsulfonium hexafluoroantimonate, was obtained from General Electric.

Preparation of Cross-Linkers. Cross-linkers **6** and **20** are prepared by hydroxymethylation of *p*-cresol and 4-(*tert*-butyl)phenol, respectively[14] 4,4′-Isopropylidenediphenol is hydroxymethylated to give **21**.[15] Cross-linker **10** is prepared by hydroxymethylation of phenol with formaldehyde in the presence of sodium hydroxide.[16] 3,5-Bis(hydroxymethyl)phenol (**13**) is synthesized by reducing the dimethyl ester of 5-hydroxy-1,3-benzenedicarboxylic acid with lithium aluminum hydride.[17] Similarly, 4,4′-oxybis(benzoic acid) is reduced to give **12**.[18] Reaction of formaldehyde with *o*-cresol affords a mixture of **8** and **11** that is separated by column chromatography. Methylation of phenols **8** and **13** with iodomethane gives cross-linkers **9** and **14**, respectively.[14] The spectroscopic and physical characteristics of the cross-linkers are in agreement with literature data and their expected structures.

Table 1. Deep-UV Sensitivity Results for Resists Formulated with Cross-Linker 6, Photoacid Generator 5, and Poly(4-hydroxystyrene)

	wt %			sensitivity	contrast,
resist	6	poly(4-hydroxystyrene)	5	mJ/cm^2	γ
6a	20	70	10	0.2	7
6b	15	75	10	0.2	5
6c	10	80	10	0.2	7
6d	5	85	10	0.2	6
6e	15	80	5	0.3	6
6f	15	83	2	0.4	8

Hydroxymethylation of Poly(4-hydroxystyrene). A suspension of poly(4-hydroxystyrene) (0.8 g, 6.67 mmol) and potassium carbonate (1.16 g, 8.41 mmol) in water (20 mL) was stirred at 40 °C for 3.5 h. The product was filtered and washed with water. It was then dissolved in methanol (20 mL) and neutralized with dilute aqueous HCl. The solution was concentrated and precipitated into water. After stirring for 1 h in water, the precipitate was filtered and dried under vacuum to afford a pale yellow solid sample of **22** (0.55 g). GPC: $M_w = 31\,700$; $M_n = 9300$. ^{1}H NMR analysis indicates the presence of one hydroxymethyl group for every five phenyl rings: ^{1}H NMR (acetone-d_6) δ 1.35 (s, CH_2, 2H), 1.93 (s, CH, 1H), 2.94 (s, CH_2OH, 0.2H), 4.70 (s, CH_2OH, 0.4H), 6.62 (s, ArH, 3.8H), 8.09 (s, Ar*OH*, 1H); ^{13}C NMR (acetone-d_6) δ 40.3, 43.6, 45.2, 46.0, 62.5, 115.7, 126.8, 128.0, 129.3, 137.1, 137.5, 138.4, 154.4, 155.9; IR (KBr) 3700–3050, 2918, 1613, 1512, 1445, 1358, 829 cm^{-1}.

Resist Formulation and Processing. Poly(4-hydroxystyrene) (0.51 g, 74 wt %), the cross-linker (0.1 g, 15 wt %), and triphenylsulfonium hexafluoroantimonate (**5**) (0.07 g, 10 wt %) are dissolved in diglyme (2.3 g) and filtered through a 0.45-μm filter. Spin-coating onto silicon wafers at 3700 rpm for 30 s followed by heating at 110 °C for 2 min gives 1.0 ± 0.05 μm films. Unless otherwise stated, all samples are postbaked at 120 °C for 3 min. Solvent development of the resists is done by dipping the wafer into a beaker of rapidly stirred 30–40% aqueous AZ312MIF solution.

A resist solution of copolymer **22** is prepared by mixing the copolymer (90 wt %) with triphenylsulfonium hexafluoroantimonate (**5**) (10 wt %) in diglyme.

Tuning of Resist Sensitivity. Resist *6b* is modified by the addition of a small amount of piperazine, ranging from 0.1 to 1.0 wt %. All samples are prebaked at 110 °C for 2 min. Postexposure bake is done at 120 °C for 3 min. Solvent development of the resists is done in 40% aqueous AZ312MIF.

Results and Discussion

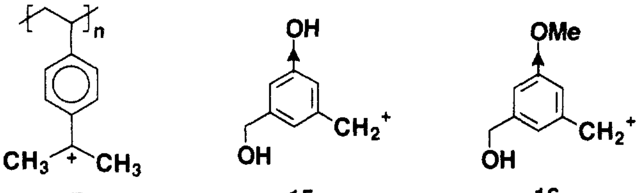
On the basis of previous studies conducted in this laboratory, the electrophilic aromatic substitution reaction between poly(4-hydroxystyrene) and benzylic alcohols **1**–**3**, is believed to be the rate-determining step in the cross-linking process.[7,12] The proposed intermediate is a carbocation–molecule pair (**4**) derived from the protonated benzylic alcohol (Scheme 2). The overall rate of polymer cross-linking is determined by the rate of formation of this carbocation–molecular pair, which, in turn, is governed by its stability. The positive charge in **4** is stabilized through dispersal over the aromatic ring by the benzylic resonance structures. Further charge stabilization, either through inductive or mesomeric effects, can be achieved by incorporation of electron-donating substituents. In this work, the phenolic hydroxyl group was chosen both for its strong positive mesomeric effect and because it imparts solubility in the alkaline developer solution. The two hydroxymethyl reactive groups of compound **6** selected for initial testing are located at the *ortho* positions of the phenolic hydroxyl group, allowing resonance conjugation in the derived carbocationic structure. The methyl group blocks the 4-position, precluding any ring substitution reaction between two molecules of the cross-linker.

Table 2. Deep-UV Sensitivities with Various Cross-Linkers[a]

cross-linker	deep-UV sensitivity, mJ/cm^2	cross-linker	deep-UV sensitivity, mJ/cm^2
1	1.9	**11**	0.2
2	3.5	**12**	0.2
3	2.3	**13**	0.5
6	0.2	**14**	1.2
8	0.2	**20**	0.3
9	0.4	**21**	0.4
10	0.2	**22**	0.6

[a] All experiments carried out with 1 μm thick film of resist; postexposure baking done at 120 °C for 3 min.

Scheme 3



7 15 16

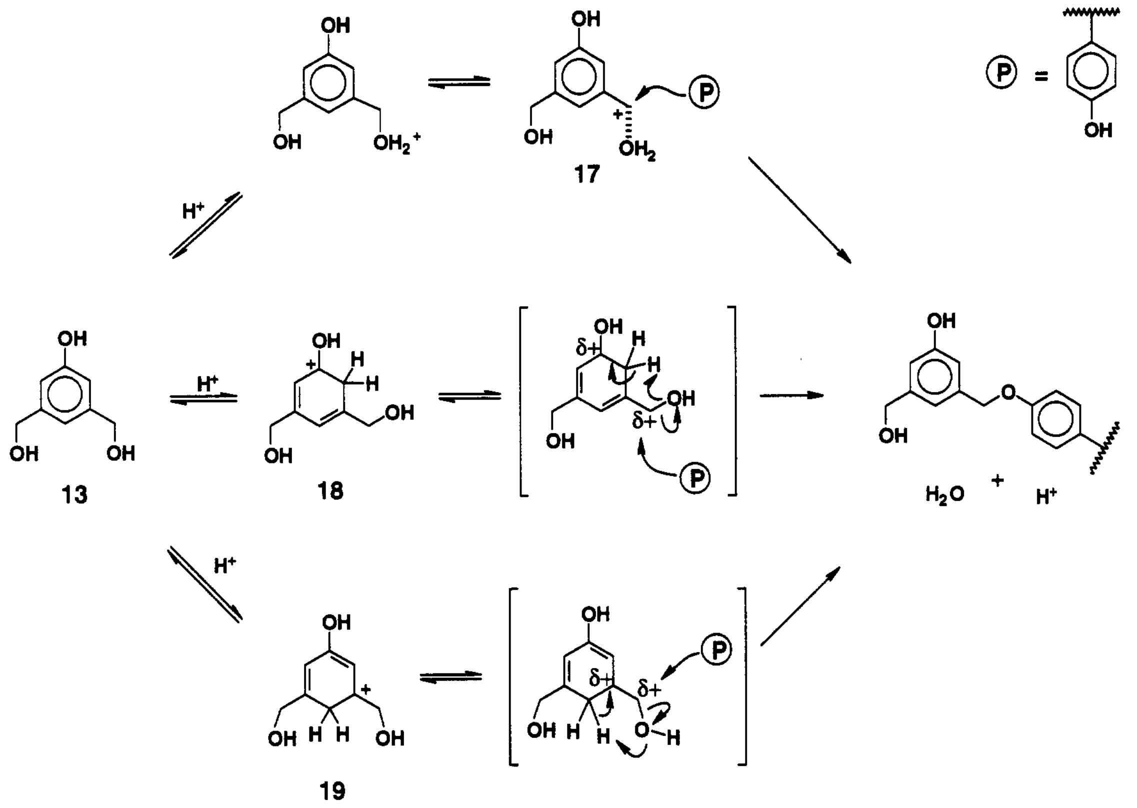
Resists of different compositions, *6a*-*6f*, were prepared with cross-linker **6** and tested with deep-UV radiation (Table 1). Incorporation of the phenolic hydroxyl group drastically increases the efficiency of the cross-linker, as reflected by 1 order of magnitude improvement in the resist sensitivities when compared with the results obtained earlier with cross-linkers **1**–**3** (Table 2). This finding confirms that the rate of cross-linking of poly(4-hydroxystyrene) via electrophilic alkylation processes is indeed governed by the stability of the carbocationic intermediate. The more stable the carbocation, the faster its formation and the higher the rate of alkylation. Cross-linker **6** forms a much more stable carbocation than **1**, **2**, or **3** as the positive mesomeric effect of the phenolic hydroxyl group provides extra delocalization of the positive charge. The importance of stabilizing the carbocation in the design of highly sensitive resist materials has previously been demonstrated[9] with highly stabilized tertiary benzylic carbocation **7** (Scheme 3) formed as the reactive species during the photoinitiated cross-linking process of a different substrate.

Resist *6b* is also extremely sensitive to other modes of irradiation. For example, its E-beam sensitivity is 0.1 μC/cm^2 and it shows a sensitivity of less than 10 mJ/cm^2 to synchrotron X-ray radiation.

Design of the Cross-Linkers: Structure–Activity Relationship. Detailed mechanistic studies involving cross-linking reactions that occur in the solid state are notoriously difficult to perform. Model studies involving low molecular weight[7] or monofunctional analogs[19] of the various components can sometimes be used to provide valuable insight into the cross-linking process.

In this study we have attempted to use sensitivity measurements and their relationship to the rate of initial cross-linking to shed further light on the structure–activity relationship for benzylic alcohol cross-linkers. To achieve this goal a series of structurally related cross-linkers

Scheme 4



(Scheme 1) was assembled and their sensitivities were measured under rigorously identical conditions (Table 2). In all cases, the amounts of cross-linkers, triphenylsulfonium hexafluoroantimonate (**5**), and poly(4-hydroxystyrene) were kept constant at 15, 10, and 75 wt %, respectively. Deep-UV exposures were done with the same experimental setup, and all samples were heated at 120 °C for 3 min in the postexposure bake step. Solvent development of the resulting images were done under similar conditions. Because the processing conditions were identical in all cases, variations in resist sensitivity observed upon slight modification of the cross-linker structure should reflect the change in the substitution reaction rate, i.e. lower sensitivity implies slower reaction rate.

The design strategy used for the selection of the most effective cross-linkers was to arrange the substituents on the aromatic ring so that any benzylic carbocationic intermediate derived from their activation would be stabilized by the strong positive mesomeric effect of methoxy, phenolic hydroxyl, or phenyl ether (e.g. **12**) group. As shown in Table 2, all the resists studied have very high sensitivities in the deep UV. Yet significant differences of >1 order of magnitude are observed between the most sensitive structures (e.g **6** or **11**) and the least sensitive (e.g. **2**) ones. These differences are readily correlated to the stability of the carbocationic intermediates that are derived from each of the cross-linkers.

The intramolecular hydrogen bonding between the phenolic hydroxyl and the benzylic hydroxyl groups in cross-linkers **6** and **8** does not appear to play a significant role in improving the resist sensitivity since similar sensitivities are obtained with both cross-linkers, despite the fact one of the benzylic hydroxyl groups in **8** cannot participate in such intramolecular hydrogen bonding.

The lower sensitivity observed in **9**, as compared to **8**, is attributed to the weaker positive mesomeric effect of the methoxy group relative to the hydroxyl group.[20]

A comparison of the sensitivities measured for cross-linkers **6**, **10**, and **11** demonstrates that increasing the number of reactive sites on the cross-linker molecule from two to four does not result in a significant increase in resist sensitivity. This suggests that once the cross-linker is connected to two polymer chains, its reduced mobility and increased steric requirements prevent further effective participation of the remaining sites in the cross-linking process.

At first glance, the results obtained with cross-linkers **13** and **14** appear unexpected. The negative inductive effect of the phenolic hydroxyl or methoxy group would be predicted to destabilize the carbocationic structures **15** and **16** (Scheme 3), rendering **13** and **14** less effective cross-linkers than **1**–**3**, for which this unfavorable situation does not apply. In fact, both **13** and **14** show higher sensitivities than **1**–**3** (Table 2), suggesting the alternate reaction mechanism shown in Scheme 4.

Various factors such as temperature and solvent determine whether protonation of a phenolic compound occurs on the oxygen atom of the hydroxyl group (*O*-protonation) or on the aromatic ring (*C*-protonation). In the gas phase, the proton affinity of the oxygen atom is 15 kcal/mol smaller than that of the aromatic ring;[21] however in 10% SbF_5–HSO_3F, *O*-protonation is reported to be 0.6 kcal/mol more favorable than *C*-protonation.[22] In the latter case, however, the amount *C*-protonation increases both with increasing temperature and with the amount of SbF_5.[22] Olah and Mo have found that at −15 °C the protonation of phenol changes from complete *C*-protonation to *O*-protonation when the solvent is changed from SbF_5–HSO_3F to SbF_5–HF.[23] Similar findings have been made for anisole.[23] Therefore, in the cases of compounds **13** and **14**, it is reasonable to assume that an equilibrium exists between *O*- and *C*-protonation. The preferred sites for *C*-protonation will be the 2- and 4-positions relative to the phenolic hydroxyl or methoxy groups, since the hydroxymethyl groups are weakly

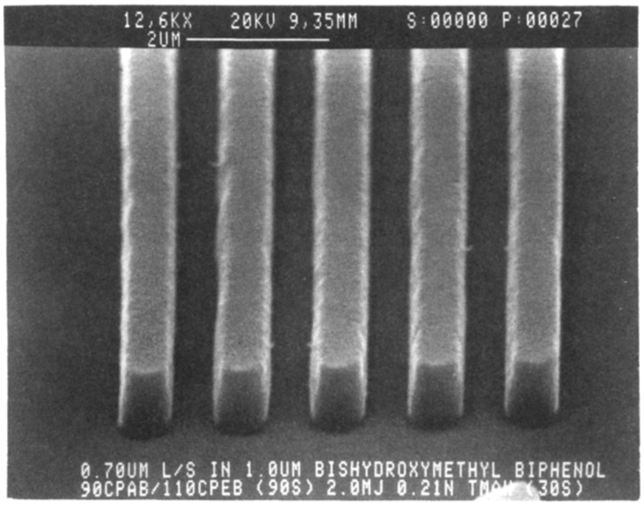
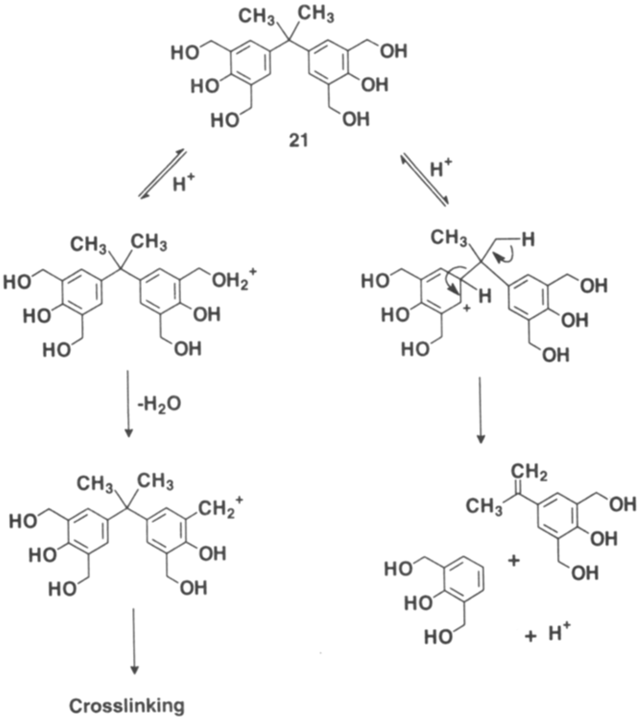


Figure 1. Scanning electron micrograph of 0.7-μm lines and spaces projection printed in resist containing cross-linker **11**, poly(4-hydroxystyrene), and onium salt **5**.

Scheme 5



electron withdrawing. A subsequent concerted removal of water and attachment of the polymer affords the product (Scheme 4). Intermediates **18** and **19** are expected to be more stable than **17** due to the strongly positive mesomeric effect of the phenolic hydroxyl group stabilizing the partial positive charge.

The observation that cross-linker **14** is less reactive than **13** provides further evidence that stabilization of carbocationic species is key to these reactions, since the methoxy group has a weaker positive mesomeric effect than the hydroxyl group.[20]

The lower resist sensitivities obtained with cross-linkers **20** and **21**, as compared to **6** and **10**, are likely the result of steric hindrance arising from the presence of the additional methyl groups that restrict the approach of the nucleophilic polymer. Alternatively, *C*-protonation causing fragmentation of the cross-linker molecule (Scheme 5) would also result in lower sensitivity, as it does not lead to any cross-linking and therefore contribute to a lower reaction rate. *C*-protonation of bisphenol A resulting in fragmentation has been previously observed in solution.[24]

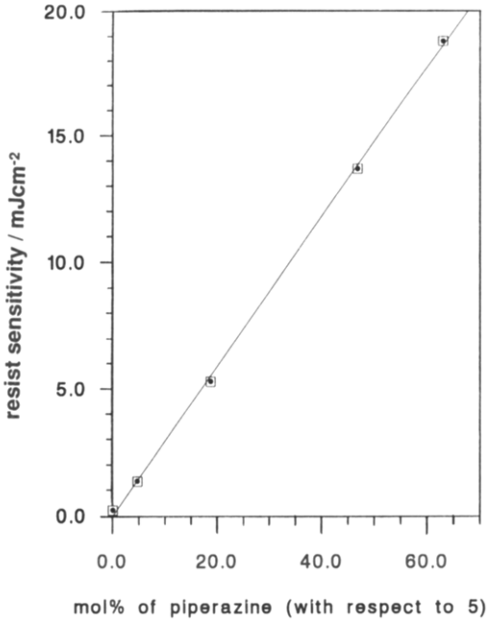


Figure 2. Tuning of resist sensitivity with addition of piperazine to resist *6b*. Postexposure bake performed at 120 °C for 3 min, followed by aqueous base development.

The possible reason behind the lower sensitivity of the resist prepared with copolymer **22**, as compared to a similarly proportioned mixture of poly(4-hydroxystyrene) and **6**, is discussed in the accompanying paper.[19]

Imaging of the Resists and the Tuning of Their Sensitivity. Feature sizes of below 1μm have been obtained in experiments testing the resolution of several resists containing different cross-linkers such as **6**, **10**, **11** and **20**, using 248-nm deep-UV projection printing. For example, Figure 1 shows a scanning electron micrograph of 0.7-μm lines and spaces printed in a resist containing cross-linker **11**, poly(4-hydroxystyrene), and onium salt **5**.

Most existing E-beam and other exposure systems have been designed for the relatively high dosage exposures that are necessary for conventional low-sensitivity resists. The sensitivities of resists *6a–6f* have now surpassed the capabilities of many existing exposure tools. We have explored the possibility of tuning the resist sensitivity over a broad range by modifying its composition. From the results in Table 1, it is apparent that this cannot be achieved by reducing the amount of cross-linker **6**. Decreasing the amount of onium salt **5** from 10 to 2 wt % only leads to a slight decrease in resist sensitivity (Table 1). To lower the sensitivity by a more significant amount, such as 1 or 2 orders of magnitude, the amount of onium salt in the resist formulation would have to be reduced drastically. This would make the resist even more susceptible to environment contamination.[25,26] As an alternative to varying the existing formulation of the resists, we have explored the addition of an organic base, piperazine, to resist *6b* to partially neutralize the acid generated in the photochemical reaction. The resist sensitivities at various mole percentages of piperazine were measured under identical processing conditions to obtain a calibration plot (Figure 2) By using this plot, it is possible to reproducibly tailor the resist sensitivity to specific exposure dose requirements. An additional feature of this approach is that, by adding a basic compound to the resist formulation, the resist might be made more stable to small amounts of airborne base contaminants.

Conclusion

A new class of cross-linking negative resists based on electrophilic aromatic substitution has been formulated and tested. In general, extremely high sensitivities result together with aqueous base development. The ability to tune the resist sensitivity by the use of an additive increases the versatility of the materials, allowing them to be used with a variety of equipments with different exposure powers. The influence of structural features of the various cross-linkers, such as the number of reactive sites and the sizes and relative positions of the substituents on the aromatic ring, on the crosslinking efficiency have been studied. This study demonstrates the direct correlation between sensitivity, rate of cross-linking of poly(4-hydroxystyrene) by alkylation, and stability of the carbocationic intermediate involved in the overall process. The most efficient and most sensitive cross-linkers of poly(4-hydroxystyrene) are characterized by structures that allow stabilization of the carbocationic intermediates by dispersion of their positive charges through the resonance effects of electron-donating substituents.

Acknowledgment. Thanks are due to Dr. J. T. Fahey, IBM, East Fishkill Facility, for assistance in deep-UV imaging. Financial support of this research by the Semiconductor Research Corp. and IBM Corp. is acknowledged with thanks. This work was performed in part at the National Nanofabrication Facility, which is supported by the National Science Foundation under Grant ECS-8619049, Cornell University, and industrial affiliates.

References and Notes

(1) Thompson, L. F. In *Introduction to Microlithography*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; ACS Symposium Series 219; American Chemical Society: Washington, DC 1983; pp 2–13; Willson, C. G. *Ibid*, pp 87–159.
(2) Terasawa, T.; Hasegawa, N.; Imai, A.; Tanaka, T.; Katagiri, S. *Proc. SPIE* **1991**, *1463*, 197.
(3) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394.
(4) Fréchet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Eng.* **1982**, 260. Willson, C. G.; Ito, H.; Fréchet, J. M. J.; Houlihan, F. *Proceedings of IUPAC 28th Symposium on Macromolecules: Amherst*, 1982, p 448. Fréchet, J. M. J.; Eichler, E.; Willson, C. G.; Ito, H. *Polymer* **1983**, *24*, 995. MacDonald, S. A.; Willson, C. G.; Fréchet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.
(5) Feely, W. E. *Proc. SPIE* **1986**, *631*, 48. Feely, W. E.; Imhof, I. C.; Stein, C. M.; Fisher, T. A.; Legenza, M. W. *Polym. Eng. Sci.* **1986**, *16*, 1101. Thackeray, J. W.; Orsula, G. W.; Pavelechek, E. K.; Canistro, D.; Bogan, L. E.; Berry, A. K.; Graziano, K. A. *Proc. SPIE* **1989**, *1086*, 34.
(6) Vollenbroek, F. A.; Nijssen, W. P. M.; Kroon, H. J. J.; Yilmaz, B. *Microelectron. Eng.* **1985**, *3*, 245.
(7) Reck, B.; Allen, R. D.; Twieg, R. J.; Willson, C. G.; Matuszczak, S.; Stöver, H. D. H.; Li, N. H.; Fréchet, J. M. J. *Polym. Eng. Sci.* **1989**, *29*, 960. Stöver, H. D. H.; Matuszczak, S.; Willson, C. G.; Fréchet, J. M. J. *Macromolecules* **1991**, *24*, 1741. Fréchet, J. M. J.; Matuszczak, S.; Reck, B.; Stöver, H. D. H.; Willson, C. G. *Macromolecules* **1991**, *24*, 1746.
(8) Dammel, R.; Dössel, K. F.; Lingnau, J.; Theis, J.; Huber, H.; Oertel, H.; Trube, J. *Microelectron. Eng.* **1989**, *9*, 575. Kajita, T.; Kobayashi, E.; Ota, T.; Miura, T. *Proc. SPIE* **1993**, *1925*, 133.
(9) Fréchet, J. M. J. U.S. Patent 5,084,522, 1992. Yoshida, M.; Fréchet, J. M. J. *Polymer* **1994**, *35*, 5. Ito, H.; Sooriyakumaran, R.; Maekawa, Y.; Mash, E. A. *Polym. Mater. Sci. Eng.* **1992**, *66*, 45.
(10) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055. Schwalm, R. *Proc. Polym. Mater. Sci. Eng.* **1989**, *61*, 278. Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Chem. Mater.* **1990**, 2, 299. Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Chin, T. *Chem. Mater.* **1991**, *3*, 462.
(11) Nonogaki, S.; Hashimoto, M.; Iwayanagi, T.; Shiraishi, H. *Proc. SPIE* **1985**, *539*, 189. Iwayanagi, T.; Hashimoto, M.; Nonogaki, S.; Koibuchi, S.; Makino, D. *Polym. Eng. Sci.* **1983**, *23*, 935.
(12) Fahey, J. T.; Shimizu, K.; Fréchet, J. M. J.; Clecak, N. J.; Willson, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1. Fahey, J. T. Ph.D. Thesis, Cornell University, 1991.
(13) Fréchet, J. M. J.; Fahey, J. T.; Lee, S. M.; Matuszczak, S.; Shacham-Diamand, Y.; MacDonald, S. A.; Willson, C. G. *J. Photopolym. Sci. Technol.* **1992**, *5*, 17. Fréchet, J. M. J.; Matuszczak, S.; Lee, S. M.; Fahey, J. T.; Willson, C. G. *Polym. Eng. Sci.* **1992**, *32*, 1471. Fréchet, J. M. J.; Lee, S. M. *Proc. SPIE* **1993**, *1925*, 102.
(14) Konig, K. E.; Lein, G. M.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553.
(15) Mitsui Petrochemical Industries, Ltd., Jpn. Kokai Tokkyo Koho 80 64,537, 1980; *Chem. Abstr.* **1977**, *93*, 204258*v*.
(16) Mitsui Petrochemical Industries, Ltd., Jpn. Kokai Tokkyo Koho JP 58,116,433 [83,116,433], 1983; *Chem. Abstr.* **1984**, *100*, 7356*n*.
(17) Uhrich, K. E., Ph.D. Thesis, Cornell University, 1992.
(18) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 2548.
(19) Lee, S. M.; Fréchet, J. M. J. accompanying paper in this issue.
(20) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
(21) DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853.
(22) Larsen, J. W.; Eckert-Maksic, M. *J. Am. Chem. Soc.* **1974**, *96*, 4311.
(23) Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 353.
(24) Feast, W. J.; Matuszczak, S. *Polym. Commun.* **1986**, *27*, 162.
(25) MacDonald, S. A.; Clecak, N. J.; Wendt, H. R.; Willson, C. G.; Snyder, C. D.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R.; McGuire, A. E.; Holmes, S. J. *Proc. SPIE* **1991**, *1466*, 2.
(26) MacDonald, S. A.; Hinsberg, W. D.; Wendt, H. R.; Clecak, N. J.; Willson, C. G.; Synder, C. D. *Chem. Mater.* **1993**, *5*, 348.