Mechanism of the Acid-Catalyzed Cross-Linking of Poly(4-hydroxystyrene) by Polyfunctional Benzylic Alcohols: A Model Study

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ABSTRACT: The mechanism responsible for the acid-catalyzed cross-linking of a photoresist based on poly(4-hydroxystyrene) was studied by ^{1}H NMR spectroscopy. The reaction involving cross-linkers that contain benzylic alcohol groups is proposed to proceed via both a direct *C*-alkylation as well as an initial *O*-alkylation followed by a subsequent acid-catalyzed rearrangement to the final *C*-alkylated product. The study reveals that a thermal cross-linking process is competing to a significant extent with the acid-catalyzed one. Two mechanisms involving different intermediates, quinone methides and carbocationic species, are proposed for these two competitive processes. The mechanistic understanding provided by this study can be used to explain some unusual features of this resist system such as the lack of correlation between the apparent resist sensitivity and the concentration of the cross-linker or the temperature of the reaction.

Introduction

Recently, we have reported the design of a new class of negative-tone photoresists with remarkably high sensitivities.[1] A typical formulation contains (i) a photoactive compound, (ii) a phenolic polymer, poly(4-hydroxystyrene), and (iii) a substituted phenol containing at least two hydroxymethyl groups such as **1** or **2** (Scheme 1) used as the cross-linker.

On exposure to suitable radiation, the photoactive compound releases hexafluoroantimonic acid[2] that catalyzes the electrophilic aromatic substitution of the benzylic alcohol cross-linker onto the phenolic matrix resin. When this process is repeated for the second benzylic alcohol group on the cross-linker, cross-linking is achieved and insolubilization results.

In practice, acid generation is followed by a thermal step that provides the activation energy necessary to overcome the activation barrier to electrophilic substitution. This postexposure thermal step, referred to as the postexposure bake or "postbaking", is typically done at 70–140 °C. Because higher reaction temperatures generally result in higher reaction rates, resist sensitivity was expected to increase with increasing postexposure bake temperature, up to the limit of the thermal stability of the resist. However, as will be seen (Table 1), the sensitivity of resists formulated with **2** is not affected significantly by changes in postexposure bake temperature within the range 80–115 °C. In addition, previous study on the use of benzyl alcohol **3** as cross-linker shows that the resist sensitivity improves with increasing weight percentage of the cross-linker.[3] In contrast, varying the amount of cross-linker **2** in the resist formulation from 5 to 20 wt % does not have much effect on the sensitivity.

Scheme 1

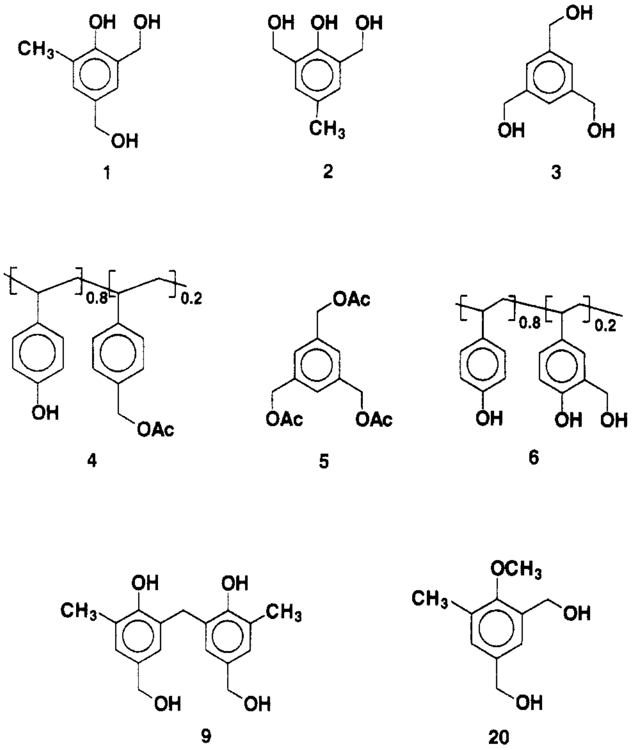

Table 1. Deep-UV Sensitivities of a Resist Containing Cross-Linker 2, Poly(4-hydroxystyrene), and an Onium Salt at Various Postexposure Temperatures

bake temp,[a] °C	sensitivity,[b] mJ/cm^2	bake temp,[a] °C	sensitivity,[b] mJ/cm^2
80	0.3	110	0.3
85	0.3	115	0.3
90	0.3	118	0.3
100	0.3	120	0.2
105	0.3	125	0.2

[a] All samples were postbaked for 3 min. [b] Developed in 40% aqueous AZ312MIF developer.

Earlier studies have shown that copolymer **4** affords a more sensitive imaging material than a mixture of poly(4-hydroxystyrene) and 1,3,5-tris(acetoxymethyl)benzene (**5**),[3,4] suggesting that incorporation of cross-linker onto the matrix resin increases sensitivity, as a single alkylation step (rather than two) is sufficient to cross-link the polymer. In contrast, we have observed that the resist derived from copolymer **6** is less sensitive than a similar resist obtained from cross-linker **2** and poly(4-hydroxystyrene).[1]

A mechanistic study using ^{1}H NMR experiments was undertaken to explain these unusual observations. In

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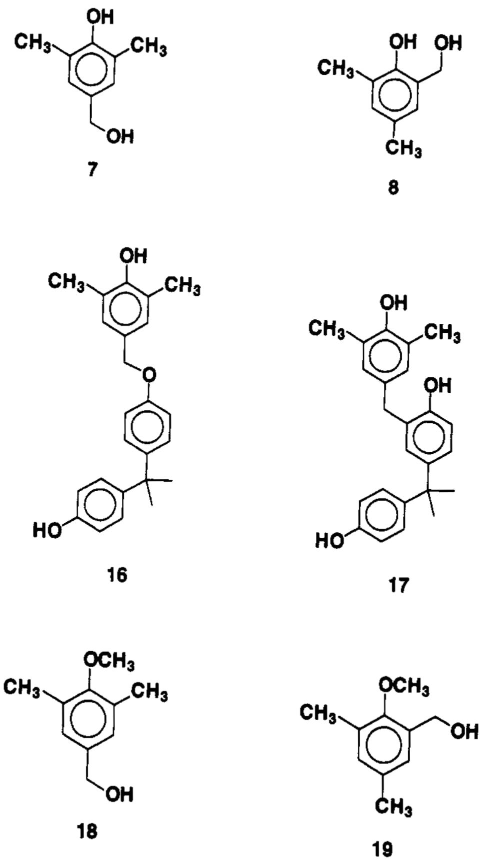
Scheme 2



principle, the methylene resonance of the benzylic alcohol group in the cross-linker molecule can be used as a probe to monitor the cross-linking reaction that occurs upon irradiation of the solid film. Chemical changes affecting the cross-linker molecule can be detected by changes in the chemical shift and quantified by integration data for the methylene signal. In practice, however, this study is complicated by the fact that the resist is insolubilized after irradiation and postbaking, making a study by solution phase NMR impossible. To solve this problem, model compounds 7 and 8 (Scheme 2) that carry a single benzylic alcohol group were used in model studies.

Because the two hydroxymethyl groups on cross-linker 1 might have different reactivities, the two isomeric model compounds 7 and 8 were examined. The observation that cross-linkers 1 and 2 give similar resist sensitivities only implies that the hydroxymethyl group in the 4-position is at least as reactive as that in the 2-position. It is however possible that the 4-hydroxymethyl group is more reactive than the 2-hydroxymethyl group, its effect being simply masked in the two-step cross-linking process by the slower reaction of the latter.

Poss *et al.* have shown that in an aqueous solution of ascorbic acid, the acid-catalyzed substitution reactions of 2- and 4-hydroxybenzyl alcohols possibly proceed via protonated quinone methide intermediates. The higher reactivity of 4-hydroxybenzyl alcohol is attributed to the higher stability of the *p*-quinone methide intermediate in comparison to the *o*-substituted counterpart.[5,6]

Any finding of higher reactivity for model compound 7 when compared to 8 could be exploited in the design of materials with unprecedented sensitivities using cross-linkers, such as 9, that possess two such groups.

Experimental Section

Instrumentation. Resist film thickness was measured with a Tencor Alpha-Step 200 surface profiler. ^{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. Differential scanning calorimetry was done on a Mettler DSC 30 instrument. Size-exclusion chromatography was carried out with THF as solvent on a Waters 590 chromatograph connected to a Waters 410 differential refractometer and a Wyatt Technology Dawn F laser photometer; data analysis was performed with Astra 202 software (Wyatts Technology). Deep-UV exposures were done with a medium-pressure mercury arc lamp through a 254-nm interference filter.

Materials. The preparation of cross-linkers 1 and 2 are reported in the preceding paper.[1] Model compound 7 was prepared by the method of Massy and McKillop.[7] Hydroxymethylation of 2,4-dimethylphenol according to the literature procedure gives compound 8.[8] Phenols 7 and 8 are methylated with iodomethane to afford compounds 18 and 19.[1] 4,4′-[Oxybis(methylene)]bis(2,6-dimethylphenol) (10) and 2,2′-[oxybis(methylene)]bis(4,6-dimethylphenol) (13) were prepared from the condensation reactions of 7 and 8, respectively.[9]

Sample Solution Preparation and Processing. Poly(4-hydroxystyrene) (83 mol %), the hydroxymethylated phenol (14 mol %) and triphenylsulfonium hexafluoroantimonate (3 mol %) were dissolved in diglyme and filtered through a 0.45-μm filter. The solution was spin-coated onto silicon wafers, followed by prebaking at 110 °C for 2 min to give 1.0 ± 0.05 μm films. The exposed samples were postbaked at 120 °C for 3 min. The sample films were then dissolved in deuterated acetone and the ^{1}H NMR spectra recorded. A known amount of triphenylmethane was added as an internal standard for comparison of peak areas.

Results and Discussion

Two different test solutions were prepared with benzylic alcohols 7 and 8. The relative molar concentrations of the individual components are similar to those in actual resist formulations. A control experiment was first carried out by spin-coating each of the two solutions onto a silicon wafer, followed by heating at 110 °C for 2 min and then 120 °C for 3 min to mimic the prebaking and postbaking steps in resist processing. Figure 1 shows the spectrum obtained with 7. New ^{1}H NMR resonance peaks are observed at 4.35 and 4.65 ppm, about 0.2 ppm upfield from that of the benzylic methylene protons of the starting materials, 7 and 8, respectively. This is accompanied by a decrease in the amount of starting material (Figure 1b) that is consumed in the reaction, as well as some evaporation of the benzylic alcohol. On exposure to radiation, there is a further decrease in the amount of starting material. In addition, two broad peaks are observed near 4.9 and 3.7 ppm (Figure 1c).

Identification of Reaction Intermediates. The methylene protons in 7 are labeled *7*. Peak *10* corresponds to the methylene protons in dibenzyl ether 10 formed by self-condensation of benzyl alcohol 7 (Scheme 3). It appears as a sharp singlet and the assignment is confirmed by comparison with an authentic sample of 10. A similar condensation reaction has been reported for various diphenylcarbinols.[10]

The broadness of peaks *11* and *12* suggests that these protons are part of a polymer system. This implies that the benzylic alcohol molecule has been bound to the poly(4-hydroxystyrene) polymer. Therefore, peak *11* is at-

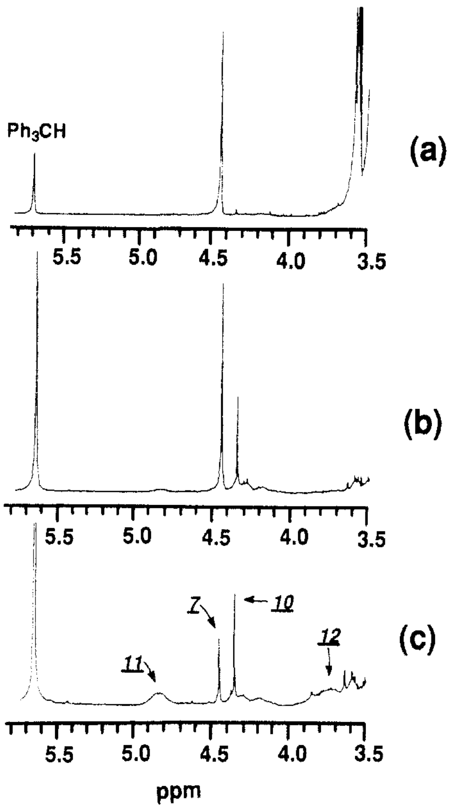
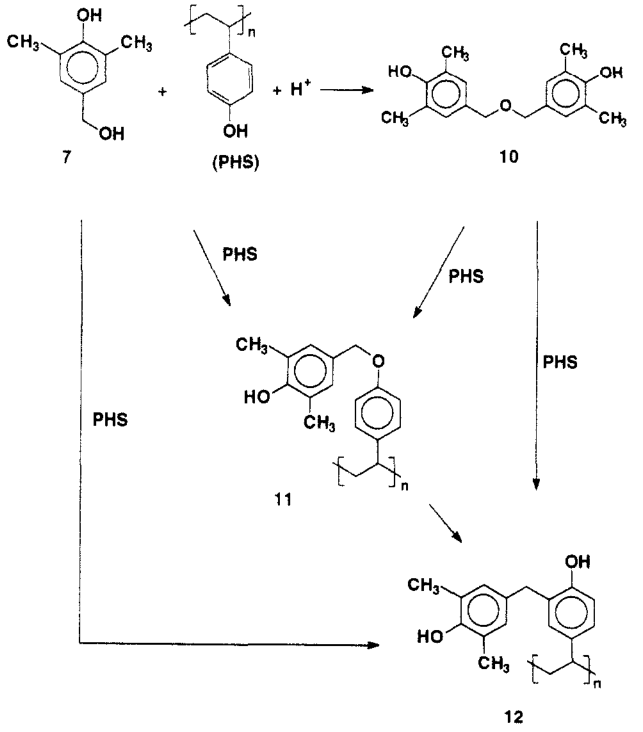


Figure 1. ^{1}H NMR spectra of model study with 7: (a) unheated sample, (b) sample heated at 110 °C for 2 min and then 120 °C for 3 min, (c) sample heated at 110 °C for 2 min, exposed to 0.55 mJ/cm^2 at 254 nm, and then 120 °C for 3 min.

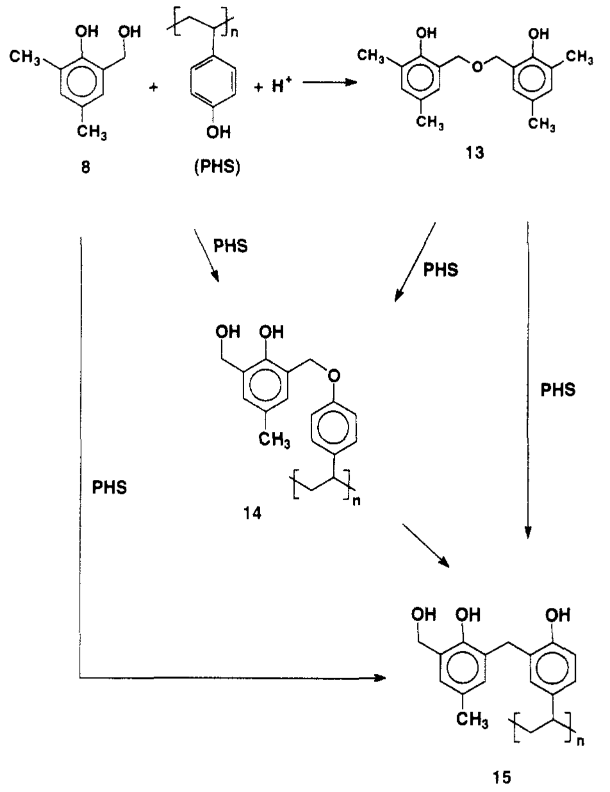
Scheme 3



tributed to the methylene protons in the *O*-alkylation product 11; whereas 12 is from the product of *C*-alkylation, 12. The *O*-alkylation product 11 is known to undergo acid-catalyzed rearrangement to the *C*-alkylation product 12 (Scheme 3).[11]

The reactivity of an authentic sample of dibenzyl ether 10 with poly(4-hydroxystyrene) under the resist processing conditions was examined. Upon exposure to radiation, formation of both the *O*- and *C*-alkylation products 11 and 12 is observed in the ^{1}H NMR spectrum. This confirms that dibenzyl ether 10 is a possible intermediate in the reaction of phenolic benzyl alcohol 7 with poly(4-hydroxystyrene). Analogous results are obtained with compound 8 (Scheme 4).

Scheme 4



Sensitivity and Thermal Stability of the Resists. Careful inspection of the experimental results reveals that, in addition to the dibenzyl ethers 10 and 13, small amounts of the *O*-alkylation products 11 (Figure 1b) and 14 are also formed upon heating of the samples even in the absence of exposure to radiation. To verify this occurrence, sample solutions of similar compositions were prepared with bisphenol A, instead of poly(4-hydroxystyrene), triphenylsulfonium hexafluoroantimonate, and 7 (or 8). The sample solutions were spin-coated onto silicon wafers, heated at 110 °C for 2 min, and then analyzed by ^{1}H NMR. In this way, the formation of any substitution reaction product can be easily observed without the signal broadening resulting from polymer attachment. For model compound 8, only trace amounts of *O*- and *C*-alkylation products are observed in the heated sample. There is no sign of any dibenzyl ether formation. In the case of 7 (Figure 2), significant quantities of *O*- and *C*-alkylation products 16 and 17 (Scheme 2) are formed after baking. It is apparent that, upon heating, 7 is more reactive than 8 toward substitution reaction.

To check whether or not similar thermal reactions happen in the resist, sample solutions of cross-linkers 1 or 2, bisphenol A, and the onium salt were made and tested. For both 1 and 2, formation of the dibenzyl ethers, as well as the *O*- and *C*-alkylation products, are observed. The extent of reaction is much higher for 1 than for 2 (Figure 3). These model experiments with bisphenol A show clearly that some thermal cross-linking occurs in the resists during the baking stages. Kajita *et al.* have also examined the use of cross-linker 2 in negative-tone resist formulation and concluded that it is thermally cross-linkable with poly-

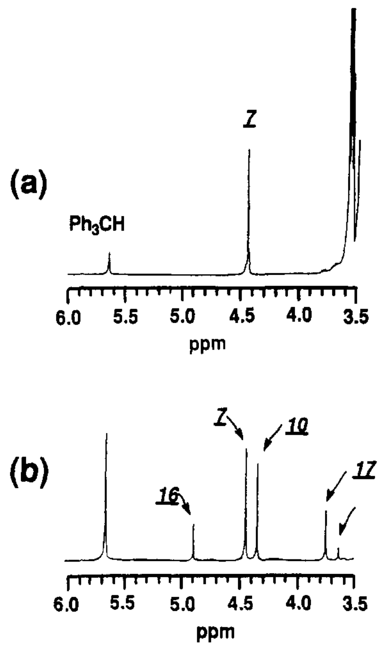


Figure 2. ^{1}H NMR spectra of model study with 7 and bisphenol A: (a) unheated sample, (b) sample heated at 110 °C for 2 min and then 120 °C for 3 min.

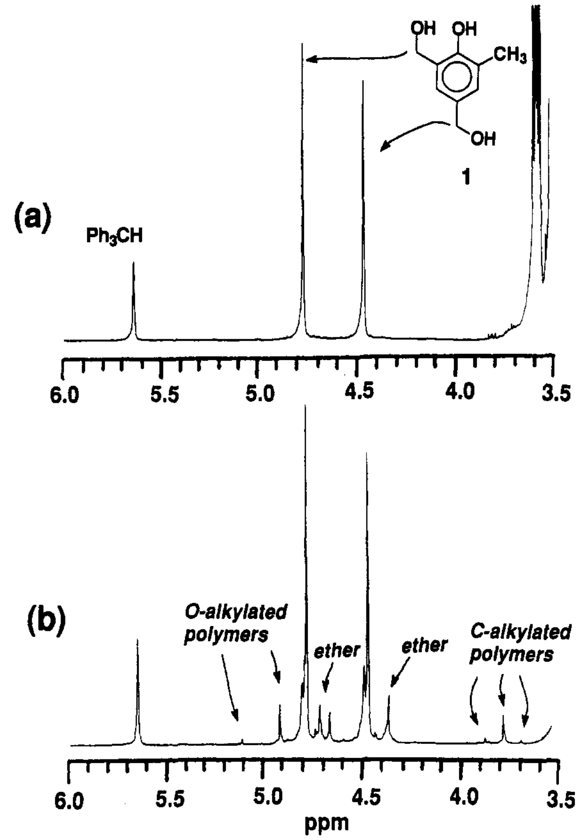


Figure 3. ^{1}H NMR spectra of model study with 1 and bisphenol A: (a) unheated sample, (b) sample heated at 110 °C for 2 min and then 120 °C for 3 min.

(4-hydroxystyrene) at high temperatures.[12] The observation that model compound 7 is much more reactive than 8 suggests that a hydroxymethyl group located at the 4-position relative to the phenolic hydroxyl group is more reactive thermally than one at the 2-position.

Even more convincing evidence of this background thermal cross-linking is provided by gel-permeation chromatography (GPC) analysis of a heated resist sample consisting of cross-linker 1 with poly(4-hydroxystyrene) and the onium salt. The analysis with a light-scattering detector, which is more sensitive toward high molecular weight fractions of a polymer than a refractive index detector, reveals the formation of a small amount of high molecular weight polymer covering a broad range of molecular weights. In contrast, analysis with a refractive index detector shows little change for the heated sample. This suggests that the thermal cross-linking process does not proceed uniformly throughout the resist but only leads to the formation of a small amount of high molecular weight material, while the rest of the polymer is still largely unchanged.

Experiments have shown that, for resists formulated with cross-linkers 1 and 2, the sensitivities are unaffected by variations in the postbaking temperatures (80–115 °C) (Table 1). This finding is unusual since the thermal step provides the activation energy that is required for actual electrophilic cross-linking. However, this behavior may be readily explained by consideration of the slow, purely thermal, cross-linking that occurs upon heating. An increase in the postbaking temperature increases the rate for the acid-catalyzed cross-linking reaction, as well as the uncatalyzed thermal cross-linking reaction. Because the two reactions appear to be accelerated to a roughly similar extent by increases in postbaking temperature, there is no net gain in the contrast between the exposed and unexposed resist regions. As a result, raising the postbaking temperature does not lead to a measurable improvement in the resist sensitivity.

As mentioned in the introduction, copolymer 6, in which the benzylic alcohol group is attached to the polymer, affords a less sensitive imaging material than a physical mixture of poly(4-hydroxystyrene) and cross-linker 2. This finding can also be rationalized by considering the purely thermal cross-linking of the resist. GPC measurements have confirmed the formation of a small amount of extremely high molecular weight material in the polymer matrix after the resist film was subjected to the prebaking and postbaking processes. A comparison to the GPC data of a similarly processed physical mixture of poly(4-hydroxystyrene) and 1 (or 2) reveals that copolymer 6 is much more prone to thermal cross-linking. This lower thermal stability of copolymer 6 results in less differentiation between the thermal- and acid-catalyzed cross-linking reaction rates, which ultimately translates into lower resist sensitivity for copolymer 6.

Relative Reactivities of the Various Cross-Linkers. Resist samples of model compounds 7, 8, 18, and 19 were irradiated at 254 nm with exposure dosages ranging from 0 to 1 mJ/cm^2. The exposed samples were then heated at 120 °C for 3 min and the resulting materials were analyzed by ^{1}H NMR spectroscopy. Since accurate measurements of the peak areas under the broad polymer signals are difficult, the amount of alkylated polymer formed, x, is estimated using the following formula: $x = [1 - (\text{relative amount of benzyl alcohol}) - (\text{relative amount of dibenzyl ether})]$. (Results for 7 and 8 are shown in Figures 4 and 5.)

The reactivities of different cross-linkers can be compared by estimating, $E_{1/2}$, the exposure dosage required for half of the starting amount of the benzylic alcohol to react (Table 2). The results obtained for model compounds 18 and 19, compared to 7 and 8, suggest that the methoxy group is less activating than the hydroxyl group in electrophilic aromatic substitution reactions. This is consistent with the fact that the hydroxyl group has a more negative σ_p^+ value than the methoxy group in the

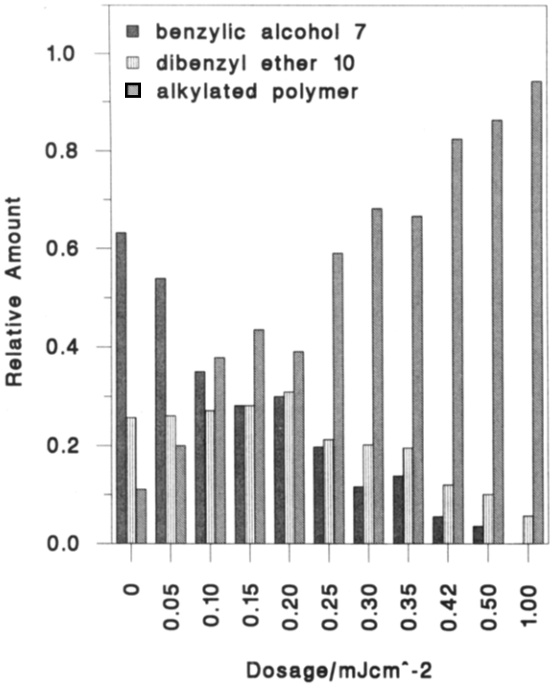


Figure 4. Compositions of the resist formulated with model compound **7** at different exposure dosages.

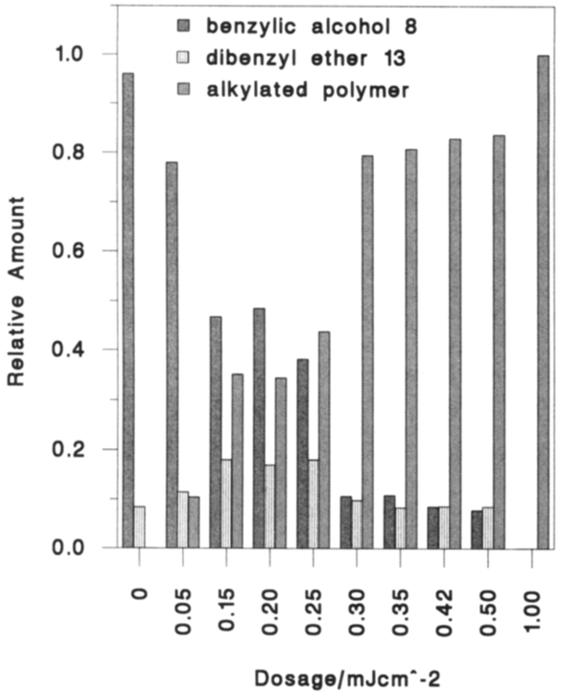


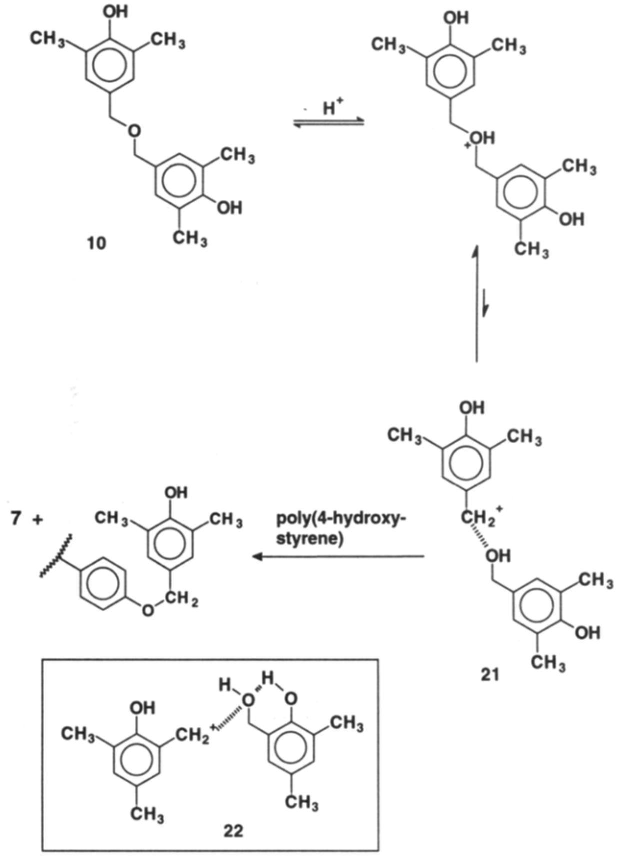
Figure 5. Compositions of the resist formulated with model compound **8** at different exposure dosages.

Table 2. Comparison of Cross-Linking Group Reactivities in Substitution Reactions with Poly(4-hydroxystyrene) in the Presence of Photogenerated Triphenylsulfonium Hexafluoroantimonic Acid

benzylic alcohol	$E_{1/2}$,[a] mJ/cm^2	benzylic alcohol	$E_{1/2}$,[a] mJ/cm^2
7	0.2	**13**	0.7
8	0.2	**18**	0.3
10	1.9	**19**	0.3

[a] $E_{1/2}$ is the exposure dosage estimated for 50% of the benzylic alcohol to react, based on analyses of sample compositions with ^{1}H NMR spectroscopy. Following the irradiation, all samples were heated at 120 °C for 3 min.

Scheme 5



Hammett equation.[13,14] Therefore, compound **20** should be less efficient than **2** in cross-linking the polymer. This is in good agreement with the imaging experiments because resists formulated and processed similarly with **2** and **20** have deep-UV sensitivities of 0.2 and 0.4 mJ/cm^2, respectively.

As mentioned above, the dibenzyl ethers **10** and **13** are possible intermediates in the reactions of the benzyl alcohols **7** and **8** with poly(4-hydroxystyrene). The data in Table 2 indicates that, under similar experimental conditions, the dibenzyl ethers **10** and **13** are much less reactive than the benzyl alcohols **7** and **8**. The slow reaction rates for the disappearance of **10** and **13**, indicated by $E_{1/2}$ values of 1.9 and 0.7, respectively (Table 2), would require significant amounts of **10** and **13** to be present at all exposure dosages shown in Figures 4 and 5. Clearly, this is not the case for exposure dosages greater than 0.4 mJ/cm^2, where the amounts of dibenzyl ethers are less than 10%. Therefore, at high exposure dosage (>0.4 mJ/cm^2) the dominant reaction pathway for the conversion of benzyl alcohols **7** and **8** to the alkylated polymers does not involve dibenzyl ethers as intermediates.

A possible explanation for the significantly lower reactivity of the dibenzyl ethers **10** and **13** relative to the benzyl alcohols **7** and **8** is that, following the heterolytic bond cleavage of the protonated ethers, recombination of the two fragments occurs. Scheme 5 shows the proposed recombination pathway for **10**. This recombination is favored over the reaction with the phenolic moiety of the polymer matrix due to the higher nucleophilicity of alcoholic fragments in comparison to the phenolic polymer.

In the case of dibenzyl ether **13**, reaction would proceed through intermediate **22**, in which the newly-formed benzylic hydroxyl group can hydrogen bond intramolecularly to the phenolic hydroxyl group. As a result, the nucleophilicity of the alcohol would be reduced and recombination with the carbocation would be less favorable compared to intermediate **21** derived from **10**. Therefore, dibenzyl ether **13** should react with the phenolic polymer significantly faster than **10**, as is indeed observed (Table 2).

Although a similar recombination could occur in the fragmentation of protonated benzyl alcohols **7** and **8**, several factors make this recombination unlikely. First of all, in the fragmentation of **7** and **8**, water and not an alcohol, as in the case of **10** and **13**, is the leaving group. Water, which has been shown to be a weaker nucleophile toward carbocation in acetonitrile than primary alcohols,[15] does not compete as readily with the phenolic polymer for the cationic site. Furthermore, the removal of water by evaporation during the postbaking process and diffusion of the small water molecule, in comparison to the large alcohol, away from the cationic site allow polymer alkylation to become the dominant reaction process. Therefore, benzyl alcohols **7** and **8** are expected to be more reactive, under acid-catalyzed conditions, than dibenzyl ethers **10** and **13** toward poly(4-hydroxystyrene).

The Mechanisms of the Substitution Reactions. As reflected by their large $E_{1/2}$ values (Table 2), the conversion of dibenzyl ethers **10** and **13** into the alkylated polymers is a very slow process; therefore, it can be assumed that in experiments conducted with exposure dosages of less than 1.0 mJ/cm^2, the amounts of **10** and **13** detected by ^{1}H NMR should roughly reflect their total formation during the course of the reactions. The exposure dosage is assumed to be directly proportional to the amount of acid generated in the sample. In the absence of exposure to light, the thermal reaction alone occurs to afford the dibenzyl ethers **10** and **13** and much smaller amounts of the alkylated polymers (Figures 4 and 5). When the samples are exposed to low deep-UV dosages of up to about 0.25 mJ/cm^2, comparable amounts of alkylated polymers and dibenzyl ethers are formed (Figures 4 and 5). Compared to the unexposed samples, these only show slight increases in the amounts of dibenzyl ethers formed. Therefore, acid catalyzes mainly the formation of the alkylated polymers and, to a smaller extent, the dibenzyl ethers. At exposure dosages above 0.25 mJ/cm^2, i.e., at higher acid concentrations, the alkylated polymers become the dominant products in the reactions of **7** and **8** and the formation of dibenzyl ethers **10** and **13** decreases, at least in comparison to the amounts of dibenzyl ethers produced in the absence of acid during the exclusively thermal reaction. This observation suggests that, at high acid concentration, the acid-catalyzed substitution reaction of **7** (or **8**) with poly(4-hydroxystyrene) dominates over the competing thermal reaction.

Two different mechanisms are proposed for the thermal and the acid-catalyzed reactions that occur in the resists. Scheme 6 shows the reactions for **7**. The thermal reaction is proposed to proceed via the unprotonated quinone methide **23**, which reacts selectively with another molecule of benzylic alcohol **7** rather than the phenolic polymer (due to the higher nucleophilicity of benzylic alcohols in comparison to phenols) to form the dibenzyl ether **10**. This is consistent with the observation that **7** is much more reactive in the thermal reaction than **8** (Figures 4 and 5), as the *p*-quinone methide **23** is expected to have higher stability than the *o*-quinone methide **24** derived from **8**.[5,6] Under acid catalysis, however, the reaction of benzylic alcohols is more likely to involve carbocationic species that are more reactive, and hence less selective, toward nucleophiles. Therefore, the poly(4-hydroxystyrene) polymer, present in much higher concentration, can compete with the benzyl alcohol itself in its reaction with the carbocation, and dibenzyl ether production is suppressed. Again, the intermediacy of carbocations, instead of quinone methides, in the acid-catalyzed reactions of **7** and **8** is supported by the finding that, in the presence of the photogenerated acid, **7** and **8** appear to have similar reactivities. The similar reactivities are expected because benzyl alcohols **7** and **8** should form carbocations of similar stabilities. Therefore, for exposure dosages of ca. 0.2 mJ/cm^2, a dose that corresponds to the sensitivity of the actual resist, the amount of alkylated polymer formed in the two systems are similar.

Scheme 6

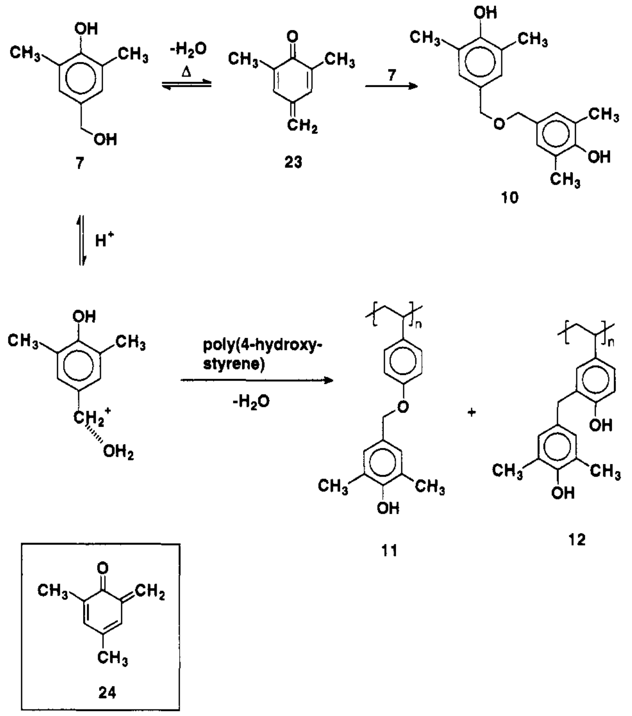


Table 3. Comparison of Dibenzyl Ether Formation at Different Concentrations of Model Compound 8

relative mole percentage of 8 (vs PHS)	relative amount of dibenzyl ether 13	
	after 0.1 mJ/cm^2	after 0.2 mJ/cm^2
0.082	0.08	0.08
0.166	0.14	0.16
0.330	0.23	0.28

Influence of the Formation of Dibenzyl Ether on Resist Sensitivity. Since dibenzyl ethers **10** and **13** are much less reactive than the benzylic alcohols, their formation is expected to slow down the cross-linking process. As mentioned in the introduction, the resist sensitivity is not affected by its content of cross-linker **1**. Because this finding is unusual, a test solution with a lower relative concentration of compound **8** was prepared and used in ^{1}H NMR model studies to help understand this behavior. These experiments show that a significantly smaller amount of dibenzyl ether **13** is formed when a lower relative concentration of **8** is present (Table 3). Therefore, the sensitivity is not affected by changes in the concentration of **8** since a higher initial concentration of the cross-linker is offset by the increased formation of the unreactive dibenzyl ether.

In addition to their lower reactivity, the dibenzyl ethers are expected to slow down the dissolution of the polymer matrix since they are less polar than the cross-linkers, the hydroxymethylated phenols.[10] This, in turn, reduces the differences in solubilities between the exposed and unexposed areas of the resist and leads to lower resist sensitivity.

Conclusion

Mechanistic studies with ^{1}H NMR spectroscopy have provided a more complete understanding of the thermal- and acid-catalyzed substitution reactions between the cross-linker molecule **1** or **2** and poly(4-hydroxystyrene). The thermal- and acid-catalyzed reactions are proposed to have quinone methides and carbocationic structures as intermediates, respectively. Because of the higher energy barrier to form the *o*-quinone methide intermediate in the thermal reaction, model compound **8** provides greater thermal stability than **7** during resist processing. On the other hand, as the activation energies for the formation of the carbocationic intermediates are similar, compounds **7** and **8** exhibit similar reactivities in radiation-promoted acid-catalyzed substitution reactions occurring in the solid polymer coating.

Several intriguing features of this class of resists, namely the lack of dependence of resist sensitivity on postexposure bake temperature and the relative lack of importance of cross-linker concentration, can be rationalized on the basis of the proposed mechanisms. The technique has also been applied to compare the reactivities of different cross-linker molecules based on benzylic alcohols.

This study and the preceding article have provided valuable insight into the photoinitiated cross-linking of phenolic polymer by alkylation reactions. It confirms that the stability of the carbocation intermediate governs the efficiency of a cross-linker based on electrophilic addition reactions to poly(4-hydroxystyrene). The study also points out the need to consider thermal stability when designing cross-linkers of ever-increasing reactivities. A deficiency in the thermal stability of one or more of the resist components can result in thermal background cross-linking. This reduces the solubility of the unexposed resist in the developer and leads to a loss of effective resist sensitivity. These factors must be addressed in the design of future resist materials. For example, one may investigate the use of a free radical scavenger[16] as an additional resist component to suppress the thermal cross-linking process.

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