Photo- and Thermochemistry of Select 2,6-Dinitrobenzyl Esters in Polymer Matrices: Studies Pertaining to Chemical Amplification and Imaging

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ABSTRACT: Various esters derived from 2,6-dinitrobenzyl alcohol were synthesized and evaluated as photoprotected acids. These materials were prepared from acids whose counterions vary in basicity and nucleophilicity. The effectiveness of these esters as photogenerators of acid was evaluated in terms of their quantum yield for generation of acid in polymer matrices and their thermal stability. The acids thus generated were evaluated in terms of their catalytic chain lengths and lithographic performance in poly(*p-tert*-butoxycarbonyloxy-α-methylstyrene) [poly(*t*-BOCoxy-α-methylstyrene)]. Of the esters studied, it was found that 2,6-dinitrobenzyl 4-nitrobenzenesulfonate had the best combination of the properties described above.

Introduction

The use of the *tert*-butyl protecting group[1] for polymers with acid or phenol functionalities allows the development of systems in which the ester group is removed by a thermally driven catalytic reaction that is initiated by a photogenerated acid.[2-4] As a consequence, compounds that generate strong acids upon photolysis are of increasing interest in areas such as microlithography. Onium salts that photochemically generate strong acids have been described by Crivello,[5] and their application to lithography has been described by Willson and coworkers.[2,3] However, these systems have several inherent disadvantages, including poor solubility in organic solvents and the presence of undesirable elements such as arsenic or antimony that are toxic and/or affect device characteristics. Photochemically active esters that generate strong organic acids upon photolysis offer several advantages, namely, improved solubility in organic solvents, wide flexibility in structure, and absence of metal atoms. Systems based upon 2-nitrobenzyl, 2,4-dinitrobenzyl, and 2,6-dinitrobenzyl esters of tosic acid have been described previously.[3,4] The 2,6-dinitrobenzyl tosylate possesses several desirable characteristics, such as good thermal stability and excellent quantum efficiency that results in good sensitivity. In this paper, we extend our study to the preparation and characterization of several new 2,6-dinitrobenzyl esters, discuss their photochemistry and activity in the solid state, and briefly examine lithographic behavior. Specifically, the catalytic deprotection of poly(*t*-BOCoxy-α-methylstyrene) initiated by several sulfonic acids after photogeneration from their corresponding 2,6-dinitrobenzyl esters is investigated.

Experimental Section

Materials Preparation. The syntheses of *t*-BOCoxy-α-methylstyrene and its corresponding polymer were adapted from the literature.[6] The procedures for the syntheses of the nitrobenzyl esters were adapted from literature preparations of tosylates.[7] Organic starting materials were obtained from the Aldrich Chemical Co. with the exception of 2,6-dinitrotoluene that was obtained from E. Merck. The synthesis of 2,6-dinitrobenzyl alcohol from 2,6-dinitrobenzaldehyde was described earlier.[4]

Synthesis of 2,6-Dinitrobenzyl Alcohol. To a solution of 2,6-dinitrobenzyl bromide (20.00 g, 76.9 mmol) in 200 mL of *p*-dioxane/water (70/30 v/v) was added 20 g (144.6 mmol) of potassium carbonate. The pale yellow, homogeneous solution was degassed with a stream of dry nitrogen, and the solution was heated for 60 h at 60 °C. The progress of the reaction was monitored by thin-layer chromatography (silica, methylene chloride), and when conversion to the alcohol was complete, the solution was cooled and neutralized by the addition of dilute HCl. The solvent was removed under reduced pressure, the residual oil was dissolved in methylene chloride, washed with water, and dried over $MgSO_4$, and the solvent was removed. A dark yellow solid was recovered that was purified by chromatography on silica with methylene chloride as the eluent. Finally, the product was recrystallized from carbon tetrachloride/chloroform (7.15 g, 46.9% yield).

Synthesis of 2,6-Dinitrobenzyl Mesylate. To a solution of 2,6-dinitrobenzyl alcohol (2 g, 10 mmol) in 5 mL of dry acetone was added methanesulfonyl chloride (1.15 g, 0.778 mL, 10 mmol). The clear solution was cooled to 10 °C, and to this solution was added dicyclohexylamine (1.81 g, 1.99 mL, 1 equiv) dropwise. A white precipitate of dicyclohexylamine hydrochloride formed immediately. The solution was warmed to room temperature, and stirring was continued overnight. The solution was then filtered and the solvent removed under reduced pressure. The pale yellow solid recovered was purified by chromatography on silica gel using methylene chloride as the eluent. Recrystallization from carbon tetrachloride/chloroform yielded 2,6-dinitrobenzyl mesylate (2.30 g, 82.7%) as white crystals.

Synthesis of 2,6-Dinitrobenzyl Pentafluorobenzenesulfonate. This reaction was carried out in a two-compartment reactor in which the two compartments were separated by a porous frit. A solution of 2,6-dinitrobenzyl alcohol (1 g, 5.05 mmol) and pentafluorobenzenesulfonyl chloride (1.47 g, 5.55 mmol) in dry acetone (4 mL) was cooled to 10 °C under an atmosphere of dry nitrogen. Dicyclohexylamine (0.91 g, 5.05 mmol) was added dropwise to this solution. A heavy white precipitate formed immediately, and after 1 min, the reaction mixture was filtered under vacuum into the other compartment of the cell. The white precipitate of dicyclohexylamine hydrochloride was washed with 2 mL of fresh cold acetone. The solvent was removed at reduced pressure to yield a yellow solid. Thin-layer chromatography (methylene chloride, silica) showed the presence of two new compounds together with unreacted 2,6-dinitrobenzyl alcohol. The new compound having the highest R_f was identified as 2,6-dinitrobenzyl chloride by comparison with an authentic sample. Recrystallization of the mixture from carbon tetrachloride/chloroform removed 2,6-dinitrobenzyl chloride. The mixture of 2,6-dinitrobenzyl alcohol and the desired ester was further purified by chromatography over silica gel under yellow lights using methylene chloride as the eluent. After removal of the solvent, the 2,6-dinitrobenzyl pentafluorobenzenesulfonate was recovered as white needles (0.9 g, 42%).

Materials Characterization

Nuclear magnetic resonance spectra were obtained on a JEOL JMN-FX90Q Fourier transform spectrometer. IR spectra were

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taken by using a Digilab FTS-60 Fourier transform spectrometer. Mass spectra were obtained on a HP 5995 mass spectrometer with a direct insert probe (DIP) heated to the desired temperature. Elemental analyses were obtained by Galbraith Laboratories Inc.

Thermogravimetry. Thermogravimetric analysis was performed by using a Perkin-Elmer TGS-2 or TGS-7 thermogravimetric analyzer interfaced with a System 4 microprocessor for temperature control and a TADS Model 3700 data station for data acquisition and operational control. A heating rate of 5 °C/min was used for the dynamic measurements while isothermal curves were obtained at 80, 100, and 120 °C. The N_2 flow rate was held constant at 20 cm^3/min.

Differential Scanning Calorimetry (DSC). Data for the solid samples were obtained by using a Perkin-Elmer DSC-4 differential scanning calorimeter that was interfaced with a System 4 microprocessor and a TAD Model 3700 data station. Calibrations of the temperature scale were performed with indium, lead, and tin. All samples were heated from 20 to 450 °C at a heating rate of 10 °C/min. Samples ranged in mass between 1.20 and 2.00 mg and were encapsulated in aluminum pans. All measurements were obtained in ultra high purity (99.999%) N_2 with a gas flow rate of 30 cm^3/min.

Quantum Yield Determination. The samples for the quantum yield determinations were prepared in the following manner. Poly(methyl methacrylate) (PMMA) (10 wt %) was dissolved in cyclohexanone, and 8.4 mol % (relative to the polymer) of a 2,6-dinitrobenzyl ester was added. The resulting solutions were coated onto standard silicon, NaCl, or quartz substrates with a Headway Research Spinner (Model EC 101). The PMMA/ester films were baked at 90 °C for 30 min in a convection oven. Film thicknesses were measured with a Nanospec AFT film thickness measurement gauge (Model 010 0180) and were in the range of 0.5–0.7 μm. Absorbances were determined by using a Hewlett-Packard Model 8452A diode array spectrophotometer. Pulsed laser exposures were carried out by using a Süss Model MA56A contact aligner equipped with a Lambda Physik excimer laser operating at 248 nm as the deep UV source. The pulse rate was 100 Hz, and energy deposited at the wafer plane was 13 mW/cm^2. The photochemical reaction was followed by monitoring the decrease in the nitro group absorbance at 1530 cm^{-1} with a Digilab FTS60 FT-IR spectrophotometer. Several measurements were made at different exposure times (doses) that resulted in between 2 and 20% conversion for each sample. This was done by monitoring the changes in the IR absorbance spectrum of each film upon UV exposure. The quantum yields were calculated as described previously.[4]

Lithographic Evaluation

Resist Solutions. Photoresist solutions were prepared by dissolving poly(*t*-BOCoxy-α-methylstyrene) (1 g) and the dinitrobenzyl esters (8.4 mol % relative to the polymer) into cyclohexanone (15 mL). The solutions were filtered through a series of 1.0, 0.5, and 0.2 μm Teflon filters (Millipore Inc.).

Lithography. Photoresist films were spin coated onto vapor primed hexamethyldisilazane (HMDS) oxidized silicon substrates and prebaked at 120 °C for 2 min. All resist-coated substrates were exposed as described earlier. Proximity printing was used to generate the exposure response curves, and vacuum contact printing was employed for high-resolution exposures. The irradiated films were post-exposure-baked (PEB) at 120 °C for 2 min on a hot plate. The films were developed in isopropyl alcohol for 90 s and rinsed in distilled water for 15 s. All thickness measurements were made by using a Nanospec film thickness gauge (Namometrics, Inc.) or a Dektak Model IIA profilometer.

Results and Discussion

Synthesis. The removal of the acid labile *t*-BOC group from a phenol is a facile process in solution and may be accomplished by a wide range of organic acids, including sulfonic and fluorinated carboxylic acids.[1] Accordingly, a series of photoactive esters were prepared that represented several examples of each type of acid. The

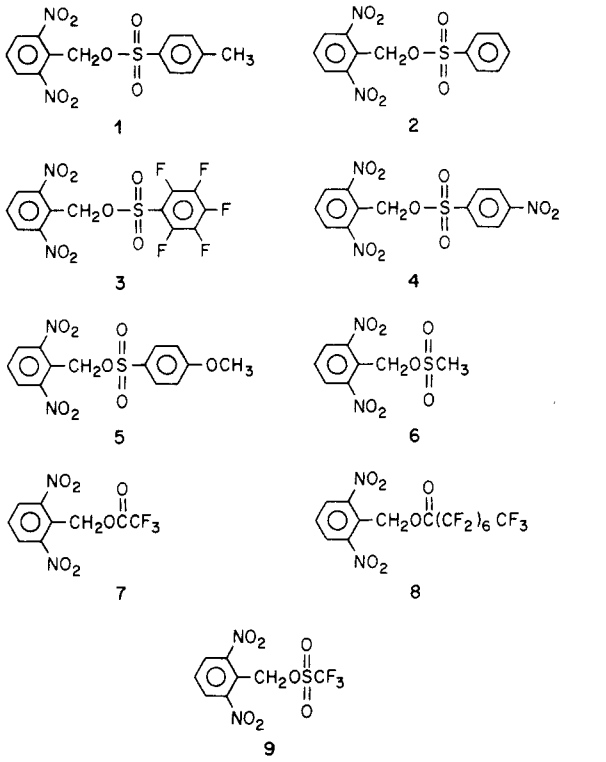
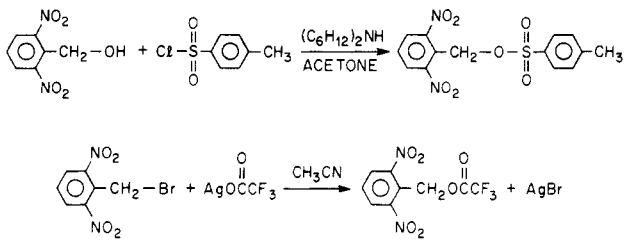


Figure 1. Structures of 2,6-dinitrobenzyl esters.

Scheme I



structures (compounds **1**–**8**) are depicted in Figure 1. Trifluoroacetic acid readily deprotects the *t*-BOC group in solution, but we were concerned about the possible volatility of its ester and loss from thin films upon mild heating. Therefore, the less volatile ester derived from perfluorooctanoic acid was also examined. The nitrobenzyl esters used in this study, with the exception of the trifluoroacetate, were prepared by the reaction of the corresponding acid chlorides with 2,6-dinitrobenzyl alcohol in the presence of dicyclohexylamine as the hydrochloride acceptor (Scheme I). The reactions were carried out at reduced temperature to avoid the possibility of attack by the dicyclohexylamine hydrochloride byproduct on the esters. This problem was particularly severe in the case of the pentafluorobenzenesulfonate derivative **3**. A ^1H NMR study showed that the ester was formed and underwent complete conversion to 2,6-dinitrobenzyl chloride in only a few minutes. This problem was overcome by removal of the dicyclohexylamine hydrochloride immediately after formation. The 2,6-dinitrobenzyl ester of trifluoroacetic acid (**6**) was prepared by the reaction of silver trifluoroacetate with 2,6-dinitrobenzyl alcohol in acetonitrile. Several routes (e.g. reaction of 2,6-dinitrobenzyl bromide or iodide with silver triflate, reaction of 2,6-dinitrobenzyl alcohol with trifluoromethanesulfonic anhydride) to prepare the trifluoromethanesulfonic acid ester **9** were unsuccessful. This result was not unexpected since the trifluoromethanesulfonate moiety is known to be a better leaving group than pentafluorobenzenesulfonate. Compound **3** containing the pen-

Table I
Characterization Data for Compounds 1–8

compd	yield, %	IR, cm^{-1}	^1H NMR, ppm	^{13}C NMR, ppm	mass spectrum, m/e	elemental anal.	C	H	N
1	58	1536, 1365, 1191, 1178, 959	8.04 (d, J = 14 Hz, 2 H), 7.80–7.60 (m, 1 H), 7.71 (d, J = 9 Hz, 2 H), 7.33 (d, J = 9 Hz, 2 H), 5.54 (s, 2 H), 2.44 (s, 3 H)	150.6, 145.7, 131.8, 130.1 (d), 130.0 (d), 128.4 (d), 127.9 (d), 123.9, 62.1 (t), 21.7 (q)	352 (M^+), 197 (M^+ – Ts), 181 (M^+ – OTs), 180 (M^+ – OTs – H), 155 (Ts^+), 122 (M^+ – Ts – H – NO – CO), 91 (C_7H_7)	calcd found	47.73 47.52	3.43 3.36	7.95 7.96
2	72	1536, 1360, 1190, 960	8.27 (d, J = 14 Hz, 2 H), 8.03–7.94 (m, 1 H), 5.60 (s, 2 H), 7.9–7.6 (m, 5 H)	151.5, 136.2, 135.3 (d), 130.5 (d), 129.6 (d), 128.8 (d), 123.2, 63.5 (t)	338 (M^+), 292 (M^+ – NO_2), 197 (M^+ – $SO_2C_6H_5$), 181 (M^+ – $SO_3C_6H_5$), 180(M^+ – H – $SO_3C_6H_5$), 141($SO_2C_6H_5$), 90 ($C_7H_6^+$)	calcd found	46.15 45.96	2.97 2.88	8.28 8.27
3	42	1520, 1480, 1340, 1180, 985, 945	8.45 (d, J = 8 Hz, 2 H), 8.10 (t, J = 8 Hz, 1 H), 5.86 (s, 2 H)	150.7, 146.9, 131.9, 131.8, 128.8, 128.9, 121.7, 63.85, 63.82	428 (M^+), 197 (M^+ – $SO_2C_6F_5$), 183 ($C_6F_5O^+$), 181 (M^+ – $SO_3C_6H_5$), 180 (M^+ – H – $SO_3C_6F_5$), 248 ($HOSO_2C_6H_5^+$), 231 ($SO_2C_6H_5^+$), 167($C_6F_5^+$)	calcd found	36.45 36.16	1.17 1.13	6.54 6.49
4	65	1535, 1365, 1190, 960	8.42 (d, J = 10 Hz, 2 H), 8.25 (d, J = 7 Hz, 2 H), 8.09 (d, J = 10 Hz, 2 H), 7.9–7.8 (m, 1 H), 5.7 (s, 2 H)	152.0, 152.5, 141.5, 133.2, 130.6, (d), 129.9 (d), 125.6 (d),122.5, 64.4 (t)	337 (M^+ – NO_2), 197 (M^+ – $SO_2C_6H_5NO_2$), 186 ($SO_2C_6H_4NO_2^+$), 181 (M^+ – $SO_3C_6H_4NO_2$), 150 (M^+ – H – $SO_3C_6H_4NO_2$ – NO), 122 (M^+ – $SO_2C_6H_5NO_2$ – H – NO – CO)	calcd found	40.73 40.74	2.36 2.33	10.96 10.85
5	75	1530, 1350, 1195, 1180, 980, 1260	7.99 (d, J = 7 Hz, 2 H), 7.74–7.50 (m, 1 H), 7.67 (d, J = 7 Hz, 2 H), 6.91 (d, J = 7 Hz, 2 H), 5.50 (s, 2 H), 3.86 (s, 3 H)	164.3, 150.7, 130.9 (d), 130.3 (d), 128.3 (d), 126.1, 123.7, 114.6 (d),61.9 (t), 55.8 (q)	368 (M^+), 197 (M^+ – $SO_3C_7H_7$), 293 (M^+ – 2NO – CH_3), 188 ($CH_3OC_6H_4SO_3H^+$)	calcd found	45.65 45.66	3.28 3.30	7.60 7.60
6	72	3088, 2948, 1533, 1354, 1176, 945	8.19 (d, J = 8 Hz, 2 H), 7.86 (t, J = 8 Hz, 1 H), 5.66 (s, 2 H), 3.11 (s, 3 H)	150.49, 128.61 (d), 122.8, 62.1 (t), 37.3 (q)	230 (M^+ – NO_3), 197 (M^+ – SO_2CH_3), 181 (M^+ – CH_3SO_3)	calcd found	34.78 34.80	2.92 3.15	10.14 9.66
7	63	1720, 1540, 1360	8.22 (d, J = 8 Hz, 2 H), 7.82 (t, J = 8 Hz, 1 H), 5.81, (s, 2 H)	159.44, 157.5, 155.5, 133.2, 131.5, 128.8, 122.8, 109.9, 60.6		calcd found	36.73 37.01	1.70 1.67	9.52 9.47
8	52	1720, 1540, 1365	8.26 (d, J = 9 Hz, 2 H), 7.87 (t, J = 9 Hz, 1 H), 5.84 (s, 2 H)			calcd found	30.30 30.06	0.84 0.76	4.71 4.91

tafluorobenzenesulfonic acid group was only marginally stable. The stability of these compounds and an explanation for it are discussed in further detail in the next section. The characterization data for the compounds discussed here are listed in Table I.

Thermal Stability. Thermal stability under lithographic processing conditions is a key requirement that any acid photogenerator must satisfy if it is to be considered for use as a resist component. Differential scanning calorimetry (DSC) was used to determine the melting and decomposition temperatures of the esters prepared in this study. The melting point temperatures, T_{mp}, onset of decomposition temperatures, T_d, and decomposition peak temperatures, T_{min}, are shown in Table II, and representative curves for one of the more stable esters **1** together with the curve observed for the least stable material **3** are depicted in Figure 2. These data were used to eliminate the less stable esters such as **3** from consideration. As the lithographic processing temperature can be as high as 120–130 °C, a material that begins to degrade at ~120 °C cannot be used. Even the more stable nitro derivative **4** is only marginally acceptable.

Table II
DSC Data for 2,6-Dinitrobenzyl Esters[a]

compd	T_{mp}, °C	T_d, °C	T_{min}, °C
1	101	197	204
2	127	188	195
3	108	123	134
4	145	158	166
5	121	199	208
6	101	192	198
7	91	261	294
8	104	281	304

[a] T_{mp} is the melting point, T_d is the temperature of onset of decomposition, and T_{min} is the decomposition peak temperature.

Mass spectrometry is another means to examine thermal stability. Compounds **1**, **2**, and **4**–**8** showed mass spectra consistent with the proposed structures and exhibited no signs of degradation upon isothermal heating at 100 °C. The initial spectrum for compound **3** is consistent with the perfluorobenzenesulfonate ester (m/e 428). After a brief interval a mass peak is seen for pentafluorobenzenesulfonic acid (m/e 248), and this peak grows

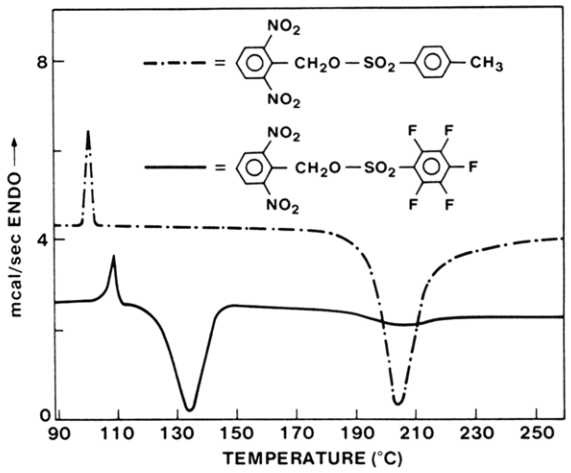


Figure 2. DSC curves for 2,6-dinitrobenzyl tosylate and 2,6-dinitrobenzyl pentafluorobenzenesulfonate.

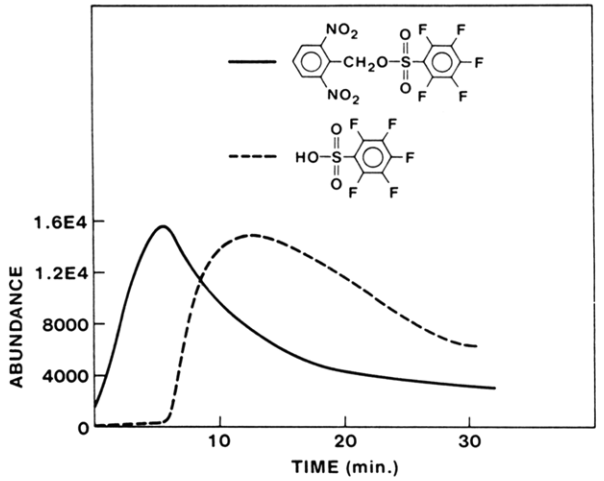


Figure 3. Plot of the ionic abundance versus time for m/e 428 (—) and m/e 248 (- - -) for 2,6-dinitrobenzyl pentafluorobenzenesulfonate.

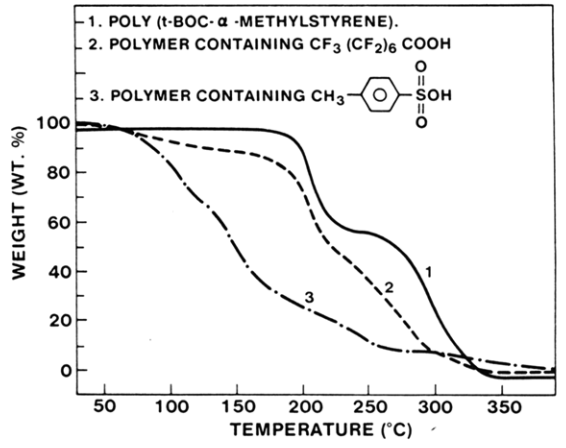


Figure 4. TGA scan of poly(t-BOCoxy-α-methylstyrene) (—) and the parent polymer containing perfluorooctanoic acid (- - -) and tosic (- · -) acid.

in intensity with continued heating. A concurrent decrease in the intensity of the peak assigned to the parent ester is observed. The decomposition behavior is most clearly seen in the plots of ionic abundance versus time for the molecular ions of pentafluorobenzenesulfonic acid and 2,6-dinitrobenzyl pentafluorobenzenesulfonate which is shown in Figure 3. A plausible explanation for the thermal stabilities observed for the series of esters evaluated

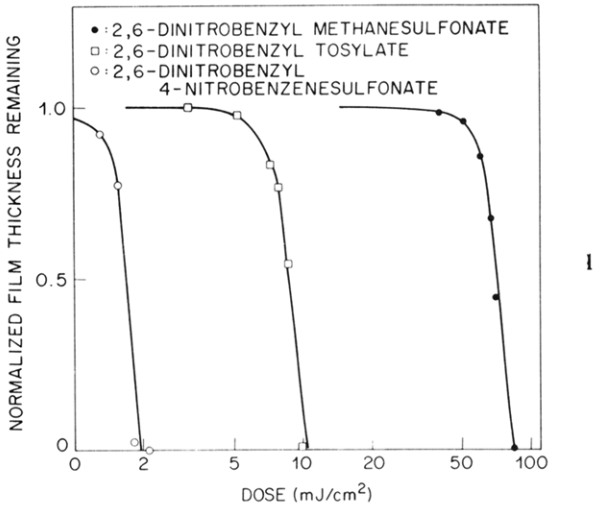


Figure 5. Exposure response curves for poly(t-BOCoxy-α-methylstyrene) containing 2,6-dinitrobenzyl mesylate, 2,6-dinitrobenzyl tosylate, and 2,6-dinitrobenzyl 4-nitrobenzensulfonate.

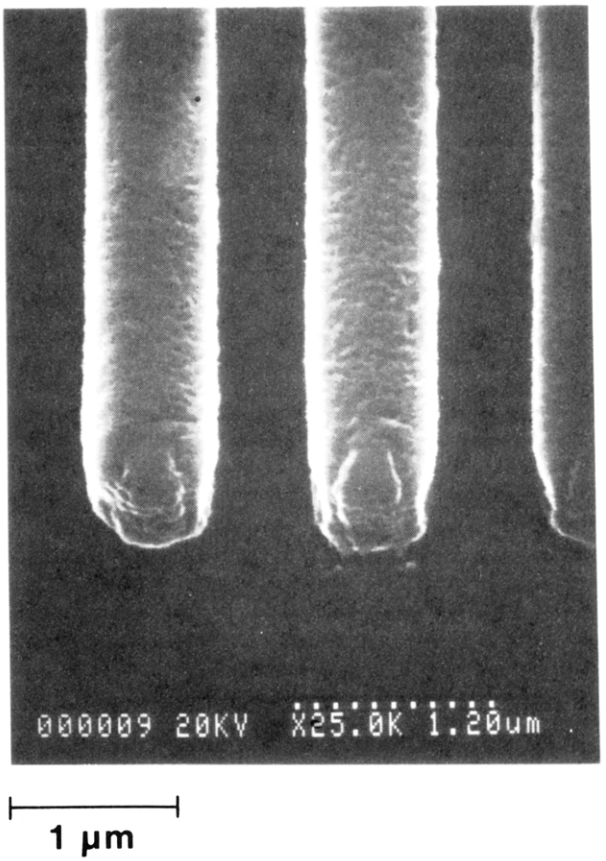


Figure 6. SEM micrograph depicting a coded 0.5 μm by 1.0 μm line/space pattern for the tosylate formulation exposed at 248 nm.

here lies in the ease of intramolecular displacement of the sulfonate moiety by a nitro group. Analogous work[8] involving intermolecular reaction of aniline or substituted anilines with a series of sulfonyl chloride shows clearly that the rates of chloride displacement are strongly influenced by the presence of an electron-withdrawing group in the para position of the sulfonyl chloride (i.e. the rate constant for $NO_2 \gg H > OCH_3$). This phenomenon may lower the thermal stability of both the p-nitro derivative **4** and the pentafluorobenzenesulfonate derivative **3**. Furthermore, it is likely that the expected ther-

Table III
Activation Energies, Quantum Yields, Catalytic Chain Lengths and Resist Sensitivity for Selected Organic Acids

acid	E_a, kcal/mol	Φ	catalytic chain length	resist sensitivity, mJ/cm^2	contrast
triphenylsulfonium hexafluoroantimonate		0.3[11]	1100[11]		
triflic	13.5	0.3	850		
tosic	11.9	0.16	200	10	6
benzenesulfonic	11.8	0.14	250	11	6
4-nitrobenzenesulfonic		0.1	800	2	8
4-methoxybenzenesulfonic		0.1	200	7	7
mesic	11.4	0.15	10	80	6

mal instability of the triflate derivative **9** and, as a consequence, our inability to prepare this compound may be rationalized in terms of the enhanced leaving group character of the triflate ion versus, for example, the marginally stable pentafluorobenzenesulfonate derivative **3**.

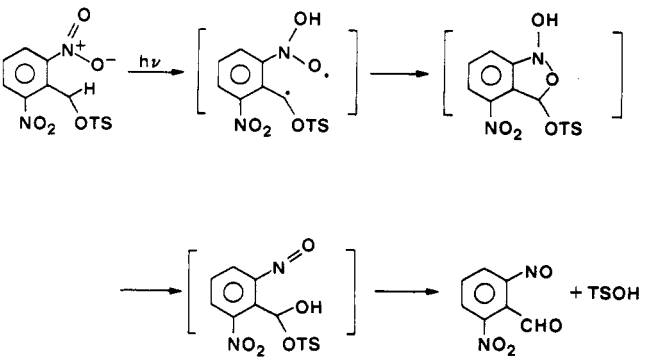
Additional materials characteristics to be considered in developing a lithographic resist system based upon the catalytic removal of a protecting group by photogenerated acid are as follows: the parent acid must effectively carry out the deprotection chemistry in the solid state, and the acid must be photogenerated efficiently. Both of these points are considered below.

Reactivity. Although removal of the acid labile *t*-BOC from a phenol by both sulfonic and fluorinated carboxylic acids is a facile process in solution, it was important to examine the same process in the solid state. Thermal gravimetric analysis (TGA) is particularly well suited for this task. The ease of deprotection of poly(*t*-BOCoxy-α-methylstyrene) by a series of acids known to catalyze *t*-BOC removal in solution was examined in the solid state by TGA. Figure 4 depicts the dynamic TGA scans of poly(*t*-BOCoxy-α-methylstyrene) and that of the polymer containing 5 mol % of tosic acid or perfluorooctanoic acid. It is clear that the incorporation of tosic acid results in a sharp decrease in the temperature required to remove the protecting group. In contrast to this result, the onset of decomposition for the sample containing perfluorooctanoic acid is essentially equivalent to that of the parent polymer. As expected, trifluoroacetic acid volatilized from the samples and meaningful data for *t*-BOC removal by this acid were not obtained. This result suggests that sulfonic acids are more effective than fluorinated carboxylic acids in removing *t*-BOC from poly(*t*-BOCoxy-α-methylstyrene) in the solid state. Within the series of sulfonic acids examined here, the onset of *t*-BOC removal occurs in the same temperature range.

The rate of *t*-BOC removal for representative acids listed in Table III was determined by isothermal studies at 80, 100, and 120 °C. With the assumption of pseudo-first-order kinetics for the initial linear parts of the curves, rate constants for *t*-BOC removal by each acid at the three different temperatures were calculated. From these data, the activation energy for the acid-catalyzed deprotection of the *t*-BOC group was determined. The values are listed in Table III. Although small differences in E_a are observed between the various acids, these differences are not significant within the limits of the experimental difficulty of dispersing the acids homogeneously throughout the polymer matrix. The large differences observed later in the lithographic behavior of the esters cannot be accounted for by differences in the E_a for *t*-BOC removal by the acids.

Quantum Yield Determination. The mechanism of the photoreaction of the nitrobenzyl esters involves insertion of an excited nitro group oxygen into a benzylic carbon–hydrogen bond. Subsequent rearrangement and cleavage generate nitrosobenzaldehyde and the corresponding organic acid (Scheme II). The effect of substitution

Scheme II

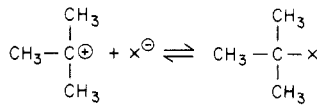


on the nitrobenzyl ring for a series of tosylates and carboxylic acids was examined previously.[4,9,10] It was found that the presence of electron-withdrawing groups on this ring generally decreases the quantum efficiency for photorearrangement to acid. Additionally, the efficiency of photoreaction was found to be lower when the molecular size of the ester moiety was small.[10] Therefore, the efficiency of photogeneration of organic acid from the 2,6-dinitrobenzyl esters of representative acids known to catalyze *t*-BOC removal from the α-methylstyrene polymer was determined quantitatively by excimer laser exposure at 248 nm. The quantum yields are listed in Table III. Surprisingly, no variation in quantum yield was observed with decreasing size of the acid group. The photoefficiency of the methanesulfonate ester was observed to be comparable to that obtained for the larger molecules such as the tosylate ester. Substitution on the aromatic ring does appear to have some effect on the photoefficiency of the reaction. The presence of an electron-withdrawing nitro group on the sulfonic acid moiety decreases the quantum efficiency to 0.1.

Catalytic Chain Length. The effectiveness of any masked acid as a catalyst for removal of the *t*-BOC protective group lies not only in the activation energy required for reaction and the photoefficiency of acid generation but also in the catalytic chain length for deprotection. The IR intensity of the carbonyl stretch of the *t*-BOC group at 1756 cm^{-1} was measured before and after exposure and PEB (120 °C for 4 min) to determine the extent of deprotection, while the quantum yield measurements were used to determine the amount of acid generated. The ratio of these two values then gives the catalytic chain length for polymer deprotection, and the values are given in Table III. The reported values for the quantum efficiency of acid generation from triphenylsulfonium hexafluoroantimonate and the catalytic chain length for *t*-BOC removal of the corresponding acid[11] are also presented in the table. The catalytic chain length for triflic acid was calculated by assuming a quantum yield for generation of the acid from the onium salt precursor of 0.3. It is interesting to note that the aromatic sulfonic acids exhibit reactivity that is an order of magnitude higher than that for the aliphatic methanesulfonate ester, while

the value observed for triflic acid is 850. The reduced acidity and higher nucleophilicity[12] of the methanesulfonic acid may allow it to undergo side reactions in the polymer matrix, thus decreasing its ability to catalyze the removal of the protective group. Specifically, attack of a nucleophilic anion on the *tert*-butyl cation formed as the initial product of deprotection can result in termination and thus (Scheme III) reduce the observed catalytic length for the aliphatic acids.

Scheme III



Lithographic Evaluation. Exposure response curves were generated for ester/poly(*t*-BOCoxy-α-methylstyrene) formulations listed in Table III. Representative curves are shown in Figure 5, and sensitivity and contrast data are presented in the table. The required dose to clear large area features is 100 mJ/cm^2 for 2,6-dinitrobenzyl methanesulfonate using a PEB of 120 °C for 2 min. In contrast to this result, formulations using the same concentration (8.4 mol%) of either 2,6-dinitrobenzyl tosylate or 2,6-dinitrobenzyl benzenesulfonate, under the same processing conditions, required approximately 10 mJ/cm^2 to achieve the same effect. Substitution of the aromatic sulfonic acid ring with the electron-withdrawing NO_2 group affords an increase in sensitivity to 2 mJ/cm^2. One could expect the pentafluorobenzenesulfonate derivative **3** to be even more sensitive than the corresponding *p*-nitrobenzenesulfonate in its lithographic behavior but its low thermal stability renders it unacceptable for this application. The differences in sensitivity for the 2,6-dinitrobenzyl esters examined here result from the lowered nucleophilicity observed for the sulfonic acids and follows the sequence CH_3SO_3H < tosic < *p*-nitrobenzenesulfonic. This sequence is also consistent with the observed catalytic chain length. The nitrobenzyl ester/*t*-BOCoxy-α-methylstyrene resist is capable of high-resolution imaging with good sensitivity. Figure 6 depicts a coded 0.5 μm by 1.0 μm line/space pattern printed in a 1.0-μm thick layer of the tosylate resist formulation. These results are typical of the esters examined here.

Conclusions

The chemistry of a family of 2,6-dinitrobenzyl esters has been investigated and found to be effective acid generators for deep UV chemically amplified resists. These materials photogenerate organic acids which, upon mild heating, catalyze the removal of a *t*-BOC protecting group from poly(*t*-BOCoxy-α-methylstyrene). The thermal behavior of the esters has been examined and the quantum yield determined for selected sulfonate esters. The quantum yield is only slightly affected by the structure of the sulfonate group. A lithographic evaluation of several of the sulfonate esters when used in conjunction with poly(*t*-BOCoxy-α-methylstyrene) has been made. A correlation has been found between the nucleophilicity of the sulfonate anions and the catalytic chain lengths observed for *t*-BOC removal in the lithograhic process. These data have been shown to be related to the lithographic sensitivity of resists formulated with the esters. Sensitivities ranging from 2 to 100 mJ/cm^2 in the deep UV have been observed, and 0.5-μm resolution has been demonstrated.

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Miscibility of Copolymer Blends

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ABSTRACT: The miscibility of two homopolymer–copolymer pairs were studied. In the first pair, poly(4-hydroxystyrene) and poly(*n*-butyl acrylate-*co*-*tert*-butyl acrylate), miscible blends were obtained only when the *n*-butyl acrylate content of the copolymer was 64% or higher. In the second pair, poly(*tert*-butyl acrylate) and poly(styrene-*co*-4-hydroxystyrene), a miscibility window was found when the amount of 4-hydroxystyrene in the copolymer was between 28 and 66 mol %. The results were analyzed with the use of current theories.

Introduction

Many recent studies of the miscibility of a copolymer with a homopolymer made use of a mean-field theory, which considered the pair interaction parameters of all the components in the blend.[1-7] Analysis of experimental data with the above theory has met with success in the prediction of miscibility behaviors.

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