octamine (**20′**) as shown by GPC peak observed at 5.85 count, which agreed with the expected value from the calibration line. But it was rather difficult to separate the product (**20′**) from a large amount of the byproduct diphenylurea.

Acknowledgment. This work was financially supported in parts by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, No. 574700210, a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, No. 60400009, and the 1986 Special Grant-in-Aid from the Ministry of Education, Education and Research, Japan. T.A. acknowledges the support of the Mitsui Interbusiness Institute and Dr. Sekimoto and Kawamurea of Nihon Kayaki Co. for the pharmaceutical tests of some compounds synthesized. We acknowledge T. Ogawa, C. Kubo, R. Itoh, T. Hiramatsu, and S. Morimoto, M. Isozaki, and K. Hirayama of Shimane University for their experiments of the parts of this work.

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Nitrobenzyl Ester Chemistry for Polymer Processes Involving Chemical Amplification

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Received November 9, 1987

ABSTRACT: Three esters, 2-nitrobenzyl, 2,4-dinitrobenzyl, and 2,6-dinitrobenzyl tosylate, were synthesized and evaluated as photoprotected toluenesulfonic acids. These materials are of interest because they are nonionic, highly soluble agents for the deep UV photogeneration of acid and may be particularly useful in certain microelectronic applications where the demand for a low dielectric constant material dictates the use of nonionic materials in processing. The effectiveness of these tosylate esters as photogenerators of acid was evaluated by determining their quantum efficiency and thermal and hydrolytic stability and by comparing the lithographic sensitivities of resist systems consisting of the esters and poly[*p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene]. The quantum efficiencies ranged from 0.02 to 0.18 depending upon nitro substitution patterns and did not change significantly with excimer laser exposure.

Introduction

Photochemically labile protective groups are known to have numerous synthetic applications[1] and have also been shown to exhibit utility in microlithography.[2,3] Materials that generate acidic species are of particular interest for this latter application. Onium salts that photochemically generate strong acids may be employed in chemical amplification resist processes,[4-6] while 2-nitrobenzyl photochemistry has been used in the development of solution-inhibition, deep-UV resists.[3,7-9] Recently, the nitrobenzyl protecting group was utilized in chemical amplification resist systems.[10] An ester-based system exhibits a number of advantages over alternative acid precursors[11] for electronic applications. Specifically, the nitrobenzyl derivatives are easily synthesized, are soluble in a variety of organic solvents, are nonionic in character, and contain no refractory elements such as arsenic or antimony. In addition, their absorption characteristics are well suited for deep-UV exposure. In this study, we examine 2-nitrobenzyl ester photochemistry and its utility in chemical amplification processes. The thermal and solvolytic stability of selected esters is investigated, and the effect of substitution on the quantum yield for acid generation is examined. The results are discussed in relation to the lithographic performance of these materials.

Experimental Section

1. **Materials.** The syntheses of *p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene and its corresponding polymer were adapted from the literature.[4,12] Organic starting materials were obtained from the Aldrich Chemical Co. with the exception of 2,4-di-

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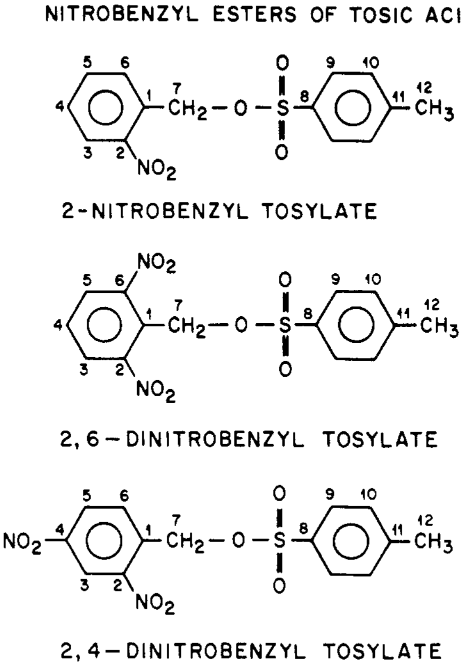


Figure 1. Structural representation of the nitrobenzyl esters of tosic acid.

nitrobenzyl chloride which was obtained from E.M. Science Inc. Poly(methyl methacrylate) (PMMA) (MW 60000) was obtained from the Aldrich Chemical Co. Titration for acid content was accomplished by using a standard sodium carbonate solution and methyl orange as the indicator.

Preparation of 2-Nitrobenzyl Tosylate by Reaction of Silver Tosylate. A solution of 3.50 g (16.2 mmol) of 2-nitrobenzyl bromide dissolved in 10 mL of acetonitrile was added dropwise, in the dark, to a cooled (0–5 °C) solution of 5.74 g (20.6 mmol) of silver tosylate in 57 mL of acetonitrile under dry nitrogen. Upon mixing, a green precipitate of silver bromide was observed. After the addition was complete, the reaction mixture was allowed to slowly return to room temperature, in the dark, and was stirred for 48 h. The reaction mixture was then poured into 100 mL of ice water. The resulting suspension was extracted with 100 mL of ether and the aqueous phase washed several times with 10-mL aliquots of ether. The combined ether washings were dried over anhydrous magnesium sulfate. Filtration, followed by evaporation of solvent, gave the crude product. Recrystallization from methylene chloride/hexane followed by chromatography over silica gel using ethyl acetate as the eluent afforded 3.75 g (75% yield) of white crystals (mp 98–100 °C; lit.[13] 100–101 °C). Mass spectrum: (*m/e*) 307 (M^+), 261 ($M^+ - NO_2$), 197 ($M^+ - NO_2 - SO_2$), 152 ($M^+ - SO_2 - C_7H_7$), 136 (M^+ – OTs), 135 (M^+ – OTs – H), 91 (C_7H_7). IR (cm^{-1}, NaCl): 1520 (NO_2 asymmetric stretch); 1340 (NO_2 symmetric stretch); 1360 (SO_2 asymmetric stretch); 1190, 1180 (SO_2 symmetric stretch); 980 (S–O–C stretch). ^1H NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 8.15 (d, J = 7 Hz, 1 H, H-3); 7.60–7.80 (m, 3 H, H-4–6); 7.88 (d, J = 9 Hz, 2 H, H-9); 7.35 (d, J = 9 Hz, 2 H, H-10); 5.47 (s, 2 H, H-7); 2.44 (s, 3 H, H-12). ^{13}C NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 146.70 (s, C-2); 145.35 (s, C-8); 134.24 (d, C-5); 132.56 (s, C-1); 130.40 (s, C-11); 130.07 (d, C-10); 129.31 (d, C-4); 128.88 (d, C-6); 128.01 (d, C-9); 125.09 (d, C-3); 68.09 (t, C-7); 21.67 (q, C-12).

Preparation of 2-Nitrobenzyl Tosylate by Reaction of Tosyl Chloride. A solution of dicyclohexylamine (9.94 mL, 50 mmol) in 20 mL of acetone was added dropwise, under argon, to a solution of 7.65 g (50 mmol) of 2-nitrobenzyl alcohol and 10.5 g (55 mmol) of tosyl chloride. The temperature was maintained between 20 and 25 °C with cooling. Precipitation of the ammonium salt was observed during the addition. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 2 h. It was then diluted with 50 mL of acetone and the precipitate filtered off and washed with 100 mL of acetone. The filtrate and washings were combined and the solvents were removed. The residue was then recrystallized 3 times from hot carbon tetrachloride to afford 9.85 g (64.2%) of white crystals (mp 98–99 °C) which have spectral characteristics identical with those of 2-nitrobenzyl ester prepared by the previous procedure.

Preparation of 2,4-Dinitrobenzyl Tosylate. A solution of 2,4-dinitrobenzyl chloride (5.00 g, 23.1 mmol) in 10 mL of dry acetonitrile was added dropwise, under argon, to a solution of silver tosylate (8.18 g, 29.3 mmol) in 60 mL of dry acetonitrile. The reaction was stirred at reflux temperature for 2 days. Silver chloride was removed by filtration; the filtrate was concentrated, dissolved in ether (150 mL), and extracted several times with distilled water. After drying over anhydrous magnesium sulfate, the organic layer was filtered and carbon tetrachloride added until crystallization ensued. The resulting brownish crystals (5.1 g) were recrystallized from a mixture of chloroform and ether to give 3.0 g (37%) of light tan needlelike crystals (mp 117–120 °C). Mass spectrum: (*m/e*) 352 (M^+), 306 ($M^+ - NO_2$), 242 ($M^+ - NO_2 - SO_2$), 181 (M^+ – OTs), 180 (M^+ – OTs – H), 155 (Ts^+), 135 (M^+ – OTs – NO_2), 134 (M^+ – OTs – NO_2 – H), 91 (C_7H_7). Anal. C, H, N, S, O: found, 47.52, 3.36, 7.96, 8.97, 31.76; calcd, 47.73, 3.43, 7.95, 9.10, 31.82. IR (cm^{-1}, NaCl): 1539 (NO_2 asymmetric stretch); 1349 (NO_2 symmetric stretch); 1198, 1178 (SO_2 symmetric stretch); 992 (S–O–C stretch). ^1H NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 8.97 (d, J = 2 Hz, 1 H, H-3); 8.52 (d of d, J = 2.25, 8.4 6 Hz), 1 H, H-5); 8.05 (d, J = 8.82 Hz, 1 H, H-6); 7.85 (d, J = 8.4 Hz, 2 H, H-9); 7.41 (d, J = 8.4 Hz, 2 H, H-10); 5.56 (s, 2 H, H-7); 2.46 (s, 3 H, H-12). ^{13}C NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 137.59 (s, C-1); 128.06 (d, C-6); 130.07 (d, C-5); 147.67 (s, C-4); 120.53 (d, C-3); 146.54 (s, C-2); 67.17 (t, C-7); 145.89 (s, C-8); 128.23 (d, C-9); 130.28 (d, C-10); 132.13 (s, C-11); 21.72 (q, C-12).

Synthesis of 2,6-Dinitrobenzyl Alcohol. To a solution of 10.00 g (76.5 mmol) of 2,6-dinitrobenzaldehyde in 75 mL of methanol was slowly added a solution of 1.1 g (29.1 mmol) of sodium borohydride dissolved in 16 mL of 0.2 N NaOH at 10–25 °C. The reaction mixture was stirred at room temperature for 30 min. The methanol was then removed under vacuum and the water residue extracted several times with ether. The ether washings were dried over anhydrous magnesium sulfate and filtered. After removal of solvents and recrystallization from chloroform/carbon tetrachloride, 9.07 g (67%) of tan crystals (mp 96–98 °C; lit.[15] 95 °C) of the desired product was obtained. IR (cm^{-1}, KBr): 3300 (O–H stretch alcohol); 3050 (C–H stretch Ar); 1514 (NO_2 asymmetric stretch); 1350 (NO_2 symmetric stretch). ^1H NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 8.25–7.97 (m, 2 H, Ar H-3,5); 7.70–7.54 (m, 1 H, Ar H-4); 4.95 (d, 2 H, H-7); 4.57 (t, 1 H, O–H). ^{13}C NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 150.82 (s, C-2,3); 130.99 (s, C-1); 129.15 (d, C-5,3); 127.63 (d, C-4); 56.88 (t, C-7).

Synthesis of 2,6-Dinitrobenzyl Tosylate. A solution of dicyclohexylamine (2.25 mL, 11.4 mmol) in 5 mL of dry acetone was added dropwise to a solution of 2,6-dinitrobenzyl alcohol (2.00 g, 11.3 mmol) and tosyl chloride (2.37 g, 12.4 mmol) in 15 mL of dry acetone at 20 °C. After the addition was complete, the reaction mixture was stirred overnight at room temperature. The workup was identical with that for 2-nitrobenzyl tosylate. Recrystallization afforded 2,6-dinitrobenzyl tosylate (2.30 g, 58%) as white crystals (mp 96–98 °C). Analysis (C, H, N, S, O): found, 47.52, 3.36, 7.96, 8.67, 31.76; calcd, 47.73, 3.43, 7.95, 9.10, 31.82. Mass spectrum: (*m/e*) 352 (M^+), 197 (M^+ – Ts), 181 (M^+ – OTs), 180 (M^+ – OTs – H), 155 (Ts^+), 122 (M^+ – Ts – H – NO – CO), 120 (M^+ – H – OTs – 2NO), 91 (C_7H_7). IR (cm^{-1}, NaCl): 1536 (NO_2 asymmetric stretch); 1365 (NO_2 symmetric stretch); 1191, 1178 (SO_2 symmetric stretch); 959 (S–O–C stretch). ^1H NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 8.04 (d, J = 14 Hz, 2 H, H-3,5); 7.6–7.80 (m, 1 H, H-4); 7.71 (d, J = 9 Hz, 2 H, H-9); 7.33 (d, J = 9 Hz), 2 H, H-10); 5.54 (s, 2 H, H-7); 2.44 (s, 3 H, H-12). ^{13}C NMR (ppm, $CDCl_3$) (for the assignments see Figure 1): 150.61 (s, C-2); 145.67 (s, C-8); 131.81 (s, C-11); 130.10 (d, C-4); 130.02 (d, C-10); 128.39 (d, C-9); 127.96 (d, C-3,5); 123.99 (s, C-1); 62.08 (t, C-7); 21.66 (q, C-12).

2. Quantum Yield Determination. The samples for the quantum yield determinations were prepared in the following manner. PMMA (20 wt %) was dissolved in cyclohexanone, and 20 wt % (relative to the polymer) of a nitrobenzyl tosylate or 2-nitrobenzaldehyde was added. The resulting solutions were applied to standard silicon, NaCl, or quartz substrates with a

Headway Research Spinner (Model EC 101). The ester films were baked at 90 °C for 30 min, and the benzaldehyde sample was dried under vacuum at ambient temperature for 30 min. Film thicknesses were measured with a Nanospec AFT film thickness measurement gauge (Model 010 0180) and were in the range 2–3 μm. Absorbances were determined by using a Hewlett-Packard Model 8452A diode array spectrophotometer. 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 between 2 and 20% conversion for each sample.

Continuous light exposures were done by using a Southern New England 50-W low-pressure mercury lamp with a principal output at 254 nm (>95%). As described previously,[7] samples were placed at a distance from the lamp where the light output was found to vary no more than 5% over the exposed area and was in the range 0.4–0.5 mW/cm^2. Light intensities were measured with an Eppley wire-wound copper–constantan thermopile and read-out meter. Pulsed laser exposures carried out by using a Questek Model 2240 KrF excimer laser operating with a primary output at 248.7 nm. The pulse width was ~15 ns and the laser was run at pulse powers varying from 1 to 30 mJ/cm^2 at 1–20 Hz. The laser beam intensity was modulated by using a combination of slits of various sizes and expansion lenses. The beam intensity was measured with a calibrated Scientech calorimeter and digital read-out meter and was found to vary no more than 5% over the exposed areas.

The quantum yields of the three tosylate esters were determined in films of PMMA cast onto NaCl. This was done by monitoring the changes in the IR absorbance spectrum of each film upon UV exposure. The quantum yields were calculated in the following manner. The ratio (NO_2/PMMA) between the peak area under the symmetric NO_2 stretch (1520 cm^{-1}) and the reference carbonyl peak of PMMA (1700 cm^{-1}) was calculated for each tosylate ester before and after UV exposure. The ratio of the values of NO_2/PMMA obtained before and after irradiation, multiplied by a hundred, gives the percent ester remaining after exposure. From this, the percent conversion after UV exposure is found by subtraction. This value is then inserted into the calculation of quantum yield (eq 1), where moles per centimeter is the initial

$$\Phi = \frac{\text{mol/cm}^2 \times \%\ \text{conversion}}{\text{flux(time)} \times \%\ \text{absorbed}} \qquad (1)$$

concentration of ester in the film, flux(time) is the product of the radiation flux multiplied by time in einsteins/cm^2, and, finally, % absorbed is the amount of light absorbed by the film at the wavelength of irradiation.

3. Lithographic Evaluation. Photoresist solutions were prepared by dissolving poly[*p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] (1 g) and the 2-nitrobenzyl ester (0.2 g) into cyclohexanone (10 mL). The solutions were filtered through a stack of 0.5 and 0.2 μm Teflon filters (Millipore Inc.)

Photoresist films were spun onto vapor-primed hexamethyldisilazane (HMDS) treated silicon substrates. The samples were prebaked in a forced-air convection oven.

The resist-coated substrates were exposed by using a Karl Suss Model MA56A, deep-UV contact printer or a GCA Model 4800 step and repeat exposure tool modified for 248.7-nm operation.

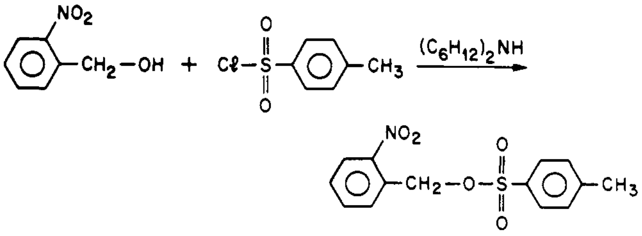
The samples were baked after exposure in an air oven. Development was done in a 1:4 solution of 25% tetramethylammonium hydroxide and distilled water followed by a rinse in distilled water.

All thickness measurements were made by using a Nanospec film thickness gauge (Nanometrics, Inc.) or a Dektak Model IIA profilometer.

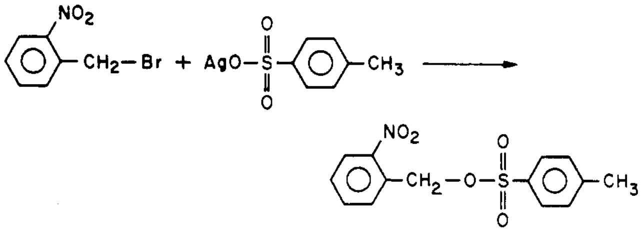
4. Thermogravimetric Analysis. All data were obtained on a Perkin-Elmer System 4 thermal analysis controller and TGS-2 thermogravimetric analyzer. The heating rate was typically at 5 °C/min in air. Isothermal analyses were carried out at 100 °C for 30 min in air.

5. Material Analysis. Nuclear magnetic resonance spectra were obtained on Jeol JNM-FX90Q Fourier transform spectrometer. IR spectra were taken by using a Digilab FTS-60 Fourier transform spectrometer. Mass spectra were obtained by using a HP 5995 mass spectrometer with a direct insertion probe (DIP) heated at 100 °C for 30 min. Elemental analyses were obtained from Galbraith Laboratories Inc.

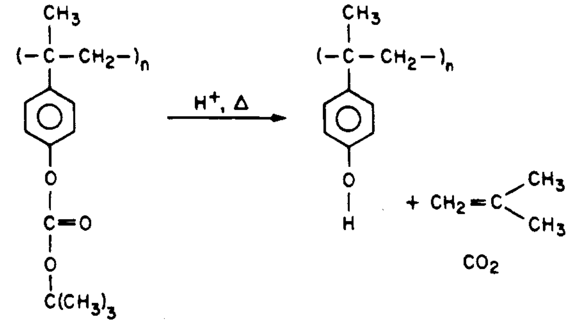
Scheme I



Scheme II



Scheme III



Results and Discussion

Materials. The nitrobenzyl tosylate esters depicted in Figure 1 were prepared by either of two synthetic pathways: the reaction of *p*-toluenesulfonyl chloride with the corresponding alcohol (Scheme I) or the reaction of silver tosylate with the benzyl halide (Scheme II). While both procedures afford the esters in high yield, the former is preferred because silver contamination is avoided.

The use of these materials in chemical amplification resist processes requires that they generate an acid upon photolysis, be stable toward hydrolysis, and be thermally stable. The generation of poly(*p*-hydroxy-α-methylstyrene) from poly[*p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] is known to occur in the presence of catalytic amounts of acid[2] (Scheme III) and is readily confirmed by both IR spectroscopy and a change in dissolution behavior of the polymer. These techniques were used to confirm the photogeneration of tosic acid from the respective esters. As seen in Figure 2, the characteristic *t*-BOC ester band centered at 1756 cm^{-1} is replaced with a hydroxyl absorbance at 3500 cm^{-1} after irradiation of the polymer in the presence of 2-nitrobenzyl tosylate followed by mild heating. This is accompanied by a change in solubility of the polymer from an aqueous base insoluble state to one that is soluble in aqueous media. Similar observations are made for the 2,4- and 2,6-dinitro esters.

Equally important are the hydrolytic and thermal stability of the esters. If even trace amounts of acid are generated in the resist solution prior to irradiation, differential solubility between exposed and unexposed resist will be lost. The question of hydrolytic stability was examined by proton NMR spectroscopy of 2-nitrobenzyl

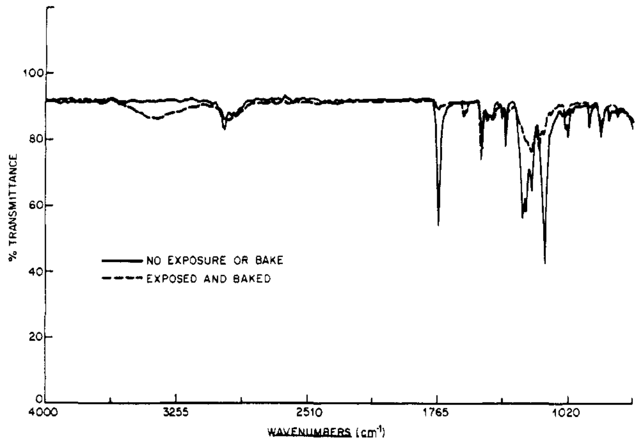


Figure 2. IR scan of 2-nitrobenzyl tosylate/poly[*p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] before and after irradiation followed by a postexposure bake.

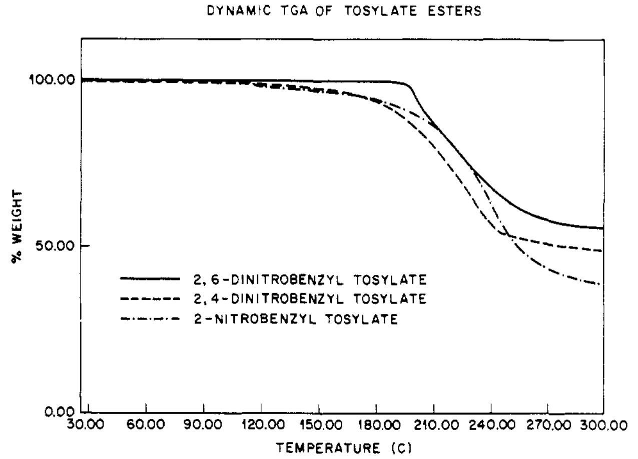


Figure 3. Dynamic TGA scans of the nitrobenzyl tosylates.

tosylate in deuteriated acetone contaminated with water. There is no noticeable change in the spectrum of this ester after several days at room temperature; moreover, hydrolysis is still not detected after 24 h at 50 °C. Titration also revealed no evidence of hydrolysis to tosic acid plus nitrobenzyl alcohol even after prolonged exposure to water at room temperature.

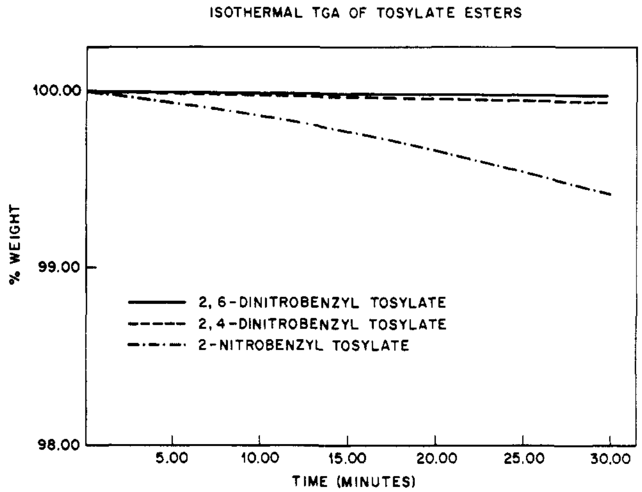


Figure 4. Isothermal TGA scans of the nitrobenzyl tosylates at 100 °C.

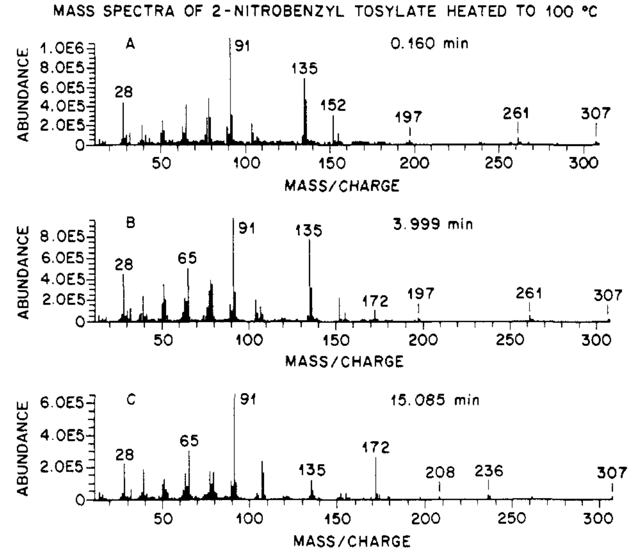


Figure 5. MS study of 2-nitrobenzyl tosylate after heating at 100 °C for 0, 4, and 15 min.

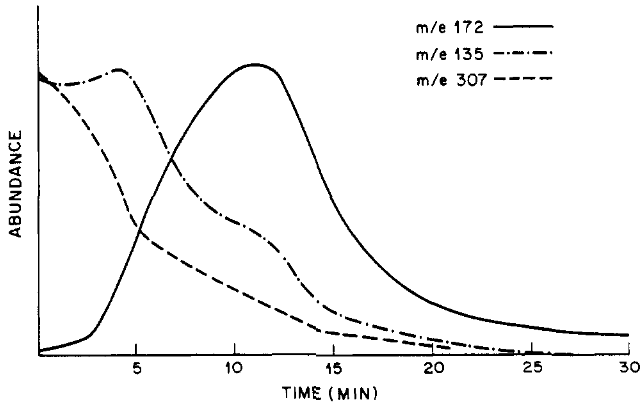


Figure 6. Plot of the ionic abundance versus time for *m*/*e* 307, 172, and 135.

A preliminary, dynamic, thermogravimetric analysis shows that all the tosylate esters exhibit reasonable thermal stability (Figure 3). However, many applications require materials that withstand prolonged exposure at elevated curing temperatures, i.e., 100 °C. Therefore, an isothermal study was done at this temperature for all three materials (Figure 4). This study indicates that 2,4-dinitrobenzyl tosylate and 2,6-dinitrobenzyl tosylate undergo no observable weight loss after half an hour of heating. However, a slow weight loss is apparent in the case of 2-nitrobenzyl tosylate. Moreover, visual examination of the samples after heating indicates that the dinitrobenzyl tosylates remained unchanged, while 2-nitrobenzyl tosylate underwent substantial decomposition. The question of thermal stability was examined more closely by mass spectroscopy. Mass spectra taken at various times during the isothermal heating of 2-nitrobenzyl tosylate (Figure 5) show that, initially, the spectrum is consistent with the ester. After a brief interval, a mass peak is clearly seen for tosic acid (*m*/*e* 172) which grows with continued heating. Also, a marked decrease of the peaks attributed to the ester (Figure 5) is observed. This is most clearly seen in the plots of ionic abundances versus time for the molecular ions of tosic acid (*m*/*e* 172) and 2-nitrobenzyl tosylate (*m*/*e* 307) shown in Figure 6. Concomitant with the appearance of tosic acid is an increase in intensity of the peak at *m*/*e* 135, an indication that a second fragment of mass 135 is being generated. In contrast to this, the 2,4-dinitrobenzyl and 2,6-dinitrobenzyl tosylates show no peak for tosic acid, even after 30 min of heating. The thermal formation of tosic acid from 2-nitrobenzyl tosylate was confirmed by titration. The thermolysis was carried out either by heating the crystalline ester at 100 °C or by

Scheme IV

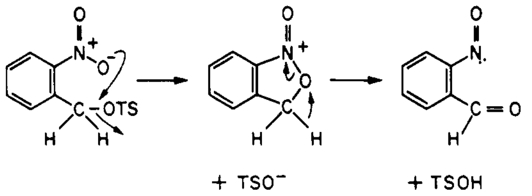


Table I
Quantum Yield Values for 2-Nitrobenzaldehyde and the Nitrobenzyl Esters for 254- and 248-nm Irradiation

material	254[a] nm	248[b] nm	248[c] nm
2-nitrobenzaldehyde	0.5	0.63	0.61
2-nitrobenzyl tosylate	0.04	0.05	0.05
2,4-dinitrobenzyl tosylate	0.02	0.02	0.02
2,6-dinitrobenzyl tosylate	0.18	0.17	0.16

[a] Low-pressure Hg lamp. [b] KrF excimer laser operating at 27 mJ/cm^2/pulse. [c] KrF excimer laser operating at 0.9 mJ/cm^2/pulse.

refluxing a solution of the ester in dry toluene for a period of 1 h. The extent of tosic acid generation was 53% and 15%, respectively.

A plausible mechanism for this reaction that is supported by mass spectral data is an intramolecular displacement of the tosylate moiety by the 2-nitro group to afford tosic acid (m/e 172) and 2-nitrosobenzaldehyde (m/e 135) (Scheme IV). Similar explanations have been proposed for the decomposition of 2-nitrobenzhydryl tosylate.[15] Here, the presence of the second phenyl group activates the tosylate displacement such that the material is decomposed, in situ, during the tosylation reaction. The thermal stability of both 2,4-dinitrobenzyl and 2,6-dinitrobenzyl tosylate is probably due to the introduction of a second nitro group at the para or ortho position, a substitution pattern known to deactivate benzylic substrates toward solvolysis reactions.[16] Moreover, 2,6-dinitrobenzyl tosylate may have its thermal decomposition inhibited by the severe steric constraints inherent in this molecule.

Quantum Yield Determination. The mechanism of the photoreaction of the nitrobenzyl tosylates involves insertion of an excited nitro group oxygen into a benzylic carbon–hydrogen bond. Subsequent rearrangement and cleavage generates nitrosobenzaldehyde and tosic acid (Scheme V).

The efficiency of photogeneration of tosic acid from the three nitrobenzyl esters examined here was determined quantitatively by using both conventional UV light and excimer laser exposure. The quantum yield (Φ) for the photorearrangement of 2-nitrobenzaldehyde to 2-nitrosobenzoic acid was used as a reference. The value of Φ obtained for this rearrangement by conventional UV irradiation is in excellent agreement with that reported in the literature.[8] The values obtained for 248-nm excimer laser irradiation are 20–25 higher and may result from laser-induced heating of the film during exposure[17,18] or from multiphotonic excitation leading to additional reactive pathways for NO_2 loss.[19,20] It is known that the quantum efficiency of this rearrangement is temperature dependent.[21]

In contrast, the quantum yields found for the tosylate esters show less variation when the different exposure methods are used (Table I) and are in close agreement with those reported for the nitrobenzyl trimethylacetate[8] and nitrobenzyl cholate[7] analogues. In addition, the values found for the esters upon excimer laser exposure are nearly the same at dose rates of 1 and 27 mJ/cm^2/pulse. The trends observed for the photoreaction of the tosylate esters are also similar to those reported for the nitrobenzyl carboxylates.[7,8] The presence of an electron-withdrawing group on the benzyl ring generally decreases the quantum efficiency of rearrangement for protected carboxylic acids, as is observed for 2,4-dinitrobenzyl tosylate (Table I), compared with the 2-nitro derivative. As expected from previous results, the 2,6-dinitrobenzylic ester exhibits a significant improvement in Φ. This effect has been attributed to a combination of steric and statistical effects.[7]

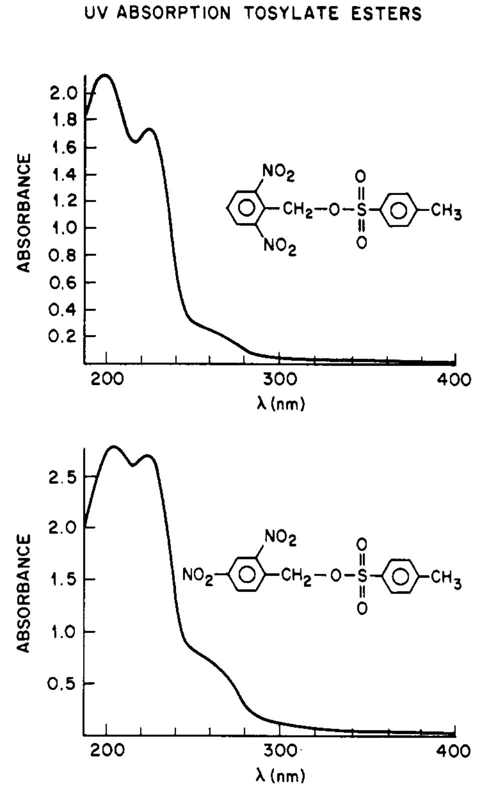
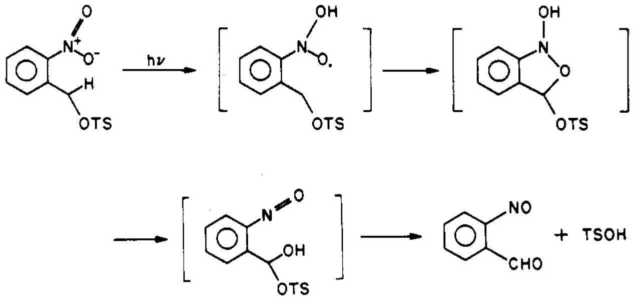


Figure 7. UV absorption spectra of 2,4- and 2,6-dinitrobenzyl tosylate/poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene].

Scheme V



Lithographic Evaluation. The composite nitrobenzyl ester systems are of interest because of their application in deep-UV lithography, particularly for 248-nm excimer laser exposures. We were interested in the lithographic properties of these materials to understand better how to correlate sensitivities determined by using a conventional lamp with those of a pulsed laser light source.

As discussed earlier, the 2-nitrobenzyl ester is thermally unstable and, as a result, is not lithographically useful. The 2,4- and 2,6-dinitro esters exhibit no marked tendency to thermally degrade with time and were therefore evaluated further for utility in a chemical amplification resist scheme.

The UV absorption curves for the ester/poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] formulations are shown in Figure 7. The calculated absorbances at 248 nm

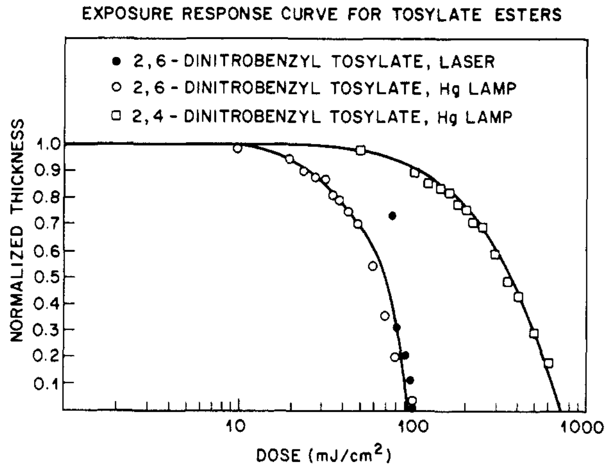


Figure 8. Exposure response curves for 2,4- and 2,6-dinitrobenzyl tosylate/poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene].

Table II
Correlation of the Lithographic Sensitivities of the Dinitrobenzyl Tosylate Resists with Φ

ester	Φ	1/Φ	lithographic sensitivity, mJ/cm^2 (normalized to 1)
2,4-dinitrobenzyl tosylate	0.02	50 (9)	700 (7.8)
2,6-dinitrobenzyl tosylate	0.18	5.5 (1)	90 (1)

for a 5000-Å film are 0.52 and 0.23 for the 2,4-dinitrobenzyl tosylate and 2,6-dinitrobenzyl tosylate systems, respectively. While the latter is higher than desired for high aspect ratio, submicron imaging at 248 nm, the absorbance for the 2,6-dinitrobenzyl ester resist system is sufficiently low to allow near-uniform absorption of light through the thickness of the film and high-resolution imaging.

Exposure response curves were generated for each resist system and are shown in Figure 8. The required dose to clear large area features by using conventional exposure is 700 mJ/cm^2 for the 2,4-dinitrobenzyl tosylate composite. Under similar exposure conditions, the required dose for the 2,6-dinitrobenzyl tosylate system is 90 mJ/cm^2. The large difference in sensitivity in these resist formulations parallels the difference in quantum yields measured for the two esters (Table II). The ester that undergoes more efficient photodecomposition to tosic acid affords the more sensitive resist.

The sensitivity of the 2,6-dinitrobenzyl tosylate/poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] resist was also determined using 248-nm excimer laser exposure. The dose required to clear large area features is 95 mJ/cm^2, a value that is comparable to that obtained with conventional UV irradiation (Figure 8). These results are also in parallel with the quantum yield measurements that indicate no difference in photoreactivity between conventional UV and excimer laser exposure.

Conclusion

Nitrobenzyl tosylate photochemistry was evaluated for its utility in chemical amplification resist processes. Quantum yield measurements indicate that the 2,6-substituted derivative undergoes the most efficient decomposition to tosic acid. The values of Φ measured with low-intensity continuous light at 254 nm did not significantly vary from those determined with high-intensity pulsed laser light at 248 nm. The quantum yields determined with laser exposure were nearly the same at 1 and 27 mJ/cm^2/pulse doses. It was also found that 2-nitrobenzyl tosylate and its derivatives are stable to hydrolysis. However, a thermolysis reaction was found to occur at 100 °C in the parent compound. Of the materials examined here, 2,6-dinitrobenzyl tosylate is the material best suited for chemical amplification resist applications. Lithographic sensitivity and contrast measurements on 2,6-dinitrobenzyl tosylate/poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene] have borne this out. Studies regarding the effects of alternate sulfonic acids and other electron-withdrawing groups are anticipated.

Registry No. 2-Nitrobenzyl tosylate, 20444-09-1; 2-nitrobenzyl bromide, 3958-60-9; silver tosylate, 16836-95-6; 2,4-dinitrobenzyl tosylate, 114719-50-5; 2,4-dinitrobenzyl chloride, 610-57-1; 2,6-dinitrobenzyl alcohol, 96839-34-8; 2,6-dinitrobenzaldehyde, 606-31-5; 2,6-dinitrobenzyl tosylate, 114719-51-6; tosyl chloride, 98-59-9; poly[p-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene], 84775-35-9; tosic acid, 104-15-4.

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