Design of Polymeric Imaging Materials Based on Electrophilic Aromatic Substitution: Model Studies

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ABSTRACT: Model experiments have been used to study the cross-linking reactions that are operative in a new negative-tone resist system based on photoacid-catalyzed electrophilic aromatic substitution of copolymers containing benzyl acetate pendant groups. NMR monitoring of the formation of diphenylmethane units in the acid-catalyzed reaction of various benzyl acetates with themselves and with activated aromatic compounds such as 4-isopropylphenol gave insight into the cross-linking reaction. The influence of the leaving group, stabilizing substituents, and nucleophile on the overall process and the possible formation of O-alkylated products or intermediates were studied.

Introduction

We have recently described several families of extremely sensitive chemically amplified resist materials that operate on the basis of photoinduced changes in side-chain polarity[1,2] or multiple main-chain cleavage processes.[3-5] Another important class of resists that received much attention involves polymers that cross-link upon irradiation.[6-8] Cross-linking systems generally have limited resolution due to image distortion that results from swelling during the solvent development step.

Our recent work has focused on the design of polymers that undergo efficient radiation-induced cross-linking yet are free of resolution loss due to swelling[9] during development. One design includes an acid-catalyzed electrophilic aromatic substitution as the key cross-linking reaction. Electrophilic aromatic substitution is attractive in the context of resist design as it has the potential to lead to chemically amplified systems with high sensitivity. The chemical amplification results from the fact that the reaction is acid catalyzed. Acid is consumed in the initiation of the reaction but it is regenerated in the subsequent substitution step.

This paper describes a series of model studies that have provided information that guided the resist design, while the following paper in this issue focuses on the application of this information to the design of a practical resist system.

While solution studies cannot fully represent the processes that occur in glassy polymers as they are used in resist applications, they do offer valuable insight into key elements of the various steps of the reactions that are involved. Therefore a series of model studies was carried out involving monitoring of the electrophilic aromatic substitution reaction between benzyl acetates and phenols in solution with NMR.

Electrophilic aromatic substitution reactions between benzyl derivatives and aromatic nucleophiles have been studied extensively.[10] In particular, thorough studies by Olah,[11-14] Brown,[15,16] and DeHaan[17] and their co-workers have provided valuable information on many facets of the mechanism of the reaction in different solvents and in the presence of a variety of Lewis acid catalysts such as $AlCl_3$, $SnCl_4$, $TiCl_4$, and $SbCl_5$.[11,13,14] General consensus exists regarding both the experimental difficulties associated with obtaining reproducible and meaningful reaction rate data[13] and regarding the apparent complexity of the reaction mechanisms.[11,17] In particular, the nature of the transition state was found to change with the substitution on the benzyl derivatives.[12,13] Reaction orders reported for the Lewis acid catalysts varied between one[13] and two to three,[17] and reaction orders for the electrophilic benzyl derivative and the aromatic nucleophile were reported to be either zero[17] or one.[13]

Our model studies were not designed primarily to contribute further to the understanding of the mechanisms of the electrophilic aromatic substitution reaction in solution. Rather, the solution reactions were used as simplified models of the solid-state reactions crucial to resist function. Another significant issue that demanded this study was the fact that the most practical materials that produce acid upon hydrolysis are those that afford Brönsted rather than Lewis acids, and, in the resist applications, the acid is produced in a concentration of 10 mol % or below.

These studies were thus focused on the chemical reactions that are responsible for image formation in the practical system. They were designed to determine the rate-limiting step and relative reaction rates as a function of variation in the structure of the reactants. It should be pointed out that relative reaction rates obtained for different model compounds in solution may not reflect the solid-state imaging sensitivities of the corresponding polymers. The higher concentrations but lower mobilities characteristic of the solid state may affect reaction pathways and thus reaction rates. Nevertheless, we can expect structurally similar reactants to show similar relative rates in solution as in solid state, to the extent that the rate-limiting step remains the same in both cases.

Experimental Section

General. The NMR studies were carried out in 5- and 10-mm-o.d. NMR tubes using deuteriochloroform as the solvent. An IBM/Bruker AF-300 NMR spectrometer operating at 300.13-MHz proton frequency was used. The concentrations of all model compounds were 0.2 M unless stated otherwise. Neat trifluoromethanesulfonic (triflic) acid (10 mol %) was added by syringe directly into the NMR tubes containing mixtures of the reactants. Triflic acid is immiscible with chloroform and was therefore added last so that it could be solubilized by coordination to the acetates and the phenol. All reaction mixtures were homogeneous. Since triflic acid reacts with tetramethylsilane (TMS), the residual

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signal from nondeuterated chloroform at 7.26 ppm relative to TMS was used as a chemical shift reference. ^{13}C NMR chemical shifts were measured relative to $CDCl_3$ at 77.0 ppm. Chemical shifts are reported in parts per million relative to TMS. Reactions were run at room temperature (22 °C) unless stated otherwise.

Reaction progress or conversion was measured by integration of the ^{1}H NMR signal areas from starting materials and products. In reactions of benzyl acetates, for example, the conversion of acetate methyl (2.1 ppm) to acetic methyl (2.2 ppm) was monitored as was the conversion of the acetate methylene protons (5.1 ppm) to diarylmethylene protons (3.6-4.1 ppm). The values reported for the reactant half-lives are averages of two or three experiments.

Deuteriochloroform was dried over molecular sieves prior to use. Benzyl acetate, α-methylbenzyl acetate, 2-methylfuran, 2-furfurylacetate, and trifluoromethanesulfonic acid were used as obtained from Aldrich. 4-Isopropylphenol (Aldrich) was distilled in vacuo prior to use.

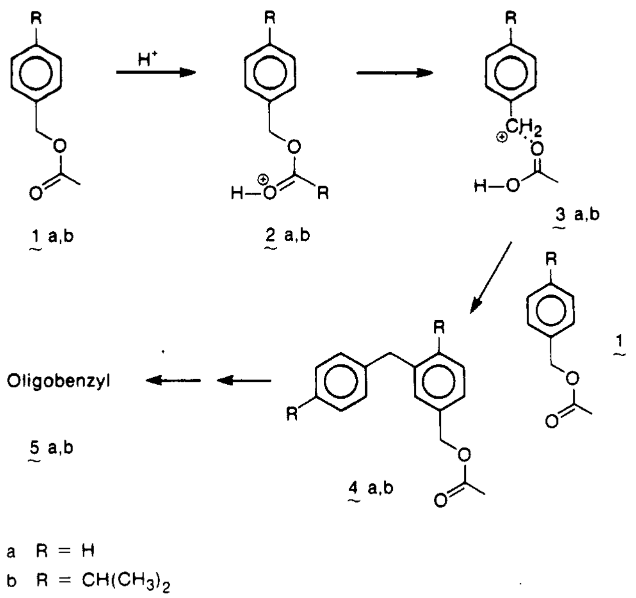
Synthesis. 4-Isopropylbenzyl acetate (1b) was prepared by stirring 4-isopropylbenzyl alcohol (9.01 g, 0.06 mol) with acetyl chloride (6.28 g, 0.08 mol) and anhydrous potassium carbonate (28.0 g, 0.2 mol) in 150 mL of 1,2-dimethoxyethane overnight. An additional 4 mL of acetyl chloride was then added and the reaction mixture was stirred for 6 days. Following filtration and solvent evaporation, the residue was taken up in methylene chloride (50 mL) and the organic phase was washed once with saturated sodium chloride and dried over anhydrous magnesium sulfate. After solvent evaporation, vacuum distillation (0.25 mbar, 75 °C) gave 7.1 g of 4-isopropylbenzyl acetate (62% yield). ^{1}H NMR: 7.29 (dd, aromatic); 5.11 (CH_2O); 2.95, 1.28 (isopropyl). ^{13}C NMR: 170.8 (carbonyl); 148.9, 133.2 (quaternary aromatic); 128.4, 126.5 (CH, aromatic); 66.1 (CH_2O); 33.8, 23.8 (isopropyl); 20.9 (CH_3).

4-Methoxybenzyl Acetate.[18] 4-Methoxybenzyl alcohol (0.05 mol, 6.91 g) was stirred with excess acetic anhydride (65 mL, 0.5 mol) at room temperature for 48 h. Acetic acid and acetic anhydride were evaporated under vacuum, and the oily residue was dissolved in 150 mL of diethyl ether. The ether solution was washed twice with 10% potassium carbonate and once with saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate and filtered and the solvent evaporated to give 8.4 g of clear oily product. Yield: 93%. ^{1}H NMR: 7.27, 6.90 (dd, aromatic); 5.03 (CH_2); 3.81 (OCH_3); 2.08 (CH_3). ^{13}C NMR: 159.59, 128.02 (quaternary atomatic); 130.05, 113.88 (CH aromtic); 66.04 (CH_2O); 55.19 (OCH_3); 20.97 (CH_3).

4-Isopropylphenyl Benzyl Ether (10). This compound was prepared by a modification of the procedure of Lenz and Patel.[19] Benzyl chloride (12.66 g, 0.1 mol), 4-isopropylphenol (14.3 g, 0.105 mol), and anhydrous potassium carbonate (27.6 g, 0.2 mol) in 200 mL of dry acetone were stirred under nitrogen for 5 days. The reaction mixture was cooled and filtered and the solvent evaporated. The oily residue was dissolved in 50 mL of methylene chloride and washed twice with 40 mL of 10% aqueous sodium hydroxide, twice with distilled water, and twice with saturated sodium chloride. After it was dried over magnesium sulfate, the solvent was evaporated. Vacuum distillation (0.1 mbar, 120 °C) (ref) gave 15.0 g of 4-isopropylphenyl benzyl ether. Yield: 66%. Mp: 30 °C. ^{1}H NMR: 7.3–7.5 (phenyl); 6.9–7.25 (aromatic); 5.07 (CH_2O); 2.95, 1.28 (isopropyl). ^{13}C NMR: 127.85, 128.53, 127.25, 137.25 (benzyl aromatic); 141.30, 127.47, 114.58, 156.88 (phenyl aromatic); 70.01 (CH_2O); 33.26, 24.19 (CH, CH_3; isopropyl).

Benzyl Tosylate.[20] Benzyl alcohol (5.41 g, 0.05 mol) in 60 mL of dry diethyl ether was refluxed with sodium hydride (1.32 g, 0.055 mol) overnight under nitrogen. After the mixture was cooled to −20 °C, 18-crown-6 (0.66 g, 0.0025 mol) was added followed by a solution of tosyl chloride (9.53 g, 0.05 mol) in 40 mL of dry diethyl ether. The mixture was stirred at −20 °C for 2.5 h and then allowed to warm to room temperature while stirring. The solution was filtered under nitrogen and the volume reduced to 30 mL. Upon cooling to −78 °C, the product precipitated and was quickly filtered. Yield: 74% prior to recrystallization from *n*-hexane. Mp: 62 °C (lit.[20] 58 °C). ^{1}H NMR: 7.80, 7.34 (dd, 4 H); 7.32, 7.2 (m, 5 H); 5.05 (s, 2 H); 2.44 (s, 3 H). ^{13}C NMR: 144.8, 133.2 (quaternary aromatic); 129.8, 129.0, 128.6, 128.5, 127.9 (CH aromatic); 71.7 (CH_2); 21.6 (CH_3).

Scheme I



Results and Discussion

The simplest model reaction studied was the self-condensation of benzyl acetate in the presence of strong acid. The overall process results in the formation of diarylmethylene linkages and may be envisioned as shown in Scheme I. In an actual imaging system the protons that initiate the reaction are generated by photolysis of a compound such as triarylsulfonium triflate, which yields triflic acid. Hence, triflic acid[21] was chosen for our solution model experiments. The simple benzyl acetate moiety was selected for this study, as were analogues substituted with an isopropyl group in the para position to mimic the backbone of a styrene polymer. The reactions were most easily studied by monitoring the ^{1}H NMR signals of the benzylic methylene group, which originally appears as a sharp singlet at ca. 5.1 ppm. This resonance disappears during the reaction and is replaced by several signals around 3.9 ppm, characteristic of substituted diarylmethylenes. The acetate methyl signals provide convenient conversion markers as well.

The overall reaction rate depends on several factors including the nucleofugicity (or basicity) of the leaving group, the extent of stabilization of the positive charge developing on the benzyl carbon by electron-donating substituents on the ring,[22] and the nucleophilicity of the aromatic substrate.[23] The effect of these three variables on the conversion rate was studied by using corresponding model compounds. We followed the reactions from ca. 1% to ca. 90% conversion for all reactions, except that of benzyl acetate alone, and calculated the reactant half-life, $t(1/2)$. If reasonable care is taken to exclude moisture, reproducible half-lives were obtained.

Protonation of the benzyl acetate carbonyl ($pK_a = -6.5$) of **1a** (Scheme I) creates a cation **2a** with a neutral leaving group, acetic acid. Unimolecular heterolysis of the benzyl carbon–oxygen bond produces the very reactive benzyl cation–acetic acid complex **3a**. This reacts in turn with another molecule of benzyl acetate to afford the benzylic "dimer" **4a** and eventually, after subsequent reactions, the oligobenzyl species **5a**. The reaction proceeds slowly at room temperature under our standard conditions, with a reactant half-life of approximately 10^6 s (Table I, entry 1). The initial reaction products have narrow diarylmethylene resonances, indicative of the formation of several low molecular weight oligomers. At higher con-

Table I
Half-Lives of Different Benzyl Acetates under Standard Reaction Conditions

entry	benzyl derivative	[4-isopropyl-phenol], M	half-life, s
1	benzyl acetate	0	10^6 (±20%)
2	benzyl acetate	0.2	2×10^5 (±25%)
3	4-isopropylbenzyl acetate	0	4.5×10^4 (±25%)
4	4-isopropylbenzyl acetate	0.2	4×10^3 (±10%)
5	α-methylbenzyl acetate	0.2	8.5 (±15%)
6	α-methylbenzyl acetate	0.2	55 (±20%)
7	4-methoxybenzyl acetate	0	≤60

version, the diarylmethylene region shows only one broad peak with a longitudinal relaxation time, T_1, of 0.4 s, indicating moderate to high molecular weight species. The acid-catalyzed polymerization of benzyl halides and similar compounds is indeed known to give highly branched soluble polybenzyls.

In the analogous reaction of 4-isopropylbenzyl acetate (**1b**) with triflic acid (Table I, entry 3) the reaction takes place to give oligo(isopropylbenzyl) **5b**. The reactant half-life time (45 000 s) is 20 times shorter than that of the benzyl acetate. This is presumed to be due to the stabilization of the benzyl cation complex, or the transition state leading toward it, by the isopropyl substituent.[21,24]

As discussed in the following paper in this issue, polymeric resists often contain phenolic components to confer aqueous base solubility and to prevent swelling of the cross-linked material during solvent development. To mimic a styrene-based polymer, 4-isopropylphenol (**6**) was selected as a model for the phenolic component of the polymer. Therefore, the carbocation precursors benzyl acetate (**1a**) and 4-isopropylbenzyl acetate (**1b**) were allowed to react with triflic acid in the presence of an equimolar amount (0.2 M solution) of 4-isopropylphenol (Scheme II). In these reactions, the 4-isopropylphenol is by far the most reactive nucleophile present, due to the strongly activating hydroxyl group, and was therefore expected to be benzylated preferentially. The major products observed were indeed the corresponding 2-benzyl-4-isopropylphenols **8a,b** and the 2,6-dibenzyl-4-isopropylphenols **9a,b**. Furthermore, addition of an equimolar amount of 4-isopropylphenol causes respectively 5- and 10-fold reductions in reactant half-lives for benzyl acetate (**1a**) and 4-isopropylbenzyl acetate (**1b**) (Table I, entries 2 and 4 versus 1 and 3). This finding indicates involvement of the phenol in the bimolecular rate-determining step.

About 30% of low molecular weight oligobenzyl (**5**) is formed in the case of the reaction of **1a** with equimolar phenol. In contrast, the reaction of **1b** under the same conditions produces only about 10% of the corresponding oligobenzyl **5b**. This observation is consistent with the lower reactivity (greater selectivity) of the cationic intermediate derived from **1b**, which bears the electron-donating alkyl group. It is also in agreement with the results of competition studies of different para-substituted benzyl halides with anisole and toluene in the presence of Lewis acids.[11-13]

According to Katritzky and Brycki,[25] unimolecular and bimolecular mechanisms can proceed in parallel in electrophilic substitutions involving, as in our case, neutral leaving groups. The unimolecular process involves rate-determining formation of the very reactive benzyl cation–acetic acid complex **3a,b** in Scheme I, followed by rapid and nonselective reaction with any nucleophile present.

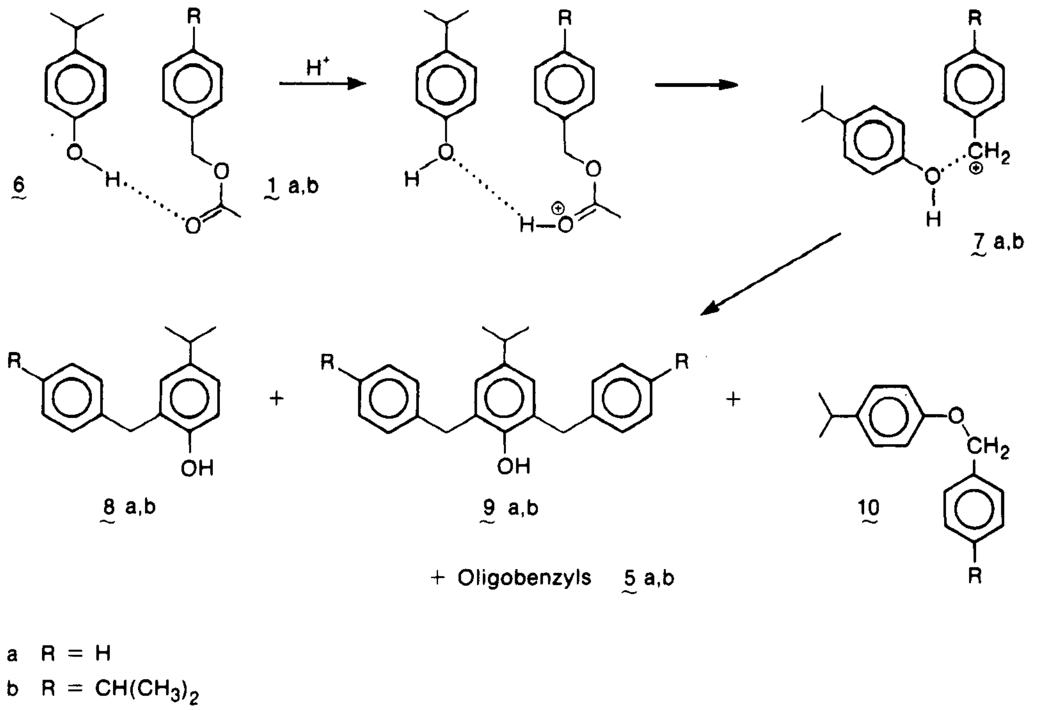
The bimolecular pathway apparently involves the phenolic substrate in the formation of the benzyl cation–acetic acid complex. It is this bimolecular pathway that is responsible for the rate increases observed in the reactions that include the phenols. IR measurements of solutions of benzyl acetates with phenols show strong hydrogen bonding between the phenol and the acetate carbonyl.[26] Studies of the solvolysis rates of trityl halides in the presence of phenols have further shown that the incipient trityl cations are stabilized by coordination to the phenol oxygen.[27] It then appears plausible that under our standard conditions, the benzyl acetates **1a,b** exist to a significant extent as complexes with 4-isopropylphenol. Upon protonation of the acetate carbonyl, the phenol is therefore available to stabilize the incipient benzyl cation by coordination through the phenolic oxygen (Scheme II, structures **7a,b**).

In fact, we observed small amounts (<10%) of benzyl 4-isopropylphenol ether **10** formation[10] during the reaction, indicating at least partial initial O-alkylation. The ether was detected by its characteristic methylene resonance at 5.05 ppm. At the end of the reaction, however, all of the ether had rearranged to the thermodynamically more stable C-benzylated phenols **8a** and **9a** shown in Scheme II. This observation is in agreement with reports of some initial O-substitution in Friedel–Crafts alkylation of phenols and anisoles, followed by rearrangement to the corresponding C-alkylated products,[28] and was confirmed by preparing 4-isopropylphenyl benzyl ether[10] and treating it with 10 mol % triflic acid, which resulted in complete conversion to C-benzylated phenols. This ether formation is of some potential significance as the insolubilization of a cross-linking resist is determined largely by the reactions that occur at very low degrees of conversion. The development and properties of potential photoresists based on this acid-catalyzed rearrangement of phenyl benzyl ethers is currently under active study.

The evidence presented above indicates that the rate-limiting step in the benzylation of phenols in our model systems is largely the formation of the benzyl cationic species in the unimolecular pathway and the approach to the related transition state in the corresponding bimolecular pathway, rather than the reaction of the cationic intermediate with the phenolic substrate. As a result, efforts to increase the solution reaction rate were next directed toward stabilizing the benzyl cationic species, rather than improving the nucleophile.

Stabilization of the Benzyl Cation. If formation of the benzyl cationic species is the rate-determining process, then any stabilization of these species will increase the overall reaction rate.[29] This stabilization can be achieved by substituting electron-donating substituents such as alkyl or methoxy groups either directly on the benzylic carbon[30,31] or on the aromatic ring.[9,16,28,31,32] The effect of alkyl substitution on the aromatic ring has already been demonstrated by the rate-enhancing effect of the 4-isopropyl substituent (Table I: entry 3 versus 1; entry 4 versus 2). Replacing one of the benzylic protons by a methyl group results in a dramatic reduction in the reactant half-life (from 10^6 s) to about 850 s (Table I, entry 7 versus 1). In the solution NMR studies, the α-methylbenzyl cation that was generated predominantly deprotonated to form a sytrene that subsequently oligomerized while little benzylation was observed. This reaction route (styrene formation) is not available with other substrates. Taken by itself, this result indicates only that introduction of the α-methyl group lowers the activation energy for elimination below that for substitution. On the other hand, in the presence of equimolar amounts of 4-isopropylphenol, the reaction proceeded still more rapidly to give ≥80% of the substitution product 1,1-diarylethane, with no styrene being observed (Table I, entry 6).

Scheme II



The 4-methoxy group (Table I, entry 7) provides the largest rate increase of the substituents tested, in accord with its superior electron-donating capacity.[11] Apparently, the 4-methoxybenzyl cation–acetic acid complex is not so stable as to become unreactive. However, structures incorporating 4-alkoxybenzyl acetate or the analogous 2-alkoxybenzyl acetates may not be easily incorporated into styrene-based polymers.

Furan Based Systems. Ultimately, stabilization of the benzyl cation by electron-donating substituents may actually slow down the overall process as the reaction of the more stabilized cation with the aromatic nucleophile may become rate limiting. In this case, further rate enhancement can be achieved by increasing the nucleophilicity of the substrate undergoing substitution. The furan ring system is more electron rich than the benzene ring, leading to electrophilic aromatic substitution reactions that are several orders of magnitude faster for analogous reactions. This suggests that use of furfuryl acetate should lead to both very fast formation of the furfuryl cation and very fast subsequent reaction with another furan ring.

However, the introduction of furan rings into these acid-catalyzed systems adds a further complication. The furan ring itself is sensitive to acid-catalyzed ring-opening polymerization. These reactions could compete with the intended cross-linking reactions. Water eliminated during these reactions could deactivate the photogenerated super acid and thus reduce the chemical amplification obtainable. For example, 2-methylfuran (0.2 M in $CDCl_3$) resinifies rapidly upon injection of 10 mol % triflic acid (entry 8, Table II). ^1H NMR spectra indicate 90% conversion after 60 s. Complete conversion was only reached after several hours. This increase in reaction rate could be caused by physical sequestering of the acid inside the precipitated resin. Alternatively the slowdown may indicate dehydration of furan, with concomitant quenching of the super acid.

In order to prevent the ring-opening reactions from interfering with acid-catalyzed cross-linking, one would have to provide for cross-linking reactions that are inherently faster than the ring-opening reactions themselves. This may be possible with systems incorporating furfuryl acetate groups. The furfuryl cation is significantly stabilized by the furan ring but still reacts very fast with other furan rings *by electrophilic aromatic substitution* in the 5-position or, to a lesser extent, the 3- and 4-positions. As in the case of the benzyl acetate systems, the furfuryl acetate serves both as the carbocation precursor and as the nucleophilic substrate.[33] Some model reactions of furfuryl acetate are listed in Table II.

Table II
Reaction of Furan Systems with Triflic Acid

entry	furan derivative	$t_{1/2}$,[a] s
8	2-methylfuran	≤60
9	furfuryl acetate	≤1
10	furfuryl acetate	≃5[b]

[a] The values given for $t_{1/2}$ are only upper limits. [b] 10 mol of triflic acid is added in the form of the triflic acid–ethyl acetate complex (triflic acid–ethyl acetate 1:5 in $CDCl_3$). General conditions are as described in Table I. In both reactions addition of triflic acid led to immediate darkening and precipitation of insoluble products.

Furfuryl acetate (Table II, entry 9) reacts immediately with triflic acid with precipitation of black insoluble products. The reaction is only slightly less rapid if, instead of neat triflic acid, the triflic acid–ethyl acetate complex is added to a solution of furfuryl acetate (Table II, entry 10). The significantly faster reactions of furfuryl acetate compared to that of 2-methylfuran are consistent with a rapid electrophilic aromatic substitution involving furfuryl cation intermediate species. These results make the furfuryl acetate group a promising carbocation precursor for future resist work. Practical realizations would involve either preparation of a polystyrene-bound furfuryl acetate or simply use of 2,5-bis(acetoxymethyl)furan as a low molecular weight cross-linker. Work along these lines with new copolymer systems is in progress.

Leaving Group Effects. An alternative approach to faster acid-catalyzed benzyl cation formation may involve using better leaving groups. Vogel[34] has reviewed the importance of the leaving group in the formation of benzyl cations. The most important criterion for good leaving groups in our case is low nucleophlicity. For closely related

Table III
Relation between the pK_a of the Leaving Group and the Reactant Half-Life

entry	derivative	pK_a of leaving group	[4-isopropylphenol], M	$t_{1/2}$, s
1	benzyl acetate	3.6	0	1 000 000 (±20%)
2	benzyl acetate		0.2	200 000 (±25%)
11	benzyl tosylate	−6.1	0	5 500 (±25%)
12	benzyl tosylate		0.2	1 800 (±25%)

functional groups, this corresponds to low basicity. Accordingly, we considered the reactions of benzyl acetate, benzyl tosylate, and benzyl triflate.

Of these leaving groups, triflic acid has the lowest pK_a (−16). Even the triflic anion is an excellent leaving group,[34] and it is widely used in alkylation reactions.[15] However, benzyl triflate is so reactive that it polymerizes spontaneously above −30 ° C to form polybenzyls. Therefore benzyl triflate is much too labile for our purposes.

p-Toluenesulfonic acid has a pK_a of −6.1, between those of triflic acid (−16) and acetic acid (3.6). Under our standard reaction conditions we found benzyl tosylate to have a half-life of ca. 5500 s (Table III, entry 11). In the presence of 4-isopropylphenol, the reactant half-life is reduced further to 1800 s (Table III, entry 12). While monomeric benzyl tosylate is somewhat moisture and heat sensitive,[35] a copolymer with styrene containing about 15% benzyl tosylate units has stability acceptable for resist applications.[36] Other potentially useful leaving groups include, for example, halogenated acetic acids, which have pK_a values intermediate between those of acetic acid and *p*-toluenesulfonic acid. Vinylbenzyl chloroacetates and fluoroacetates should be excellent commonomers for acid-catalyzed cross-linkable polymers. However, the absorption spectra of these materials may limit their use to high-energy exposure such as X-ray or electron beam irradiation.[37]

Conclusion

Our model reactions show that the electrophilic aromatic substitution reactions between benzyl acetates and phenols proceed cleanly under catalysis by 10 mol % of triflic acid. This indicates that these reactions may be well suited for extension to the design of a chemically amplified resist system containing both benzyl acetate and phenolic groups. The rate-limiting step in all cases appears to be cleavage of the benzyl carbon–oxygen bond, rather than reaction of the resulting cation with nucleophiles. Different means of enhancing the rate of the overall reaction by stabilizing the incipient benzyl cation have been investigated. Rate enhancement was observed by substituting electron-releasing substituents on the ring of the benzylic moiety and on the benzylic carbon. Additional rate enhancements have been observed when using less nucleophilic leaving groups and electron-rich furfuryl acetate systems. These studies have provided a basis for synthesizing new polymers for resist applications. The results of lithographic studies on one such system are reported in the accompanying paper.

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Registry No. 1a, 140-11-4; **1b**, 59230-57-8; α-methylbenzyl acetate, 93-92-5; 4-methoxybenzyl acetate, 104-21-2; 4-isopropylphenol, 99-89-8; 2-methylfuran, 534-22-5; furfuryl acetate, 623-17-6; triflic acid, 1493-13-6; benzyl tosylate, 1024-41-5.