Thermal Stability of Sulfonate Ester Photoacid Generators in Phenolic Matrices

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Sulfonate esters have been used extensively as photoacid generators (PAGs) in a number of chemically amplified photoresist systems. For these molecules to be useful in such systems, they must be able to withstand processing temperatures of up to 150 °C. Differential scanning calorimetry and thermogravimetric analysis have been used to investigate the thermal stability of a variety of classes of sulfonate esters. It has been discovered that the decomposition temperatures of a number of sulfonate esters are changed when placed in a polymeric matrix. In phenolic polymers a destabilization was observed, and in many cases the effect is profound. The thermal stability of various sulfonates including pyrogallol esters, nitrobenzyl derivatives and imino sulfonates were investigated in poly(4-hydroxystyrene) (PHS). It has been shown that acid is formed upon decomposition. Further, model reactions have been employed to investigate the mechanism of decomposition. It was concluded that both steric hindrance of the sulfonate ester linkage and the electronic effects of the functional groups on the sulfonate moiety play important roles in the thermal stability of these molecules in PHS. Finally, the effect of thermally generated acid from these photoacid generators on a typical chemically amplified resist system was studied by thermogravimetric analysis and FTIR.

Introduction

The use of photolabile molecules which are capable of generating acid upon exposure to radiation in imaging systems has been well documented. Photoacid generators (PAGs) have proven to be particularly effective in chemically amplified photoresists.[1,2] In these systems the photogenerated acid is used to catalyze a reaction which leads to the induction of a solubility differential between the exposed and unexposed areas of the resist film. Acid-catalyzed cross-linking has been employed in negative acting schemes, while a number of deblocking reactions have been utilized in positive resists.

Photoacid-generating molecules must meet several criteria in order to be useful components in photoresists. One of the more important requirements is that the PAG must not undergo any thermally induced acid-generating reactions during the baking protocols used in processing the resist. If acid is thermally generated, the photochemically induced solubility differentiation between the exposed and unexposed regions of the chemically amplified resist would be lost, resulting in image degradation.

Several classes of compounds have been used as PAGs in chemically amplified photoresists, including onium salts,[3] polyhalogenated compounds,[4] and a variety of sulfonate ester derivatives.[5–10] The thermal stability of PAGs is usually assessed by conventional thermal characterization techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). For example, the thermal decomposition of various *o*-nitrobenzyl sulfonate esters has been extensively studied.[11] Generally, a decomposition temperature of greater than 150 °C for a PAG is deemed sufficient for its use in photoresists. However, these measurements are made on neat samples of the compounds and may not truly reflect the actual stability of the material when it is utilized in a polymer matrix. The most commonly used polymers in resists contain phenolic units with which the PAG may interact. In this report it was observed that these interactions may destabilize the molecule.

This paper reports on the investigation into the thermal stability of several sulfonate ester classes of PAGs in phenolic matrices. These classes include β-ketosulfonate esters, phenolic sulfonate esters, iminosulfonates, phthalimidosulfonates, *o*-nitrobenzyl sulfonates, and *p*-nitrobenzyl sulfonates. The matrix used in this study was poly(4-hydroxystyrene) (PHS), one of the more widely used polymers in microlithography. Typically PHS is used as the base polymer in negative acting deep UV (DUV) resists involving an acid-

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(1) Willson, C. G. *Introduction to Microlithography,* 2nd ed; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Washington, DC, 1994; p 139.

(2) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991,** *3,* 394.

(3) Ito, H.; Willson, C. G. *Polymers in Electronics,* Davidson, T., Ed.; American Chemical Society, Washington, DC, 1984; p 11.

(4) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993,** *115,* 8340.

(5) Shirai, M.; Tsunooka, M. *J. Photopolym. Sci. Technol.* **1990,** *3,* 301.

(6) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Chem. Mater.* **1990,** *2,* 299.

(7) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988,** *21,* 2001.

(8) Brunsvold, W.; Montgomery, W.; Hwang, B. *Proc. SPIE* **1991,** *1446,* 368.

(9) Onishi, Y.; Niki, H.; Kobayashi, Y.; Horiguchi, Y.; Oyasato, N.; Sasaki, O. *J. Photopolym. Sci. Technol.* **1991,** *4,* 337.

(10) Naitoh, K.; Yoneyama, K.; Yamaoka, T. *J. Phys. Chem.* **1992,** *96,* 238.

(11) Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Chin, T. *Chem. Mater.* **1991,** *3,* 462.

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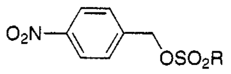
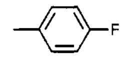
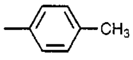
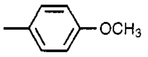
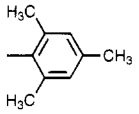
Table 1. Decomposition Temperatures of Sulfonate Esters (1–7)

	decomposition temp[a] (°C)		
		DSC	
PAG	TGA	neat	in PHS[b]
1	216	155	117
2	261	153	141
3	285	279	204
4	227	118	107
5	273	259	125
6	205	196	163
7	320	309	305

[a] Determined at 10 °C/min under N_2. [b] PAG 20 mol % (w/w) in PHS.

Table 2. Effect of a PHS Matrix on the Decomposition of 4-Nitrobenzyl Sulfonate Esters

	decomposition temp[a] (°C)	
	neat	in PHS[b]
 **8**	242	115
 **4**	259	125
 **9**	248	136
 **10**	223	151

[a] Determined by DSC (10 °C/min). [b] PAG 20 mol % (w/w) in PHS.

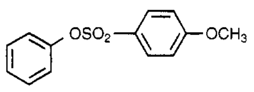
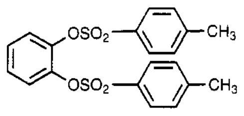
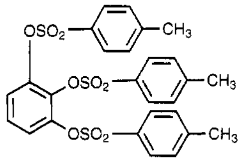
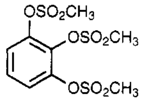
catalyzed cross-linking process and positive acting DUV resists involving the cleavage of acid-labile blocking groups. DSC analysis of blends of these PAGs and PHS indicate that this matrix has a profound destabilizing effect on some of the sulfonate esters studied. Ion chromatography confirmed that acid generation was associated with the decomposition of these PAGs. Further, model compounds and reactions were used to elucidate substituent effects and the mechanism of decomposition of these sulfonate esters in phenolic media.

The effect of the thermal generation of acid from these PAGs on a typical chemically amplified resist system was also investigated. This study was undertaken by monitoring the deprotection temperature of partially *tert*-butoxycarbonyl blocked poly(4-hydroxystyrene) (*t*-BOC PHS) in the presence of these sulfonate esters by thermogravimetric analysis. Further, the effect of PAG thermal stability on rate of thermal deprotection of the *t*-BOC moiety was examined by FTIR.

Experimental Section

Materials. Benzoin *p*-toluenesulfonate (**1**) was used as obtained from Midori Kagaku Co. Ltd. The sulfonate esters listed in Tables 1–3 were synthesized by methods reported in the literature.[5–10] The 4-nitrobenzyl sulfonates (**8**, **9**, and **11**) were synthesized as described in the general procedure below. PHS was obtained from Hoechst Celanese (M_n = 22 000; polydispersity = 2.52; T_g = 180 °C). Partially *tert*-butoxycarbonyl functionalized poly(4-hydroxystyrene) (20% *t*-BOC–PHS) was prepared by reacting PHS with *tert*-butylpyrocarbonate in the presence of potassium *tert*-butoxide.[12]

Table 3. Effect of a PHS Matrix on the Decomposition of Phenolic Sulfonate Esters

	decomposition temp[a] (°C)	
PAG	neat	in PHS[b]
 **16**	219	118
 **17**	249	243
 **7**	309	305
 **18**	261	215

[a] Determined by DSC (10 °C/min). [b] PAG 20 mol % (w/w) in PHS.

General Synthetic Procedure for 4-Nitrobenzyl Sulfonates. *4-Nitrobenzyl 4-Methoxybenzenesulfonate (**9**).* To a solution of 4-nitrobenzyl alcohol (18.00 g, 118 mmol) and 4-methoxybenzenesulfonyl chloride (25.00 g, 121 mmol) in dry acetone (150 mL), a solution of dicyclohexylamine (23.39 g, 129 mmol) in acetone (50 mL) was added dropwise at 0–5 °C under nitrogen. After addition of dicyclohexylamine the reaction temperature was increased to 25 °C and stirring continued for 2 h under nitrogen. The reaction was then filtered and the filtrate evaporated under reduced pressure. The crude white solid was recrystallized from methanol to give 22.00 g (58% of theory) of the title compound having a melting point of 102 °C (peak temperature, DSC/10 °C min). ^1H NMR of **9** (acetone-d_6) 3.90 (3H, s, CH_3O), 5.26 (2H, s, CH_2), 7.15 (2H, d, aromatic), 7.60 (2H, d, aromatic), 7.88 (2H, d, aromatic) and 8.20 (2H, d, aromatic). IR of **9** (KBr disk, cm^{-1}) 1540 (unsym NO_2), 1372 (sym NO_2), 1350, and 1181 (SO_2).

*4-Nitrobenzyl 2,4,6-Trimethylbenzenesulfonate (**10**).* Melting point 102 °C (peak temperature, DSC/10 °C min). ^1H NMR of **10** (acetone-d_6) 2.29 (3H, s, CH_3), 2.59 (6H, s, CH_3), 5.22 (2H, s, CH_2), 7.07 (2H, s, aromatic), 7.62 (2H, d, aromatic), and 8.20 (2H, d, aromatic). IR of **10** (KBr disk, cm^{-1}) 1545 (unsym NO_2), 1378 (sym NO_2), 1357 and 1166 (SO_2).

*4-Nitrobenzyl 4-Fluorobenzenesulfonate (**8**).* Melting point 85 °C (peak temperature, DSC/10 °C min). ^1H NMR of **8** (acetone-d_6) 5.35 (2H, s, CH_2), 7.42 (2H, t, aromatic), 7.61 (2H, d, aromatic), 8.05 (2H, dd, aromatic), and 8.20 (2H, d, aromatic). IR of **8** (KBr disk, cm^{-1}) 1547 (unsym NO_2), 1380 (sym NO_2), 1359 and 1167 (SO_2).

*Reaction of 4-Nitrobenzyl p-Toluenesulfonate (**4**) with 4-ethylphenol (**11**).* 4-Nitrobenzyl *p*-toluenesulfonate (2.00 g, 6.5 mmol) and 4-ethylphenol (3.98 g, 32.6 mmol) were melted together under nitrogen and the temperature raised to 125–130 °C. The reaction mixture was stirred at this temperature for 30 min and then allowed to cool to room temperature. Thin-layer chromatography of the resulting mixture (eluent 15% ethyl acetate/85% hexanes) indicated four main products plus baseline material. The baseline material was removed

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[12] Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995.

by passing the product through a short silica gel column using 15% ethyl acetate/85% hexanes as eluent. The baseline material was then recovered by washing this short column with methanol. Using ion chromatography it was shown that this baseline material contained *p*-toluenesulfonic acid (**12**). The filtrate from the column was then concentrated and the four main products isolated using a Chromatotron (silica gel 60-PF254, EM Sciences) using 15% ethyl acetate/85% hexanes as eluent. The isolated products consisted of 4-nitrobenzyl *p*-toluenesulfonate (**4**), yield 70 mg, melting point 103–105 °C (lit.[13] 105 °C). *p*-Nitrobenzyl 4-ethylphenyl ether (**13**), yield 80 mg, melting point 53 °C (peak temp, DSC/10 °C min). ^{1}H NMR of **13** ($CDCl_3$) 1.25 (3H, t, CH_3), 2.63 (2H, q, CH_2), 5.19 (2H, s, CH_2O), 6.92 (2H, d, aromatic), 7.17 (2H, d, aromatic), 7.64 (2H, d, aromatic), and 8.28 (2H, d, aromatic). ^{13}C NMR of **13** ($CDCl_3$) 15.85, 27.98, 68.72, 114.65, 123.80, 127.55, 128.91, 137.37, 144.84, and 156.14. IR of **13** (KBr disk, cm^{-1}) 1512 (unsym NO_2), 1343 (sym NO_2), 1243 (C–O–C) and 1060 (C–O–C). Mass spectrum (MS) of **13**: *m/e* 257 (M^+). 2-(*p*-Nitrobenzyl)-4-ethylphenol (**14**), yield 420 mg, melting point 114 °C (peak temperature, DSC/10 °C min). ^{1}H NMR of **14** ($CDCl_3$) 1.21 (3H, t, CH_3), 2.58 (2H, q, CH_2), 4.08 (2H, s, CH_2), 4.73 (1H, s, OH), 6.72 (1H, d, aromatic), 6.90–7.10 (2H, m, aromatic), 7.41 (2H, d, aromatic), and 8.15 (2H, d, aromatic). ^{13}C NMR of **14** ($CDCl_3$) 15.88, 27.95, 36.18, 115.45, 123.63, 125.43, 127.42, 129.46, 130.42, 137.05, 148.84, and 151.28. IR of **14** (KBr disk, cm^{-1}) 3631–3259 (O–H), 1504 (unsym NO_2) and 1339 (sym NO_2). MS of **14**: *m/e* 257 (M^+). 3-(*p*-Nitrobenzyl)-4-ethylphenol (**15**), yield 90 mg, melting point 85 °C (peak temperature, DSC/10 °C min). ^{1}H NMR of **15** ($CDCl_3$) 1.13 (3H, t, CH_3), 2.51 (2H, q, CH_2), 4.07 (2H, s, CH_2), 4.73 (1H, s, OH), 6.58 (1H, d, aromatic), 6.71–6.79 (1H, dd, aromatic), 7.12 (1H, d, aromatic), 7.30 (2H, d, aromatic), and 8.15 (2H, d, aromatic). ^{13}C NMR of **15** ($CDCl_3$) 15.08, 24.98, 38.64, 114.06, 117.04, 123.68, 129.23, 129.44, 129.91, 137.81, 148.56, and 153.67. IR of **15** (KBr disk, cm^{-1}) 3752–3132 (O–H), 1514 (unsym NO_2) and 1348 (sym NO_2). MS of **15**: *m/e* 257 (M^+).

Characterization. Blended samples of PHS containing the sulfonate esters (**1–18**) were prepared by weighing out the appropriate molar quantities of each of the components into vials containing a polystyrene ball. These samples were then mechanically milled together for 5 min. Blended samples of 20% *t*-BOC functionalized PHS containing 10 mol % of sulfonate esters (**1–7**) were prepared using a similar method. TGA and DSC were performed using a Perkin-Elmer TGA-7 and a Perkin-Elmer DSC-7 under N_2 (10 °C/min).

Compositions of the sulfonate esters were determined using a GE QE300 NMR spectrometer, ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR, with tetramethylsilane as an internal standard. FTIR spectra were collected on a Mattson Polaris FTIR spectrometer. Mass spectra were obtained on a HP 5988A mass spectrometer using a direct insert probe. Ion chromatography was performed using a AS 10 Dionex column with 10% acetonitrile in 0.1 N sodium hydroxide solution as eluent. Thin-film IR samples (~1.5 μm thick) were prepared by codissolving the polymer (20% *t*-BOC–PHS) and PAG in 2-methoxyethyl ether, filtering (0.2 μm), and spin coating onto silicon wafers. The wafers were then placed in a vacuum oven at room temperature to remove residual solvent. The wafers were subsequently baked at 90 °C for 1 min intervals. After each 1 min time interval an FTIR spectrum was collected using a total of 128 scans at 4 cm^{-1} resolution.

Results and Discussion

Thermal Characterization Method. DSC and TGA were used to determine the thermal stability of the principal classes of sulfonate ester photoacid generators (PAGs) which have been utilized in chemically amplified photoresists (Figure 1). Monitoring the onset of the decomposition exotherm by DSC proved to be the more accurate technique for determining the thermal stability of these PAGs. Previously reported decomposition data on some of these PAGs has been solely based upon TGA, which may not give a true indication of the stability of the molecule.[5,7] During the present investigation it was observed that there was no correlation between the onset of decomposition as determined by DSC and weight loss as observed by TGA. For example, the decomposition exotherm observed by DSC for tosyliminotetralone (**2**) occurs at a much lower temperature (153 °C) than the onset of weight loss associated with decomposition (261 °C, Figure 2). The lower decomposition temperature obtained by DSC compared to TGA proved to be a general phenomenon for all of the sulfonate esters studied. In particular, large discrepancies between the two methods were observed for the benzoin (**1**), iminotetralone (**2**), and *o*-nitrobenzyl (**4**) sulfonate esters (Table 1). The difference in decomposition temperature for these three PAGs as measured by both techniques, ranged from 50 °C to greater than 100 °C. The higher decomposition temperature observed by TGA is probably due to the nonvolatile nature of the products of thermal decomposition. Therefore, the onset temperature of the decomposition exotherm determined by DSC was used to compare the relative stabilities of neat samples of the PAGs and blends of the PAGs in a phenolic matrix.

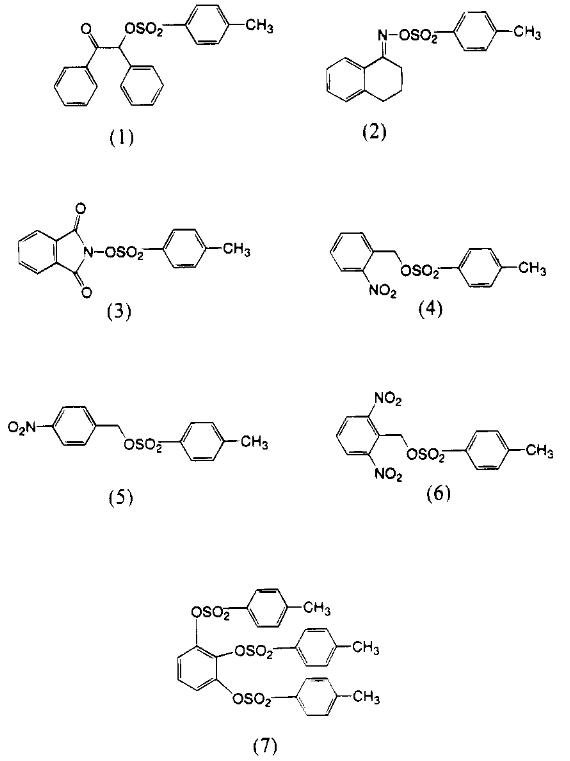

Figure 1. Sulfonate esters (**1–7**).

Thermal Stability in Phenolic Matrices. The most widely used polymer matrices in microlithography are phenolic in nature, for example, PHS and novolac (Figure 3). It is therefore important to understand the thermal stability of these sulfonate ester PAGs in a phenolic environment. DSC was used to determine the effect that the interaction of these molecules with a phenolic matrix would have on their thermal decomposition temperature.

A standard molar concentration of 20 mol % relative to PHS was chosen to compare the relative stabilities

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(13) Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3443.

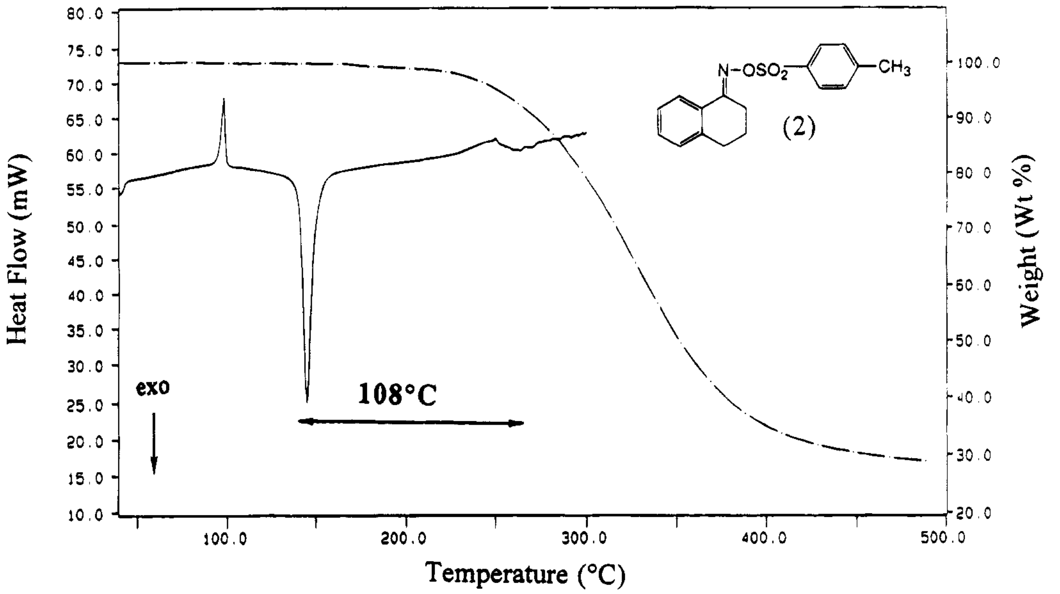

Figure 2. Thermal characterization technique: DSC vs TGA.

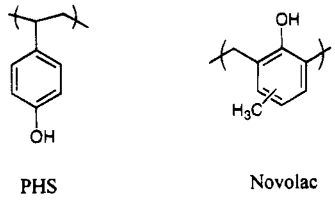

Figure 3. PHS and Novolac.

of these sulfonate ester PAGs. This concentration was preferred since below 20 mol % some of the sulfonate esters studied exhibited only weak decomposition exotherms which were difficult to determine accurately. It was observed that neither physical "milling" of the components nor codissolving the materials followed by evaporation gave intimate mixtures of the PAGs with the phenolic polymer at this molar ratio. Incomplete mixing is evident from the melting transitions of the PAGs in these mixtures as observed by DSC (Figure 4). However, the decomposition exotherms for all of the PAGs in the phenolic matrix occur at temperatures above melting, by which time the components were fluid and intimately mixed. Hot-stage optical microscopy was used to determine that homogeneous mixtures were formed after melting and that no phase segregation was present. The relative stabilities at a 20 mol % concentration of the sulfonate esters (**1**–**7**) in PHS were determined using DSC (Table 1).

β-Keto sulfonate esters are a class of photolabile sulfonate esters which photochemically generate sulfonic acid via a Norrish type I mechanism.[14] Benzoin *p*-toluenesulfonate (**1**) was chosen as a compound representative of this class of PAG. As illustrated by the DSC thermograms shown in Figure 4, the blending of benzoin p-toluenesulfonate (**1**) with PHS has a considerable destabilizing effect on the thermal stability of this PAG. The onset temperature of the decomposition exotherm is lowered from 155 °C for the neat sample of **1** to 117 °C when blended with PHS. Further, at this reduced temperature it was observed that the destructive interaction of the phenolic matrix with **1** resulted in the thermal generation of sulfonic acid. Ion chromatography of a mixture of the benzoin PAG (**1**) in PHS, isothermally held at 117 °C for 2 min, indicated that *p*-toluenesulfonic acid is indeed thermally generated from **1**. The generation of *p*-toluenesulfonic acid at this lower temperature would have a detrimental effect on the lithographic performance of a chemically amplified photoresist composition containing this PAG. For example, in the presence of **1** a partially *tert*-butoxycarbonyl (*t*-BOC) functionalized PHS polymer undergoes complete deprotection at 117 °C, due to the thermal liberation of acid (vide infra). Therefore, an understanding of the effect of a phenolic matrix on the thermal stability of these sulfonate ester PAGs is extremely important.

A reduction in decomposition temperature in the presence of PHS was found to be a general phenomenon for all of the sulfonate esters studied (**1**–**7**). However, the degree to which the decomposition temperature was affected by the phenolic matrix was dependent upon the structure of the sulfonate ester molecule (Table 1).

The photoinduced homolytic cleavage of the N–O bond has also been used as a means of generating sulfonic acid.[5,15] Two classes of PAGs have been developed using this type of photochemistry: the iminosulfonates and the phthalimidosulfonates. The thermal stabilities of two compounds representative of these classes of PAG, *N*-tosyliminotetralone (**2**) and *N*-tosyloxyphthalimide (**3**), were investigated by DSC. It was observed that both of these materials exhibit reduced thermal stability in a phenolic environment compared to neat samples of these compounds. The least stable of these two molecules in PHS was tosyliminotetralone, which exhibits a decomposition temperature of 141 °C, a reduction of 12 °C (Table 1). As was shown to be the case with the benzoin PAG **1**, *p*-toluenesulfonic acid is liberated from **2** in PHS at this reduced decomposition temperature. In contrast, the phthalimido PAG **3** is thermally stable both neat and in a phenolic environment to temperatures above 200 °C and as a result would be a suitable PAG for a phenolic based photore-

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(14) Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67.

(15) Brunsvold, W.; Kwong, R.; Montgomery, W.; Moreau, W.; Sachdev, H.; Welsh, K. *Proc. SPIE* **1990**, *1262*, 162.

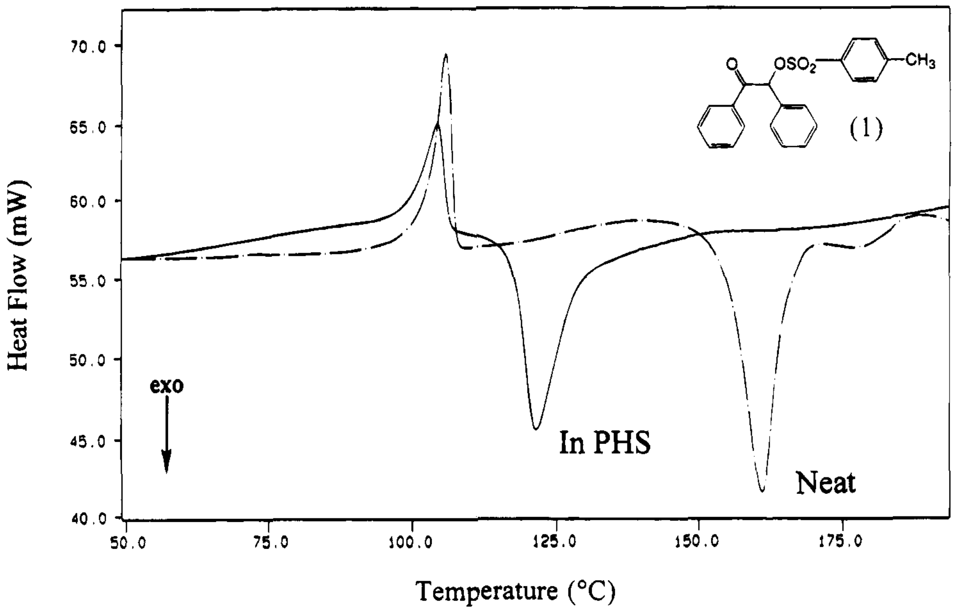

Figure 4. Phenolic matrix effect on the decomposition of benzoin tosylate (**1**).

sist. However, **3** did exhibit some reduction in thermal stability in the phenolic matrix, from 279 °C (neat) to 204 °C.

The *o*-nitrobenzyl sulfonate esters, another class of photolabile sulfonate esters, undergo intramolecular photodecomposition and thermal decomposition.[11] It has been reported that the temperature of thermal decomposition of these molecules can be controlled by incorporating bulky electron-withdrawing groups in the 6-position of the benzyl moiety. However, no data have been reported on the thermal stability of this class of PAGs in polymeric matrices.

It was observed by DSC that both the *o*- (**4**) and *p*- (**5**) nitrobenzyl *p*-toluenesulfonate isomers exhibit reduced thermal stability in the PHS matrix (Table 1). The least stable of the two isomers is 2-nitrobenzyl *p*-toluenesulfonate (**4**), which decomposed at 107 °C in PHS. However, above its melting point, this ortho isomer (**4**) is inherently unstable, and the interaction of this PAG with PHS was shown to have only a minor effect on the decomposition temperature. A greater illustration of the effect of a phenolic environment on thermal stability is shown by 4-nitrobenzyl *p*-toluenesulfonate (**5**). This para isomer (**5**) exhibits a reduction in decomposition temperature of 134 °C, from 259 °C (neat) to 125 °C in the PHS matrix. Therefore, the interaction of this benzyl sulfonate ester (**5**) with the matrix has a considerable destabilizing effect on this molecule. Also, as was observed for the benzoin PAG (**1**), ion chromatography indicated that *p*-toluenesulfonic acid was liberated from **5** at this lower temperature.

As reported in the literature[11] it is possible to increase the thermal stability of *o*-nitrobenzyl sulfonate esters by the incorporation of a bulky electron withdrawing group, such as the nitro group in the 6-position. Thus, the decomposition of the more thermally stable 2,6-dinitrobenzyl *p*-toluenesulfonate (**6**) was also studied. This derivative (**6**) proved to be the most stable of the nitrobenzyl sulfonates in a phenolic environment (163 °C), exhibiting a reduction of only 33 °C in decomposition temperature (Table 1). One possible explanation for the superior thermal stability of the 2,6-dinitro derivative (**6**) in PHS compared to the 4-nitro derivative (**5**) is that the two ortho nitro groups of **6** sterically hinder the interaction of the phenolic polymer with the sulfonate ester linkage.

To further understand the effect of the structure of these sulfonate esters on the stability of these molecules in a phenolic environment, two classes of these PAGs, the 4-nitrobenzyl sulfonates, and the phenolic sulfonates were investigated in more detail. Various model compounds were prepared to examine the relationship between the molecular structure of these sulfonate esters and their stability in a phenolic matrix.

4-Nitrobenzyl Sulfonate Esters. It has been reported that the *o*-nitrobenzyl sulfonate esters undergo intramolecular thermal decomposition via the nitro group.[11] To separate this intramolecular decomposition from any intermolecular interactions with the phenolic matrix, various 4-nitrobenzyl sulfonate ester model compounds (**5** and **8**–**10**) were prepared and their thermal decomposition studied (Table 2). These compounds were used to investigate the electronic and steric effects of various substituent groups on the decomposition temperature of sulfonate esters in a phenolic matrix.

It is well documented that alkyl and aromatic sulfonates are good leaving groups and readily undergo nucleophilic displacement reactions.[16] For example, ethers of alcohols and phenols can be prepared by reaction of alkoxides or aryl oxides with alkyl or aryl sulfonates. The observation that sulfonate esters show reduced thermal stability in a phenolic matrix suggests that the decomposition mechanism may involve nucleophilic attack at the sulfonate ester linkage.

To confirm this nucleophilic decomposition mechanism, a model reaction was carried out between 4-nitrobenzyl *p*-toluenesulfonate (**5**) and 4-ethylphenol (**11**). This reaction was carried out in the melt using a 20 mol % concentration of **5** relative to 4-ethylphenol to mimic the DSC conditions. A temperature of 125–130 °C was chosen for this reaction since it is the onset of the decomposition exotherm of **5** in PHS as observed

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(16) Crossland, R. K.; Wells, W. E.; Shiner, V. J. *J. Am. Chem. Soc.* **1971**, *93*, 4217.

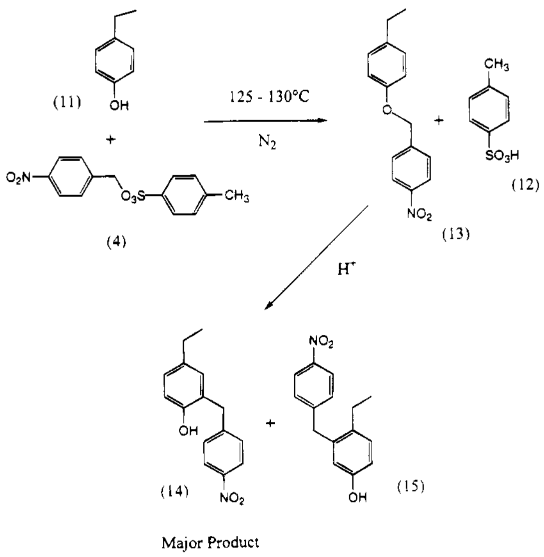

Figure 5. Model reaction.

by DSC. The products of this model reaction were isolated by thin-layer chromatography. Under these reaction conditions, four main products were isolated. These products were identified as *p*-toluenesulfonic acid (**12**), *p*-nitrobenzyl 4-ethylphenyl ether (**13**), 2-(*p*-nitrobenzyl)-4-ethylphenol (**14**), and 3-(*p*-nitrobenzyl)-4-ethylphenol (**15**). The proposed mechanism for the formation of these products is shown in Figure 5. This mechanism involves the nucleophilic attack of 4-ethylphenol at the sulfonate ester linkage of 4-nitrobenzyl *p*-toluenesulfonate to form the benzyl ether (**13**) and *p*-toluenesulfonic acid (**12**). In this strongly acidic environment the benzyl ether (**13**) rearranges to form the two C-alkylation products **14** and **15**. As expected, due to the electron donating effect of the hydroxy group, the major product of this acid-catalyzed rearrangement of **13** is the ortho isomer **14**. It is worth noting that similar acid catalyzed rearrangements of benzyl ethers in the presence of strong acid have been reported in the literature.[17]

If the reduction in thermal stability of these sulfonate esters in a phenolic environment is due to nucleophilic displacement, then the basicity of the sulfonate leaving group should play an important role in determining the decomposition temperature. To investigate the effect of the sulfonate ester leaving group on the thermal stability of nitrobenzyl esters in phenolic matrices, 4-nitrobenzyl compounds were prepared containing sulfonate ester moieties of varying basicity. The basicity of the leaving group was varied by the incorporation of electron-withdrawing and electron-donating groups onto the sulfonate ester benzene ring. The sulfonate esters used in this study in order of increasing leaving group basicity were 4-nitrobenzyl 4-fluorobenzenesulfonate (**8**), 4-nitrobenzyl *p*-toluenesulfonate (**4**), and 4-nitrobenzyl 4-methoxybenzenesulfonate (**9**, Table 2).

The stability of the sulfonate esters in the phenolic matrix decreases on going from 4-methoxybenzenesulfonate (**9**, 136 °C), to *p*-toluenesulfonate (**4**, 125 °C), to the 4-fluorobenzenesulfonate derivative (**8**, 115 °C). The order of thermal stability in PHS exactly parallels the basicity of the corresponding leaving group. In other words the compound capable of generating the strongest acid (**8**) is the least stable. This trend is in contrast to the molecules themselves which exhibit no correlation between basicity of leaving group and decomposition temperature. The observation that the incorporation of a more basic sulfonate leaving group into these nitrobenzyl PAGs results in increased thermal stability further indicates that the decomposition mechanism in a phenolic environment involves nucleophilic attack at the sulfonate ester linkage.

To investigate the effect of sterically hindering nucleophilic substitution, 4-nitrobenzyl 2,4,6-trimethylbenzenesulfonate (**11**), where the sulfonate ester is flanked by two methyl groups was synthesized. The stability of this hindered derivative in phenolic media was then compared with 4-nitrobenzyl *p*-toluenesulfonate (**4**). It was observed that the decomposition temperature of **11** is indeed higher than the unhindered sulfonate ester (**4**, Table 2). The difference in decomposition temperature (ΔT_d) between the neat compounds and mixtures of these esters in a phenolic matrix illustrates the stabilizing effect of the two methyl groups which flank the ester linkage. The ΔT_d for the tosylate derivative **4** being 134 °C, while the ΔT_d for the hindered derivative **11** is nearly half this value, 72 °C. However, it should be noted that the stabilizing effect of the two ortho methyl groups in **11** may not be due totally to steric inhibition, since their electronic effect increases the basicity of this leaving group compared to the tosyl moiety of **4**.

Thus it can be concluded that both steric hindrance of the sulfonate ester linkage and the electronic effects of the functional groups on the sulfonate moiety play important roles in defining the thermal stability of these molecules in phenolic matrices.

Phenolic Sulfonate Esters. Multifunctional phenolic sulfonates, such as the sulfonate esters of 1,2,3-trihydroxybenzene, have been used as photoacid generators in chemically amplified photoresists.[6] It was reported that as the number of sulfonate esters bonded to the aromatic ring is increased, there is a concomitant increase in the efficiency of acid generation (the molar ratio of sulfonate esters groups being normalized to one).[18] That is, sulfonate esters of 1,2,3-trihydroxybenzene are more efficient at generating acid than the corresponding esters of 1,2-dihydroxybenzene, which in turn is more efficient than the same sulfonate ester of phenol. The thermal stability of these sulfonate esters relative to the functionality of the benzene ring was therefore investigated in a phenolic matrix. Further, the effect of the sulfonate ester leaving group on the stability of these phenolic sulfonates was investigated by comparing the stability of 1,2,3-tris(*p*-toluenesulfonyloxy)benzene (**7**) with 1,2,3-tris(methanesulfonyloxy)benzene (**18**) in PHS.

The effect of the degree of functionality on thermal stability in a phenolic matrix of the *p*-toluenesulfonate derivatives of phenol, 1,2-dihydroxybenzene and 1,2,3-trihydroxybenzene is shown in Table 3. PHS has a considerable destabilizing effect on the monofunctional sulfonate ester (**16**); the decomposition temperature is reduced by 101 °C. In contrast, the di- and trifunc-

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(17) Lee, S. M.; Fréchet, J. M. J. *Macromolecules* **1994**, *27*, 5160.

(18) Ueno, T.; Schlegel, L.; Hayashi, N.; Shiraishi, H.; Iwayanagi, T. *SPE Regional Technical Conference on Photopolymers: Principles—Processes and Materials*, Society of Plastics Engineers Inc. 1991; p 121.

Table 4. Effect of Sulfonate Esters (1–7) on the Thermal Deprotection of 20% *t*-BOC PHS

PAG[a]	TGA deprotection temp[b] (°C)
control[c]	149
1	107
2	125
3	145
4	97
5	116
6	139
7	148

[a] Blended at 10 mol % relative to polymer. [b] Deprotection temperature determined at peak maximum of first derivative. [c] 20% *t*-BOC PHS containing no PAG.

tional tosyl derivatives **17** and **7** exhibited only minor reductions in thermal stability in PHS. The significant increase in thermal stability of the di- and trifunctional tosyl derivatives compared to the monofunctional ester indicates that steric crowding of these sulfonate esters plays an important role in improving thermal stability. As the functionality of the benzene ring is increased, steric crowding of the sulfonate ester linkage inhibits interaction with the PHS matrix, impeding the nucleophilic displacement of sulfonic acid. It should be noted that the decomposition temperatures of neat samples of these compounds (**16**, **17**, and **9**) also exhibit increased thermal stability with increasing functionality.

The effect of the leaving group on the thermal stability of these trifunctional phenolic sulfonates in PHS was investigated by comparing the stability of the mesyl derivative **18** with the tosyl derivative **7**. DSC indicated that **18** was considerably less stable in a phenolic environment than **7** (Table 4). The difference in thermal stability between these two PAGs (90 °C) may be accounted for by the difference in basicity of the tosyl group relative to the mesyl group. That is, methanesulfonate is a better leaving group than *p*-toluenesulfonate due to the more acidic nature of its conjugate acid relative to the tosic acid. Further, the bulky nature of the tosyl group may sterically hinder the interaction of **7** with PHS, inhibiting nucleophilic displacement.

Effect of Thermally Generated Acid on a Chemically Amplified Photoresist. The concept of chemically amplified photoresist systems was first developed by Fréchet et al.[19] One of the initial systems developed involves the acid catalyzed deprotection of the *tert*-butoxycarbonyloxy (*t*-BOC) moiety from a phenolic polymer. This type of acid-catalyzed deprotection has been extensively investigated using a number of acid labile protecting groups.[1,2]

Recently, partially protected phenolic polymer systems have been developed for use in photoresists. However, this partial protection of the PHS backbone results in free phenolic groups, which may adversely effect the thermal lability of both the protecting group and the PAG. For example, it has been reported that the thermal deprotection of the *t*-BOC moiety in partially *t*-BOC functionalized PHS is dependent upon the content of phenolic groups in the copolymer.[20] As the phenolic content of the polymer is increased the thermal deprotection temperature of the *t*-BOC group is reduced. Further, as described in this article, increased phenolic concentrations may also have a detrimental effect on the thermal stability of the PAG (vide supra). Therefore, it is important to understand the interaction of the PAG component of the resist with the partially protected phenolic polymer matrix.

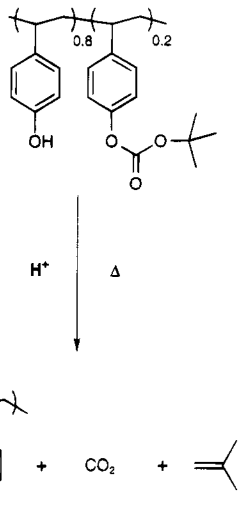

Figure 6. Thermal deprotection of 20% *t*-BOC PHS.

TGA Deblocking Study. The effect of the thermal stability of these sulfonate esters on the deprotection temperature of a 20% *t*-BOC functionalized PHS was determined in the presence of these PAGs. TGA was used to follow the weight loss associated with the thermolysis of the *t*-BOC group from the polymer backbone. Upon thermal decomposition, the t-BOC moiety liberates carbon dioxide and isobutylene, regenerating the phenolic functionality (Figure 6). To determine the comparative effect of these PAGs on the thermolysis of the *t*-BOC group, molar equivalents of the various sulfonate esters (10 mol % relative to polymer) were blended with the 20% *t*-BOC functionalized PHS. The temperature of deprotection of the *t*-BOC moiety was then monitored by TGA. As illustrated in Figure 7, TGA indicates that the 2,6-dinitrobenzyl (**6**), 4-nitrobenzyl (**5**), and benzoin (**1**) *p*-toluenesulfonates all reduce the thermolysis temperature of the *t*-BOC group compared to the control. This reduction in the thermolysis temperature of the *t*-BOC group verifies that acidic species are liberated upon the decomposition of these PAGs in PHS. The least stable of these PAGs in a phenolic matrix, benzoin *p*-toluenesulfonate (**1**), causes the greatest decrease in the deprotection temperature of the *t*-BOC polymer, a reduction of 42 °C. While the most stable of the three PAGs (**6**) has a smaller effect on the temperature of deprotection, reducing the thermolysis temperature from 149 to 139 °C (i.e., smaller amounts of acid are formed). It was observed that most of the sulfonate esters studied reduce the deprotection temperature of the *t*-BOC group in this phenolic polymer system (Table 4). The decrease in deprotection temperature was found to be dependent upon the molecular structure of the PAG. The extent of the decrease in *t*-BOC thermolysis temperatures in the presence of these PAGs is in agreement with their thermal stability in a phenolic environment. That is, the order of thermal stability of the sulfonate esters in PHS (Table 1), corresponds exactly to the order of the

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(19) Fréchet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Eng.* **1982**, 260.

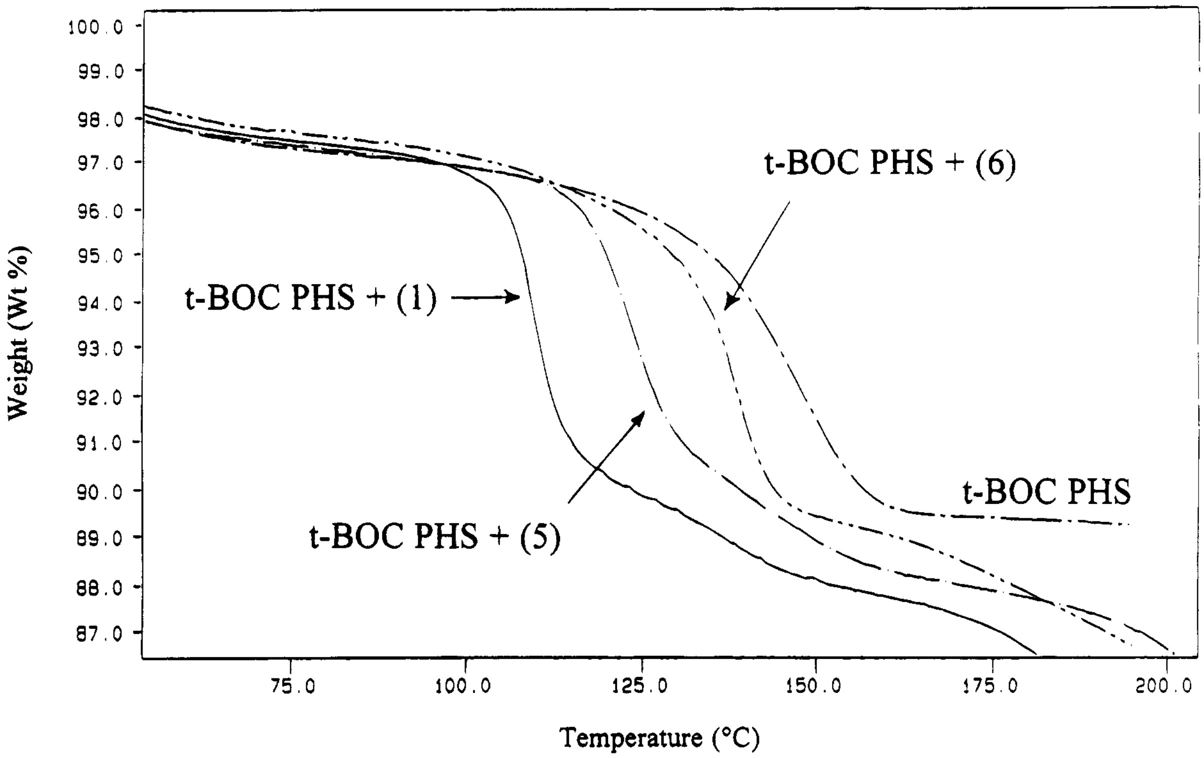

Figure 7. TGA of blends of sulfonate esters (**1**, **5**, and **6**) and 20% *t*-BOC PHS.

temperature of deprotection in the presence of these PAGs. In contrast, there is no correlation between the neat decomposition temperatures of these PAGs and their effect on the deprotection of 20 mol% t-BOC PHS. The discrepancy between the order of thermal stability of neat samples and the effect of these PAGs on the deprotection of 20 mol % *t*-BOC PHS further emphasizes the importance of measuring the stability of these sulfonate esters in a phenolic environment.

The most thermally stable PAGs in PHS, and therefore most useful in an acid catalyzed photoresist, are the phthalimido and pyrogallol sulfonate esters, which cause very little reduction in the deprotection temperature of 20 mol % *t*-BOC PHS.

FTIR Deblocking Study. As described above, DSC was used to compare the relative thermal stabilities of the sulfonate esters (**1**−**7**) in a phenolic environment, while TGA was used to determine their effect on 20% *t*-BOC PHS thermolysis. The order of thermal stability obtained for these PAGs from both of these studies proved to be in complete agreement. However, both of these thermal analysis techniques are dynamic, since they are dependent upon the heating rate used during the experiment. As a result, these techniques may not truly reflect the thermal stability of a photoresist composition. To mimic more closely the working environment of a photoresist, thin films of formulations comprising of PAG (10 mol % relative to polymer) and 20% *t*-BOC PHS were spin coated onto silicon wafers and these films isothermally treated at 90 °C on a vacuum hot plate. A temperature of 90 °C was chosen since this is a representative bake temperature used to remove solvent before exposure and to thermally activate deblocking or cross-linking chemistries after photogeneration of acid. The effect of these PAGs on the deprotection of the *t*-BOC moiety was monitored as a function of time with FTIR by following the reduction in carbonyl stretching absorbance between 1800 and 1670 cm^{-1} (Figure 8). The C=O stretching absorption is split into two, as evident by the shoulder at 1730 cm^{-1}. This shoulder is due to hydrogen bonding of the carbonyl with the phenolic functionalities of the polymer backbone. The extent of *t*-BOC thermolysis was determined by normalizing the area of the C=O absorption between 1800 and 1670 cm^{-1} relative to the strong aromatic C=C absorption between 1545 and 1480 cm^{-1}, which remains unchanged during thermolysis (Figure 8). The degree of *t*-BOC conversion was then determined and plotted against time (Figure 9).

Three PAGs were chosen for this FTIR study: 1,2,3-tris(*p*-toluenesulfonyloxy)benzene (**7**), which has a thermal stability >300 °C, 2,6-dinitrobenzyl *p*-toluenesulfonate (**6**), and tosyliminotetralone (**2**), both of which exhibit slight reductions in thermal stability in PHS (163 and 141 °C, respectively). It was observed when PAGs **1**, **4**, and **5**, which have decomposition temperatures lower than 140 °C in PHS, are used complete deprotection of the 20% *t*-BOC PHS occurs within 1 min at 90 °C.

Figure 8 illustrates the disappearance of the carbonyl stretching absorption with time at 90 °C, due to the thermolysis of the *t*-BOC moiety. The photoresist composition used in this experiment comprised 2,6-dinitrobenzyl *p*-toluenesulfonate (**6**) and 20% *t*-BOC PHS. As can be seen from this figure, a considerable reduction in the carbonyl absorption was observed with time, indicating that this photoresist composition is thermally unstable when isothermally held at 90 °C. In contrast, TGA (heating rate, 10 °C/min) indicated that this composition is thermally stable up to 139 °C. As previously stated, although TGA gives a good relative comparison of the effect of these PAGs on thermal deprotection, it does not give a true indication of the thermal stability of the resist system. This FTIR study indicates that thermally generated acid is liberated within the resist film at this lower temperature. In

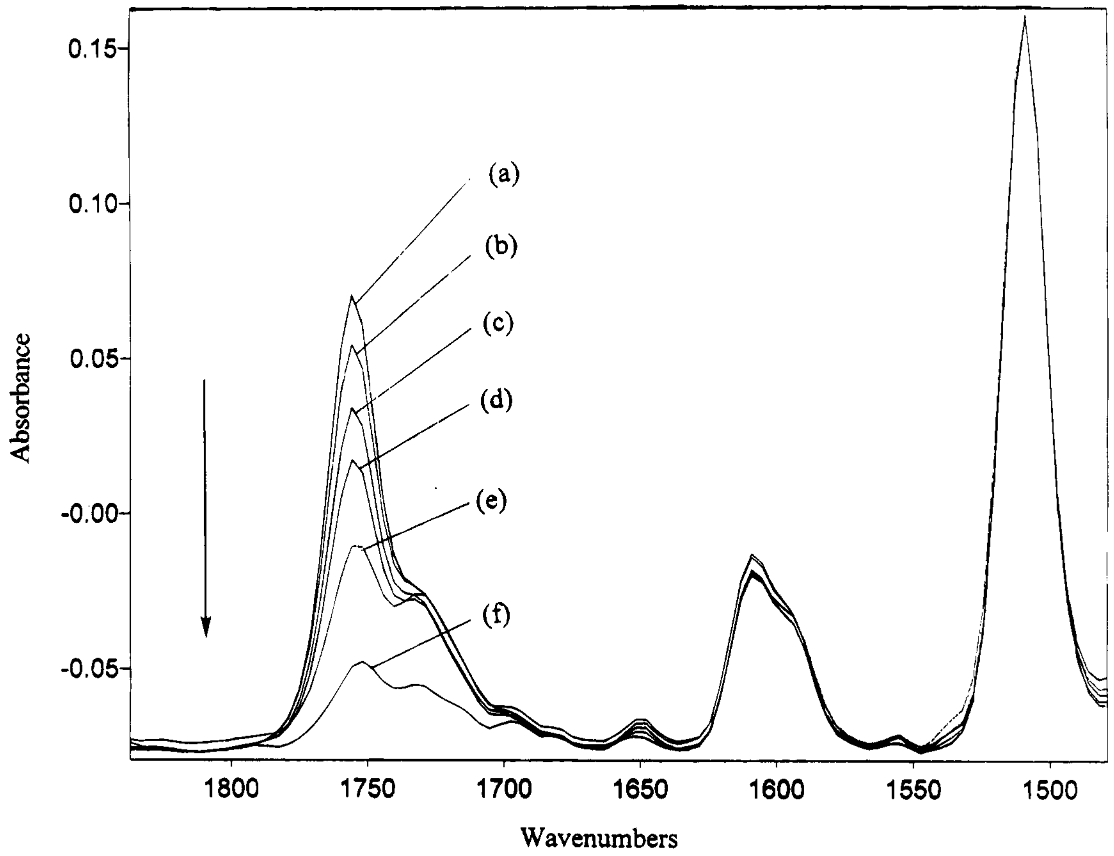

Figure 8. FTIR spectra of deblocking of 20% *t*-BOC PHS in the presence of **6** at 90 °C after (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 min.

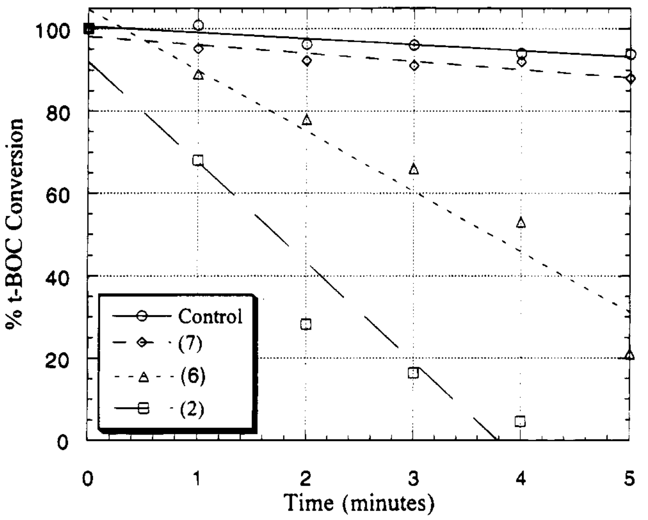

Figure 9. FTIR thermal deblocking study.

the case of the *t*-BOC system an FTIR investigation of the deprotection reaction proved to be the most sensitive technique for determining the effect of thermal acid generation on the stability of photoresist compositions.

Figure 9, illustrates the effect of PAGs **2**, **6**, and **7** on the rate of deprotection of the *t*-BOC group at 90 °C. The rate of deprotection was determined from the slope of these plots and is expressed as percentage reduction in C═O absorption per minute. The control sample which contained 20% *t*-BOC PHS and no PAG, exhibits a slight reduction in C═O absorption with time (rate of deprotection = 1.5%/min). These data is are agreement with a previous report which indicated that free phenolic groups lower the thermal stability of the *t*-BOC protecting group.[20] This FTIR investigation indicates that most of the photoacid generators studied increase the rate of thermolysis of the *t*-BOC group relative to a control sample which contained no PAG. The most thermally stable PAG in a phenolic matrix (**7**), has very little effect on the rate of thermolysis of the *t*-BOC group under these conditions. The rate of deprotection was only increased to 2.0%/min. This rate is in agreement with the TGA data which indicates that this PAG causes minimal reduction in the deprotection rate of 20% *t*-BOC PHS. In contrast, the sulfonate esters which exhibit reduced thermal stability in PHS, cause a considerable increase in the rate of thermolysis of the *t*-BOC group under these conditions. For example, tosyliminotetralone (**2**) which is the least stable PAG in PHS, promotes the greatest increase in rate of thermolysis of the *t*-BOC group (rate of deprotection = 24%/min). 2,6-dinitrobenzyl *p*-toluenesulfonate (**6**), which has a thermal stability intermediate between **2** and **7**, exhibits an increase in rate of thermolysis intermediate between **2** and **7** (rate of deprotection = 15%/min). All this data is in agreement with DSC data (vide supra).

Conclusions

The thermal stability of various sulfonate ester photoacid generators have been investigated in the presence of PHS. It was discovered that in many cases the phenolic environment has a considerable destabilizing effect on these sulfonate ester molecules. However, the degree to which the decomposition temperature was

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[20] Ito, H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2971.

affected by the PHS was dependent upon the structure of the sulfonate ester molecule. Model compounds and reactions were used to elucidate substituent effects and the mechanism of decomposition of these sulfonate esters in phenolic media. The results of this study support a decomposition mechanism which involves nucleophilic attack by phenolic moieties at the sulfonate ester linkage, resulting in the liberation of sulfonic acid. Further, model compounds indicate that both steric hindrance of the sulfonate ester linkage and the electronic effects of the functional groups on the sulfonate moiety play important roles in the thermal stability of these molecules. The effect of the thermal generation of acid from these PAGs on a typical, chemically amplified resist system was also investigated by TGA and FTIR. This investigation revealed that the onset temperature and rate of thermolysis of a 20% *t*-BOC functionalized PHS was profoundly affected by the presence of these sulfonate esters. That is, the order of thermal stability of the sulfonate esters in PHS (Table 1) corresponds exactly to the order of thermal *t*-BOC deprotection in the presence of these PAGs (Table 4). Therefore, an understanding of the effect of a phenolic matrix on the thermal stability of these sulfonate esters and the consequences of this stability on a chemically amplified resist are extremely important when designing a photoresist composition.

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