Two acids with torsion angles greater than 60°, 2,5-dichloro-6-methoxybenzoic acid (82.0°) and 2,4,6-triamino-3,5-dinitrobenzoic acid (-66.2°), crystallize as dimers rather than chains. In the structure of 2,5-dichloro-6-methoxybenzoic acid, the methoxy group is rotated nearly perpendicular to the plane of the benzene ring and it is on the same side of the benzene ring as the carbonyl group. The methoxy group sterically hinders the anti lone-pair orbital. The reason for dimer formation in 2,4,6-triamino-3,5-dinitrobenzoic acid is not as obvious. The nitro and amino groups, however, form an extensive hydrogen-bond network that may interfere with the formation of benzoic acid chains.

The torsion angle in 2,6-dimethoxybenzoic acid (-54.7°) is smaller than in the four benzoic acids with syn–anti hydrogen bonds. The structure of this acid is unique because it is the only acid in this study with an anti–anti hydrogen-bond configuration, Figure 7.[31] The anti–anti hydrogen-bond configuration in 2,6-dimethoxybenzoic acid is stabilized by an intramolecular hydrogen bond between the -OH group of the acid and the oxygen of the methoxy group (O···O = 2.853 Å, O-H···O = 105.3°).

Conclusions

A correlation has been established between aggregate inversion symmetry and crystal inversion symmetry, suggesting that hydrogen-bonded aggregates formed in solution direct the crystal growth process. Consequently, acentric aggregate structures promote the formation of acentric crystal structures.

A second correlation has been established between the formation of acentric hydrogen-bonded chains and the presence of ortho substituents on benzoic acids. An ortho substituent that forms intramolecular hydrogen bonds reduces the likelihood of acid dimer formation. Alternatively, two bulky ortho substituents cause the acid group to rotate out of the plane of the benzene ring, so that it is sterically more accessible for chain formation.

These results show that predictions about the symmetry of benzoic acid crystals and the structure of the hydrogen-bonded aggregates can be derived from their molecular structures. It also shows that ortho substitution on a benzoic acid ring can indirectly promote formation of acentric crystals.

Supplementary Material Available: Test questions and refcodes from the CCDF (3 pages). Ordering information is given on any current masthead page.

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Radiation-Induced Chemistry of Poly(4-[(*tert*-butoxycarbonyl)oxy]styrene-*co*-sulfur dioxide)

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Copolymers of 4-[(*tert*-butoxycarbonyl)oxy]styrene (TBS) and sulfur dioxide (SO₂) have been found to act as sensitive X-ray (λ = 14 Å) single-component, chemically amplified, aqueous-base-soluble positive-acting resists. The X-ray response of these materials was a function of copolymer composition and independent of molecular weight. It was observed that increasing the SO_2 content enhanced the resist sensitivity. Initial investigation into the radiation-induced reaction mechanism provided evidence that acid formation occurs via polymer main-chain scission. It is proposed that at the scission sites radical species are produced which in turn are responsible for the formation of the acidic moieties. Heat treatment of resist films after exposure converted copolymers to poly(4-hydroxystyrene sulfone) and permitted exposed film areas to be developed in an aqueous base solution. Preliminary lithographic evaluation has resolved 0.5-μm line and space patterns in 0.65-μm-thick 1.75/1 TBS/SO_2 resist films using an X-ray dose of 10 mJ/cm². No change in X-ray dose was required to resolve the same width feature in the same resist having a film thickness of 1.0 μm.

Introduction

Resist systems based on chemical amplification have provided materials which exhibit both high sensitivity and resolution when used in conjunction with photon and electron-beam lithography.[1-3] To date, these resist systems are multicomponent materials, and the radiation-induced chemistry is substantially different from that which occurs in standard novolac–diazonaphthoquinone photoresist formulations. Central to each chemically amplified resist formulation is an acid-generating species (AGS) which can be ionic or nonionic in nature and is the component that initially responds to the radiation that is used to expose the resist.[1,4] Additional components act

(1) (a) Ito, H., Willson, C. G. In *Polymers in Electronics*; ACS Symposium Series No. 242; Davidson, T., Ed., American Chemical Society: Washington, DC, 1984; pp 11–23. (b) Frechet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Engineering 82*; Grenoble, France, 1982; p 260. (c) Crivello, J. V. In *Polymers in Electronics*; ACS Symposium Series No. 242; Davidson, T., Ed.; American Chemical Society: Washington, DC, 1984; pp 3–10.

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as dissolution inhibitors,[5,6] crosslinking agents,[7,8] and binder resins.[4] In the noncrosslinking systems, location of the acid-labile group on a dissolution inhibitor generally dictates that three species must be present, whereas attachment of this group to a binder or matrix resin reduces the number of components to two. Further simplification is made possible because of the observation that copolymers of 4-[(*tert*-butoxycarbonyl)oxy]styrene (TBS) and sulfur dioxide (SO₂) alone act as highly sensitive X-ray (λ = 14 Å) single-component, chemically amplified, aqueous base-soluble positive-acting resists. An understanding of how the molecular and compositional properties of these materials affect their response to X-rays will be presented. A mechanism proposing why a distinct acid-generating species need not be present in the resist film prior to exposure will be detailed. Evidence for the mechanism will be provided from γ-radiolysis studies conducted on powdered samples and IR spectral analysis of thin-resist films exposed to X-rays. The presence of acidic moieties will be determined by titration techniques which are followed spectrophotometrically. A preliminary lithographic evaluation will indicate the resolution capability and image quality of this resist.

Experimental Section

Materials Synthesis. The monomers, 4-[(*tert*-butoxycarbonyl)oxy]styrene and sulfur dioxide, were obtained from Kodak and Matheson Gas Products, respectively. Prior to polymerization, each monomer was degassed, and sulfur dioxide was further purified by passing it through a column containing phosphorous pentoxide. Poly(4-[(*tert*-butoxycarbonyl)oxy]-styrene) (PTBS) was prepared by thermally initiated solution polymerization methods, and polymers of different molecular weights were synthesized by varying the polymerization temperature and/or initiator concentration.[9] Poly(4-[(*tert*-butoxy-carbonyl)oxy]styrene-*co*-sulfur dioxide) (PTBSS) was prepared by thermal or photoinitiated bulk or solution polymerization techniques. PTBSS of varying composition was obtained by adjusting the polymerization temperature, monomer feed ratio, and initiator concentration. Toluene and/or liquid sulfur dioxide were used as the polymerization solvents. For copolymerizations at or above 40 °C, initiation was commenced using 2,2′-azobis-(isobutyronitrile) (AIBN). At temperatures below 40 °C, polymerizations were either initiated photochemically using a UV light source which was filtered by enclosing the source in a Pyrex sleeve and limiting the light output to above 300 nm or by using radical initiators which decompose at ≤0 °C.

Materials Characterization. The molecular size and distribution properties of PTBS and PTBSS were determined by size exclusion chromatography (SEC). The system configuration consisted of a Waters Model 510 pump (flow rate = 1.0 mL/min.), Rheodyne 7125 injector (50-μL loop), Waters Model 410 differential refractometer detector, and a Viscotek Model 100 differential viscometer detector. The operating temperature of the system was set at 40 °C, and a mobile phase comprising of stabilized tetrahydrofuran was used. A set of Polymer Laboratories PLgel 5-μm particle size MIXC pore type columns was used as the size-separating medium. Data acquisition and analysis were performed by an AT&T 6312 microcomputer equipped with an ASYST Unical 3.02 software system supplied with the Viscotek instrument.

A universal calibration curve was obtained using a set of narrow molecular weight linear polystyrene standards acquired from the Toya Soda Co. Reproducibility and validity of the calibration were checked periodically using a broad molecular weight distribution polystyrene standard sample obtained from the National Institute of Science and Technology (sample I.D. NIST-706).

Sulfur concentration in the copolymers was used to determine the composition of each material. The weight percent of sulfur was determined by X-ray fluorescence as described previously[9] and by elemental analysis performed by Gailbraith Laboratories, Knoxville, TN.

Glass transition temperatures (T_g) and the thermal decomposition temperature (T_d) in N₂ of the polymers were determined using a Perkin-Elmer DSC-7 differential scanning calorimeter and TGS-7 thermogravimetric analyzer, respectively. The temperature scan rate for both the DSC and TGA experiments was 10 °C/min, and the N₂ (99.99 % purity) flow rate was 20 cm³/min. For T_g determinations, sample masses ranged between 10 and 12 mg and for T_d measurements samples masses were in the range 2–4 mg.

X-ray Lithographic Response. PTBS and PTBSS resist solutions (5–20 w/v %) were prepared by dissolving the polymers in ethyl 3-ethoxypropionate, cyclohexanone, or chlorobenzene. The solutions were filtered no less than two times through a filter stack consisting a 1.0-, 0.5-, and 0.2-μm average pore size Millipore Teflon filters. Resist films in the range 0.4–1.1-μm thickness were spin coated onto 3- and 4-in. silicon substrates at spin speeds ranging from 1100 to 4000 rpm. The resist films were baked after coating at 105 °C for 2 min on a Machine Technology Inc. (MTI) vacuum hot plate. Film thicknesses were measured using Sloane Dektak Model IIA and Tencor Alpha Step 200 profilometers and a Prometrix Spectra Map SM 200 interferometer. Prior to resist coating, the silicon substrates were vapor primed using hexamethyldisilazane in a Yield Engineering Systems (YES) oven for 5 min at 90 °C.

X-ray (λ = 8–22 Å centered at 14 Å) exposures in helium (O₂ content ≤200 ppm) were performed using a Hampshire Instruments series 5000 point source proximity print stepper. The laser pulse rate was set at 0.3 Hz, and the flux was measured to be 0.3–0.6 mJ/cm²/pulse. An X-ray mask having a structure consisting of a 0.4-μm gold absorber layer on top of a 1.0-μm silicon membrane was used for patterning purposes.

The resist films were postexposure baked (PEB) on an MTI vacuum hot plate at temperatures ranging from 120 to 140 °C for 2.5–4.0 min. Film thickness loss resulting from exposure and baking was measured using a profilometer.

The exposed and baked films were immersion developed in a 0.17 N tetramethylammonium hydroxide (TMAH) solution for 30 s and rinsed for 20 s in deionized water. The minimum dose (D_s) necessary to completely develop a 100 × 150 μm X-ray exposed area was used as the reported sensitivity for the PTBS and PTBSS polymers investigated. A Hitachi Model 570 scanning electron microscope (SEM) operating at 15 or 20 kV was used to take photomicrographs of the developed resist images.

Conversion of PTBSS to Poly(4-hydroxystyrene sulfone). The extent of the loss of the *tert*-butoxycarbonyl (*t*-BOC) group as a function of X-ray dose was calculated by recording FT-IR spectra of postexposure baked PTBSS films spun onto silicon wafers which had been polished on both sides. FT-IR spectra were obtained using a Mattson Instruments Inc., Galaxy Series Model 8020 spectrometer, in the single-beam mode.

Chain Scission Efficiency. Powdered samples of PTBSS and PTBS were irradiated at room temperature in the air with cobalt-60 γ-radiation. The dose rate was 0.45 Mrad/h. After irradiation the molecular weight of the exposed materials was measured by SEC. The change in the number average molecular weight ($\bar{M}_n$) as function of γ-irradiation dose was then used to determine $G(s)$, which represents the number of scission events for every 100 eV of energy absorbed by the irradiated material.

Identification of the Radiation-Generated Acidic Species. A 1.4-mg powdered sample of the 2.1:1 TBS:SO₂ copolymer was γ-irradiated (dose = 3 Mrad) and was dissolved in 2.5 mL of cyclohexanone containing the sodium salt of tetrabromophenol blue (TBPB) acid/base indicator. UV–visible absorption spectra of the TBPB solutions with and without the γ-irradiated copolymer were taken on a Hewlett-Packard 8452A diode array spectrophotometer. The measured change in absorbance of TBPB

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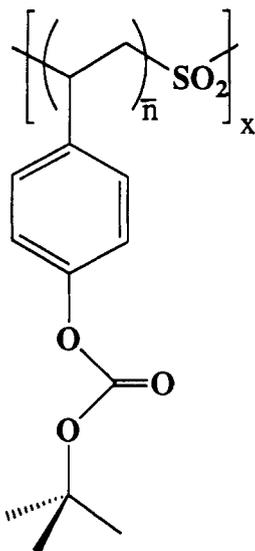
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Figure 1. Structural representation of the repeat unit in PTBSS resists.

Figure 2. X-ray exposure response curves for PTBSS resists of different composition.

Table I. PTBS and PTBSS Material Properties

composition (TBS:SO$_2$)	wt % sulfur	$10^{-5}\bar{M}_w$,[a] g/mol	MWD[b]	T_g, °C	T_d, °C
1.75:1	7.10	3.53	2.70	168	171.5
2.1:1	6.27	4.74	1.88	165	170
2.6:1	5.00	1.00	1.90	160	166.5
2.6:1	5.00	9.00	2.00	163	176
2.81:1	4.62	2.14	1.89	159	169
3.75:1	3.59	2.50	1.98	151	174
1:0		1.07	1.60	127	192

[a] $\bar{M}_w$ = weight average molecular weight. [b] MWD = $\bar{M}_w/\bar{M}_n$.

at 610 nm recorded from the two spectra was used to calculate the amount of acid present in the γ-irradiated sample by correlating the change to a linear calibration of the TBPB absorbance versus known amounts of strong acid added to the solution.[10] A correction to the total change in absorbance at 610 nm was made by subtracting from this change the loss of absorbance at 610 nm from a solution containing an equal amount of the nonirradiated 2.1:1 TBS:SO$_2$ copolymer.

Results and Discussion

Materials Synthesis and Characterization. A series of PTBSS copolymers of varying composition where the average value of n ($\bar{n}$) = 1.75–3.75 in Figure 1 and the TBS homopolymer were prepared. Selected elemental, molecular, and thermal properties of these materials are listed in Table I. In the cases of the 2.1:1 to 3.75:1 TBS:SO$_2$ copolymers the variation in copolymer composition was achieved by adjusting the reaction temperature from 40 to 65 °C and feed ratio of the monomers in the range of 1:1 to 10:1 SO$_2$:TBS. As previously reported,[9] a decrease in reaction temperature and/or use of excess SO$_2$ as the copolymerization solvent increases the incorporation of SO$_2$ into PTBSS. To obtain a copolymer having a TBS:SO$_2$ ratio less than 2, two approaches were investigated. The first consisted of radical initiation by decomposing trichloroacetyl peroxide at 0 °C. FTIR analysis of the copolymers obtained revealed that ~40% of the t-BOC groups were removed. Conversion of t-BOC is a result of the presence of trichloroacetic acid, a byproduct of the thermolysis of the peroxide. An attempt to decrease the partial deprotection of the copolymer was made using heptafluorobutyl peroxide (HFBP) as the initiator. The expected byproducts resulting from the decomposition of HFBP are nonacidic. In this case, a bimodal molecular weight distribution of the copolymer resulted, and further
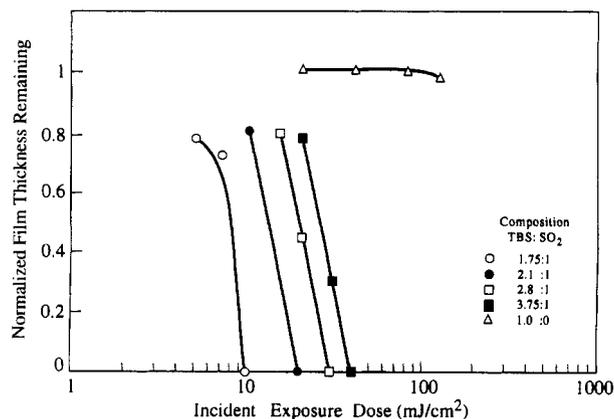
attemps to use peroxide initiators were abandoned. The second approach involved initiation using UV light.[11] The reaction temperature was set at 0 °C and these conditions yielded a copolymer having a 1.75:1 TBS:SO$_2$ composition. IR spectral data confirmed the absence of any hydroxyl functionality in the copolymer. This approach may provide a viable method for achieving a copolymer having a 1:1 TBS:SO$_2$ ratio. To investigate the effect of molecular weight on the exposure response of these materials, 2.6:1 TBS:SO$_2$ copolymers having a weight average molecular weight of 1.0 and 9.0 × 10^5 g/mol were prepared.

From the data in Table I, the T_g values increased with increasing SO$_2$ content in the copolymer. A comparison of the 1.75:1 to the 3.75:1 TBS:SO$_2$ copolymer indicates a 17 °C increase in the T_g. The higher T_g for higher SO$_2$ content copolymers can be used to increase the lithographic sensitivity of these materials by virtue of the ability of the partially patterned images to remain dimensionally stable at postexposure bake temperatures which are greater than what can be used for the two-component resist system consisting of a 3:1 TBS:SO$_2$ copolymer and a nonionic acid generator.[12] Table I also indicates that the T_d values at constant molecular weight will decrease as SO$_2$ is incorporated into the PTBS homopolymer. A comparison of the T_d values of PTBS vs the 2.6:1 TBS:SO$_2$ copolymer of approximately the same molecular weight indicates a decrease of ~26 °C. Table I additionally reveals that the T_d values for the copolymers at constant composition increased with increasing molecular weight. For example, the 2.6:1 TBS:SO$_2$ copolymer showed an ~10 °C increase in T_d as the $\bar{M}_w$ was increased from 1 to 9 × 10^5 g/mol.

X-ray Lithographic Performance. Effect of Copolymer Composition. The X-ray exposure response curves for the TBS homopolymer and for PTBSS having a composition ranging from 1.75:1 to 3.71:1 TBS:SO$_2$ are shown in Figure 2. The initial film thickness and postexposure hot plate bake conditions were 0.5 μm and 140 °C for 2.5 min, respectively. A 4-fold increase in the minimum dose necessary to dissolve a 100 × 150 μm exposed area in the 0.17 N TMAH developer was observed as the ratio of TBS:SO$_2$ in the copolymers increased from 1.75:1 to 3.75:1. The former exhibited a D_s value of 10 mJ/cm^2, whereas the latter had a value of 40 mJ/cm^2. These results differ from what was observed for the TBS homopolymer where no change in film thickness due to

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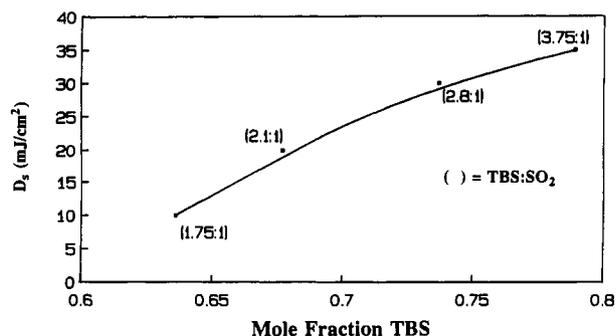
Figure 3. Plot of D_s taken from Figure 2 versus mole fraction of TBS in the copolymer.
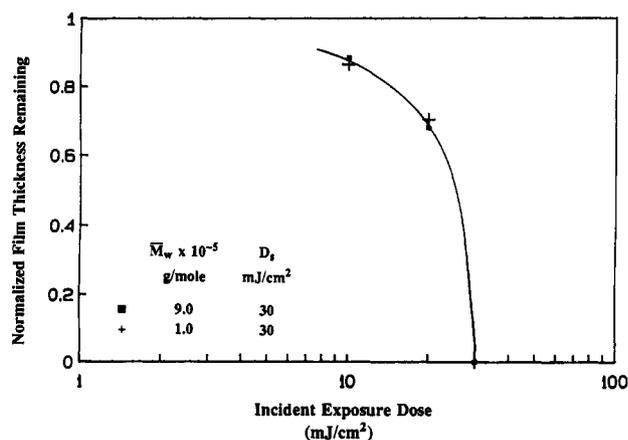

Figure 4. X-ray exposure response curves for 2.6:1 TBS:SO$_2$ copolymers at different initial weight average molecular weights.

the PEB and development step was found even for X-ray doses up to 120 mJ/cm^2. The slight thickness change that was observed for PTBS resulted solely from the exposure. At a dose of 120 mJ/cm^2 approximately 3% of the initial film thickness was lost. This loss is a direct result of the removal of the *tert*-butoxycarbonyl group during the exposure. The resulting small percentage of hydroxyl groups formed in the homopolymer were ineffective in catalyzing the deprotection reaction during the subsequent postexposure bake step. It is therefore clear that the presence of sulfur dioxide in the copolymer and postexposure baking at temperatures approaching 140 °C afford the observed high X-ray sensitivity.

Figure 3 represents a plot of D_s as a function of mole fraction of TBS (X_{TBS}) in the copolymer. This figure can be used to project what the X-ray sensitivity for copolymers having a X_{TBS} < 0.64 will be. For the case when X_{TBS} = 0.60 (1.5:1 TBS:SO$_2$) the value for D_s obtained from linear extrapolation of the region of the curve in Figure 3 corresponding to X_{TBS} ≤ 0.675 is ~3 mJ/cm^2. Preparation of a 1:1 TBS:SO$_2$ copolymer would provide for the highest posible sensitivity, but the decrease in solubility observed for copolymers ≤0.66 mol fraction TBS may result in a material that would be difficult to image and process.

For the X-ray PTBSS process, no measurable thickness loss in the nonexposed areas was observed when comparing the initial resist film thickness to the thickness remaining after development. This is consistent with the reported thermal properties of PTBSS in that the postexposure bake temperature is below the onset temperature for thermal decomposition in air for all PTBSS compositions investigated.[9]

Effect of Copolymer Molecular Weight. The influence of molecular weight on the X-ray exposure response
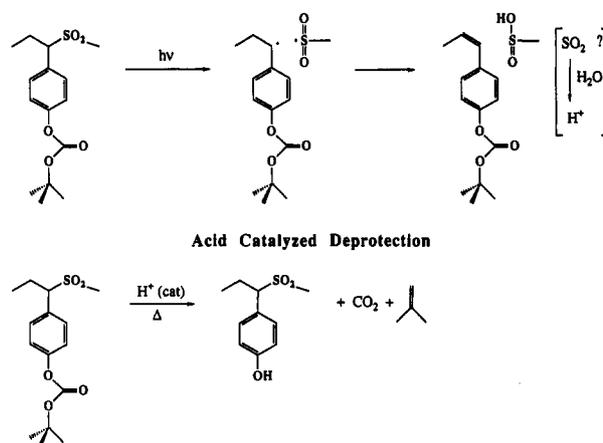
Scheme I
Radiation Induced Chemistry

Acid Catalyzed Deprotection

Table II. Change in Molecular Weight of a 2.1:1 TBS:SO$_2$ Copolymer as a Function of γ-radiation Dose

dose, Mrad	$10^{-5}\bar{M}_n$, g/mol	dose, Mrad	$10^{-5}\bar{M}_n$, g/mol
0	2.52	11	.23
3	.38	21	.12

of a 2.6:1 TBS:SO$_2$ copolymer is given in Figure 4. When postexposure baking the films at 140 °C for 2.5 min, the D_s value for the materials covering a molecular weight range of (1–9) × 10^5 g/mol remained constant at 30 mJ/cm^2. The X-ray exposure response of this resist can, therefore, be considered independent of molecular weight over the range investigated. These results should be representative of what would occur for all compositions prepared and should also lead to simplifying both the formulating and processing considerations of these resists.

Mechanism for Acid Generation. Scheme I depicts the proposed X-ray-induced reaction mechanism. Exposure to both forms of radiation results in homolytic cleavage of the carbon–sulfur bond which in turn produces benzylic and sulfonyl radical species. The latter species provides the source for the formation of acidic moieties, whereby a certin percentage of the radicals abstract a hydrogen from the solid matrix to form sulfinic or sulfonic acid groups which become the ends of the fragmented polymer chains. The remaining percentage of the sulfur-containing radicals can undergo desulfonylation generating sulfur dioxide which can then subsequently react with a proton source in the film to produce sulfurous or sulfuric acid. In a subsequent heating step, the acidic moieties catalyze the thermolysis of the *tert*-butoxycarbonyl group to form the aqueous base-soluble polymer, poly(4-hydroxystyrene-*co*-sulfur dioxide) (PHSS). The occurrence of main-chain scission and the evolution of gaseous products resulting from γ-radiolysis of olefin sulfones have been previously reported by Brown and O'Donnell,[13,14] and these results provide justification for the proposed PTBSS radiation-induced degradation mechanism.

Evidence for Main-Chain Scission. Solid samples of a 2:1 TBS:SO$_2$ copolymer were γ-irradiated in air at doses ranging from 3 to 21 Mrad. The molecular weight data obtained for the nonirradiated and irradiated samples are summarized in Table II. An approximate 7-fold decrease in the $\bar{M}_n$ can be seen for the sample irradiated at the

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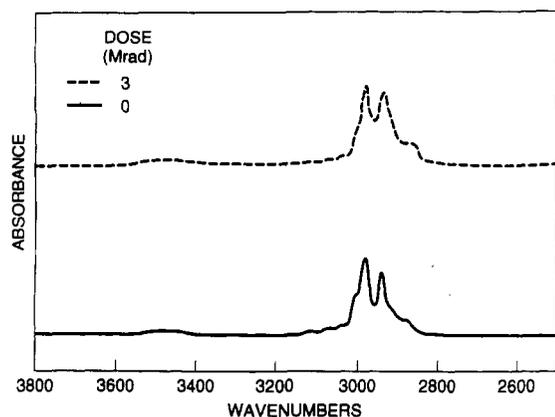(14) Brown, J. R.; O'Donnell, J. H *Macromolecules* 1972, *5*, 109.

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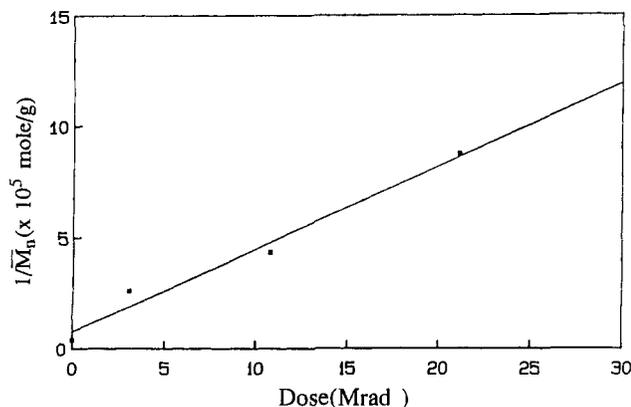**Figure 5.** IR spectra of a γ-irradiated (3 Mrad) and nonirradiated powdered sample of the 2:1 TBS:SO₂ copolymer.

Figure 6. Plot of reciprocal $\bar{M}_n$ vs absorbed dose for the 2.1:1 TBS:SO₂ resist.

Figure 7. UV-visible spectra of a TBPB cyclohexanone solution before (−) and after (- -) the addition of 1.4 mg of γ-irradiated 2.1:1 TBS:SO₂ resist.

Figure 8. IR spectra of X-ray exposed and nonexposed regions of a 2.8:1 TBS:SO₂ resist film.

Table III. X-ray Exposure Results for a 2.8:1 TBS:SO₂ Copolymer

exposure dose, mJ/cm²	% t-BOC groups removed	dissolution[a] (+/−)
10	26.5	−
20	80.8	−
40	96.5	+

[a] + = soluble.

lowest dose of 3 Mrad. Increasing the dose to 21 Mrad further decreased the value of $\bar{M}_n$ by 68%. To ascertain that the change in $\bar{M}_n$ was not due to the partial conversion of PTBSS to PHSS upon exposure, IR spectra in the region 2600–3800 cm⁻¹ for the sample irradiated at 3 Mrad and for a nonirradiated sample are compared in Figure 5. No difference in absorption intensity at 3500 cm⁻¹ between the two samples was observed, confirming that the decrease in molecular weight is solely due to the polymer backbone fragmentation.

The value of $G(s)$ was obtained by plotting the reciprocal of $\bar{M}_n$ as a function of absorbed dose. The $G(s)$ was taken to be proportional to the slope of the line in Figure 6 and for the 2.1:1 TBS:SO₂ copolymer was equal to 3.6.

Presence of Acidic Moieties. The amount of acid produced in a γ-irradiated 2.1:1 TBS:SO₂ copolymer sample was determined by following spectrophotometrically the protonation of the sodium salt of tetrabromophenol blue after the irradiated polymer was added to the solution.[10] A calibration curve was established by plotting the absorbance of TBPB at 610 nm as a function of varying amounts of titrant added. A 10⁻⁴ N HCl solution was used as the titrant, and aliquots of 10 μL up to a total of 80 μL were added. This total addition resulted in a 0.037 decrease in absorbance for every millimol of titrant added. Figure 7 portrays the absorption spectra in the region 300–800 nm for the TBPB solution in cyclohexanone before and after the addition of 1.4 mg of the γ-irradiated 2.1:1 TBS:SO₂ copolymer.

After subtracting the change in absorbance resulting from the initial presence of some partially deprotected PTBSS from the recorded change in absorbance observed
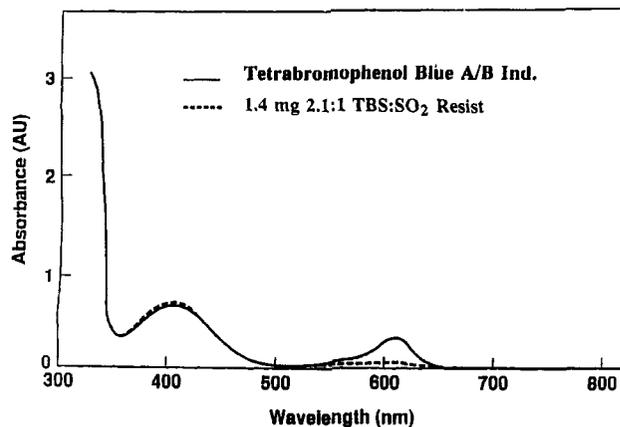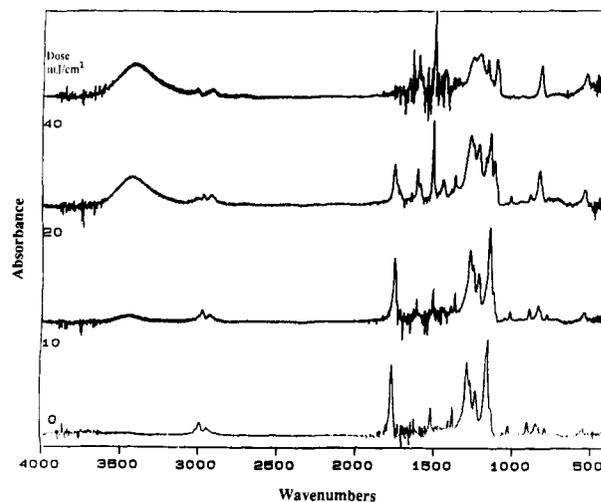
after the addition of the exposed copolymer, the final absorbance value was 0.26 and corresponded to the production of 7.0 × 10⁻⁶ mmol of acidic moieties. If it is assumed that the amount of acid produced per unit absorbed dose is constant, the G value for acid formation G(acid), which is the total number of acidic moieties produced for every 100 eV of energy absorbed by the irradiated copolymer, is calculated to be 1.6. The ratio of G(acid) to the G(scission) therefore represents a measure of the efficiency of acid generation at each scission site. For the 2.1:1 TBS:SO₂ copolymer, the ratio was calculated to be 0.45, indicating nearly 50% efficiency.

Evidence for PHSS Formation. The formation of PHSS was confirmed by analyzing IR spectra taken of X-ray exposed regions of a thin film of a 2.8:1 TBS:SO₂ copolymer which had been postexposure baked at 140 °C for 2.5 min. Table III lists the X-ray dose, the corresponding percentage of t-BOC groups removed, and whether the exposed areas at the given dose were soluble in the aqueous base developer.
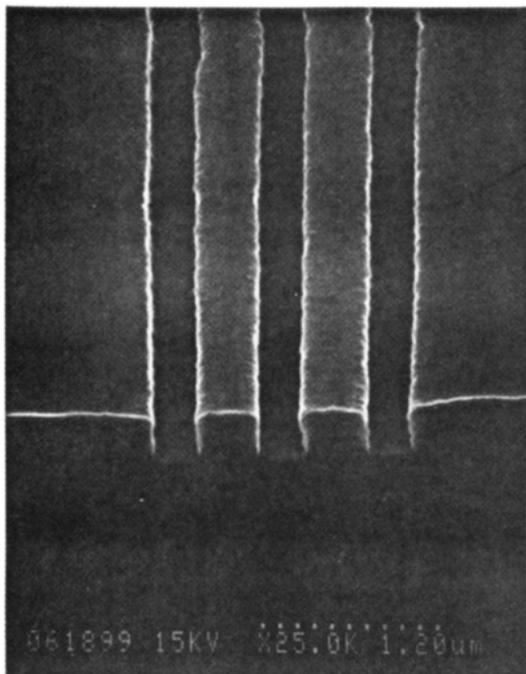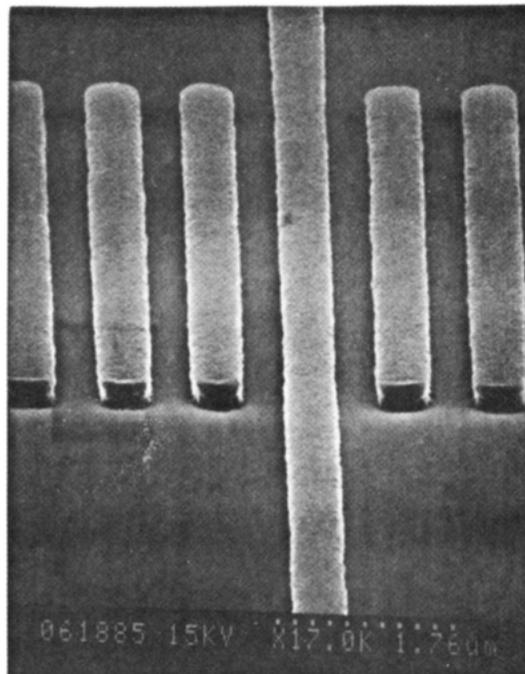
CODED 0.4 μm LINE/SPACE

CODED 0.5 μm LINE/SPACE

Figure 9. SEM photomicrographs of coded 0.4- and 0.5-μm line/space patterns formed in 0.5-μm-thick 2.1:1 TBS:SO$_2$ resist using an X-ray dose of 25 mJ/cm^2.

Figure 8 represents the IR spectra of the exposed and nonexposed regions of the resist film. The appearance and increase in absorption at 3500 cm^{-1} with increasing exposure dose is indicative of the presence of PHSS. Additional minor contributions to this absorption may result from the hygroscopic nature of PHSS and from the presence of any acidic moieties remaining in the film.

The percent conversion of the *t*-BOC group was determined by integrating the area of the carbonyl absorption band (1676–1876 cm^{-1}) of the exposed and baked film regions, and normalizing it to that region of the spectrum corresponding to the nonexposed portions of the film. Table III indicates that for a dose of 40 mJ/cm^2 and a 140 °C for 2.5 min PEB, greater than 95% of the *t*-BOC groups are removed. This represents the minimum percentage which is required for the exposed regions of the resist film to be soluble in the aqueous base developer. Previous studies have confirmed the need to achieve high *t*-BOC conversion for aqueous base development and this phenomenon has also been used to explain the high contrast values which have been reported for resists based on PTBS and PTBSS.[15]

Preliminary Lithographic Evaluation. For all X-ray exposures, the minimum mask feature size used for patterning was 0.4 μm. Figure 9 depicts scanning electron microscope (SEM) photomicrographs of coded 0.4- and 0.5-μm line and space (l/s) patterns formed in 0.5-μm-thick 2.1:1 TBS:SO$_2$ resist using an X-ray dose of 25 mJ/cm^2. No change in exposure requirements for this resist was found necessary to resolve equivalent size features in a 1.0-μm initial resist film thickness. Figure 10 depicts an SEM photomicrograph of coded 0.5-μm l/s patterns delineated in the 1.75:1 TBS:SO$_2$ resist using a dose of 10 mJ/cm^2. For both resists, the pattern profiles achieved were approximately 90°, and adhesion of all resist features
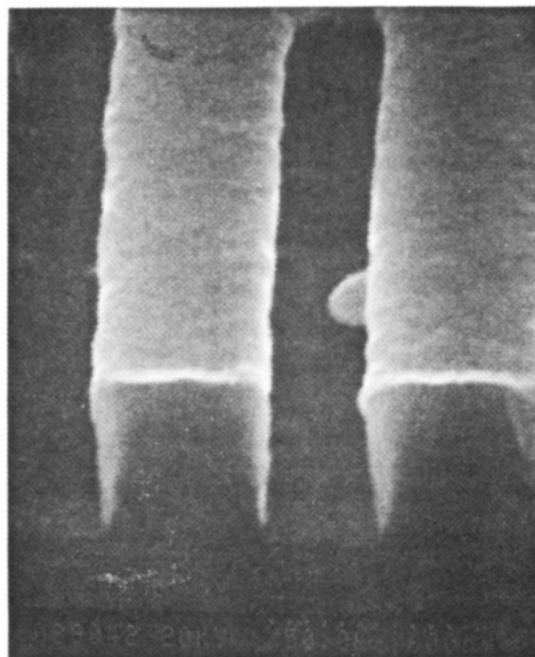
(15) Nalamasu, O.; Cheng, M.; Kometani, J. M.; Vaidya, S.; Reichmanis, E.; Thompson, L. F. *Proc. SPIE Adv. Resist Technol. Processing VII* **1990**, *1262*, 32.

CODED 0.5μm LINE/SPACE

Figure 10. SEM photomicrograph of a coded 0.5 μm l/s patterns formed in 0.65-μm-thick 1.75:1 TBS:SO$_2$ resist using an X-ray dose of 10 mJ/cm^2.

to the silicon substrates used was acceptable.

Conclusions

Copolymers of 4-[(*tert*-butoxycarbonyl)oxy]styrene and sulfur dioxide have been shown to function as sensitive X-ray (λ = 14 Å), single-component, chemically amplified, aqueous-base-soluble positive-acting resist materials. No evidence of these properties was observed for the homo-

polymer poly(4-[*tert*-butoxycarbonyl)oxy]styrene) even when exposed to X-ray doses which were more than 100% higher than those used to develop images in the least sensitive PTBSS copolymer.

For the PTBSS copolymers, the X-ray response was shown to be a function of copolymer composition and independent of molecular weight. It was observed that increasing the sulfur dioxide content enhanced the resist sensitivity.

The X-ray-induced reaction mechanism is proposed to be initiated via copolymer main-chain scission. At the scission sites, radical species are produced which in turn are responsible for the formation of acidic moieties. Such moieties may exist as either sulfinic or sulfonic acid end groups of the fragmented polymer chain. Likewise, it is reasonable to assume that the acidic moieties may exist as free molecules such as sulfurous or sulfuric acid. The ratio of G(acid) to that for G(scission) has shown that approximately 50% of all scission sites produce an acid moiety which is subsequently used during the deprotection reaction.

Preliminary lithographic evaluation of these materials demonstrated that for a 1.75:1 TBS:SO$_2$ copolymer, the X-ray dose necessary to resolve 0.5-μm features is 10 mJ/cm^2 and is independent of the initial film thickness of the resist. Approximately 90° pattern profiles are observed for these features, and this is largely attributable to the extremely high contrast (>6) of these materials. High contrast is postulated to result from the fact that dissolution in the aqueous base developer does not occur until at least 95% of *t*-BOC groups have been removed. It can therefore be expected that the dependence of line width on development conditions will be minimized or that changing the normality of the developer or increasing the development time should have little or no effect on line width.

Further studies elucidating the structure of the acid species will be conducted, and the knowledge gained will be applied to resist formulations used in photolithographic technologies.
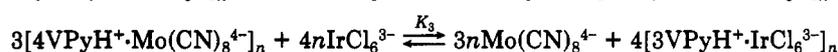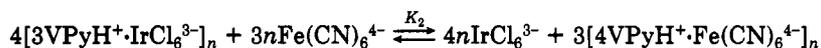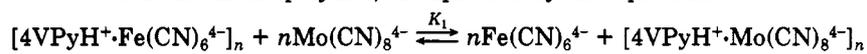
Use of Rutherford Backscattering Spectroscopy To Investigate Anion Exchange Constants of Protonated Poly(4-vinylpyridine)

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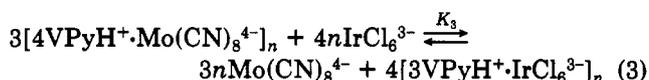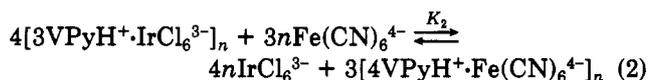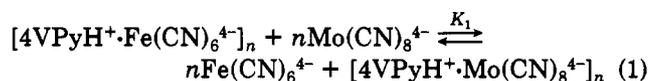
Rutherford backscattering spectroscopy (RBS) can be used to measure the competitive electrostatic binding of two anionic metal complexes in protonated poly(4-vinylpyridine), $(VPyH^+)_n$. RBS was done using a 2–3-MeV He$^+$ or He^{2+} ion beam from a tandem accelerator. The elemental composition was measured for polymer films of <0.5-μm thickness coated onto carbon substrates. Anions such as Fe(CN)$_6^{4-}$, Mo(CN)$_8^{4-}$, and IrCl$_6^{3-}$ can be persistently electrostatically bound into the $(VPyH^+)_n$, and the resulting polymer films can be quantitatively analyzed by RBS. The equilibrium constants for the equilibria between two metal complexes in the solution and in the polymer, as expressed by the equations

$$[4VPyH^+\cdot Fe(CN)_6^{4-}]_n + nMo(CN)_8^{4-} \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} nFe(CN)_6^{4-} + [4VPyH^+\cdot Mo(CN)_8^{4-}]_n$$

$$4[3VPyH^+\cdot IrCl_6^{3-}]_n + 3nFe(CN)_6^{4-} \underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} 4nIrCl_6^{3-} + 3[4VPyH^+\cdot Fe(CN)_6^{4-}]_n$$

$$3[4VPyH^+\cdot Mo(CN)_8^{4-}]_n + 4nIrCl_6^{3-} \underset{\longleftarrow}{\overset{K_3}{\longrightarrow}} 3nMo(CN)_8^{4-} + 4[3VPyH^+\cdot IrCl_6^{3-}]_n$$

can be determined using RBS analysis of surface composition and knowledge of the solution concentrations of metal complexes used to modify the surface. The product $(K_1^3 K_2 K_3)$ of the three measured constants is very close to the expected value of 1. RBS data correlate well with polymer composition established by electrochemical measurements, but RBS data are more quantitative. The electrochemical data are not as reliable, due to overlapping electrochemical responses of the anionic metal complexes.

We wish to report use of Rutherford backscattering spectroscopy (RBS) to establish essential features of the composition of polycationic films on carbon substrates. In particular, we demonstrate use of RBS to measure the relative concentration of anionic metal complexes in protonated poly(4-vinylpyridine), $(VPyH^+)_n$. The data are useful for determining equilibrium constants for anion exchange processes such as those shown in eqs 1–3. The

$$[4VPyH^+\cdot Fe(CN)_6^{4-}]_n + nMo(CN)_8^{4-} \underset{\rightleftharpoons}{\overset{K_1}{\longrightarrow}}$$
$$nFe(CN)_6^{4-} + [4VPyH^+\cdot Mo(CN)_8^{4-}]_n \quad (1)$$

$$4[3VPyH^+\cdot IrCl_6^{3-}]_n + 3nFe(CN)_6^{4-} \underset{\rightleftharpoons}{\overset{K_2}{\longrightarrow}}$$
$$4nIrCl_6^{3-} + 3[4VPyH^+\cdot Fe(CN)_6^{4-}]_n \quad (2)$$

$$3[4VPyH^+\cdot Mo(CN)_8^{4-}]_n + 4nIrCl_6^{3-} \underset{\rightleftharpoons}{\overset{K_3}{\longrightarrow}}$$
$$3nMo(CN)_8^{4-} + 4[3VPyH^+\cdot IrCl_6^{3-}]_n \quad (3)$$

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