Macromolecules **1993,** *26,* 2165–2170

A Novel Approach to Inducing Aqueous Base Solubility in Substituted Styrene–Sulfone Polymers

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Received September 14, 1992

ABSTRACT: This paper describes the synthesis of a new terpolymer, poly[(*tert*-butoxycarbonyloxy)styrene acetoxystyrene sulfone], and provides spectroscopic evidence for the chemical reactions this polymer is capable of undergoing. The (*tert*-butoxycarbonyloxy)styrene undergoes acidolysis of the *tert*-butoxycarbonyl moiety in the solid state in the presence of a strong acid. If this acid is generated by exposure to UV light, this reaction can form the basis for imaging this polymer. The acetoxy group can be cleaved from the acetoxystyrene monomer in aqueous base solution only when sulfone is incorporated into the copolymer in the appropriate amounts. After cleavage by base the resulting polymer is soluble in the base solution only if the *tert*-butoxycarbonyl group has been removed by acid. The polymer has been designed in a novel manner such that each monomer of the copolymer fulfills a different function. IR and NMR studies which emphasize and explain the role of sulfone in facilitating acetoxy hydrolysis are presented.

Introduction

Considerable research efforts are now focused on discovering and designing polymers to be used in resist formulations for submicron lithography.[1] These materials are essential to meet the needs of the electronics industry as the trend toward increased device elements and reduced feature size continues. Several lithographic schemes being considered for the production of features in integrated circuits involve the use of UV light to create solubility differences in polymeric matrices. In general, a polymer used in these schemes must contain a sufficient fraction (>50%) of a unit which undergoes a chemical reaction upon UV exposure to provide the required solubility change. Poly[(*tert*-butoxycarbonyloxy)styrene sulfone] (PTBSS)[2,3] has been shown to be an effective matrix resin for deep-UV chemically amplified[1,4,5] resist formulations. This polymer is 75 mol % (*tert*-butoxycarbonyloxy)styrene (TBS) and 25 mol % sulfone. When mixed with a photoacid generator (PAG), which produces a strong acid upon exposure to UV light, the *tert*-butoxycarbonyl (*t*-BOC) moiety is cleaved by the acid, yielding the aqueous base soluble poly(hydroxystyrene sulfone). The cleaved *t*-BOC exits the polymer film as CO_2 and isobutene gas and results in a 40 wt % loss as compared to the original polymer. Such a weight loss is undesirable and may be the cause of adhesion failure sometimes associated with this polymeric resin.[6] A program was, therefore, initiated to design polymers which are capable of producing the required solubility changes while undergoing minimum weight loss. The simplest approach to achieve this end involving preparation of a hydroxystyrene–TBS–sulfone terpolymer was abandoned due to the synthetic difficulty of incorporating the hydroxystyrene monomer. Alternative strategies were thus required.

In devising these alternatives, it is important to realize that TBS actually serves two functions in the polymer. First, this unit renders the polymer acid sensitive and, as such, it may be used as the basis for imaging upon exposure to UV light. Second, the TBS provides the basis for the solubility change required to delineate exposed and unexposed regions. Historically these two functions, imaging and solubility change, have been fulfilled by the same monomer although there is no scientific need for this. In devising a novel scheme to effect both imaging and a solubility change in a given polymer, we decided to allow these two functions to be fulfilled by two different monomers. We retained TBS as the imaging monomer and incorporated acetoxystyrene for producing the solubility changes. When copolymerized with sulfur dioxide and TBS, the acetoxy moiety is capable of cleavage in aqueous base, yielding hydroxystyrene. Base cleavage of the acetoxy group only occurs when sulfur dioxide is incorporated into the polymer and in the exposed areas of the film where TBS has undergone acidolysis to produce hydroxystyrene. Without base cleavage of the acetoxy moiety, the exposed polymer is not base soluble and thus acetoxystyrene is required for the needed solubility changes. By incorporating acetoxystyrene into the polymer, the concentration of TBS, and therefore the weight loss in the solid film, can be significantly reduced. This paper describes the synthesis of poly[(*tert*-butoxycarbonyloxy)styrene acetoxystyrene sulfone] (PATBSS). We also provide spectroscopic evidence for the base cleavage of the acetoxy moiety. This paper also presents new evidence and understanding as to why the presence of sulfone is required for aqueous base cleavage of the acetoxy moiety.

Experimental Section

Materials Synthesis. All of the polymer candidates were prepared by free radical copolymerization or terpolymerization using 2,2′-azobis(isobutyronitrile) (AIBN, Alfa Chemical Co., Inc.) as the thermal initiator. The inhibitor-free monomer, TBS, was obtained from Kodak and was used as received. The acetoxystyrene monomer, which was inhibited with 25 ppm of phenothiazine, was purchased from Hoechst-Celanese Corp. The monomer was distilled under vacuum (75 °C, 0.05 Torr) immediately prior to polymerization to separate it from the inhibitor. Anhydrous sulfur dioxide (SO_2) was obtained from Matheson Gas Products. The SO_2 was passed through a column of phosphorus pentoxide, condensed through the vacuum line into a graduated flask, and then distilled into the reaction vessel. The polymerizations were carried out both in bulk and also by using liquid SO_2 and/or toluene as diluents. The PTBSS polymer was prepared as described in the literature.[2,3] Similarly, the terpolymer PATBSS was synthesized by a thermal, free radical, solution polymerization of acetoxystyrene, TBS, and SO_2 using AIBN as the initiator.

Syntheses of the photoacid generator (PAG) and thermal acid generator were carried out as described in the literature.[5,7,8]

Polymerization Description. (1) Preparation of PATBSS. The bulk and solution polymerizations were carried out

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in a heavy-walled Kjeldahl flask modified with a vacuum/pressure stopcock allowing for the addition of monomer under vacuum and the transfer and distillation of degassed SO_2. Freshly distilled acetoxystyrene (20 g, 0.1266 mol) and degassed TBS (27 g, 0.1266 mol) were transferred under vacuum into the modified Kjeldahl reactor flask and placed in a −78 °C bath. Under vacuum, a mixture of AIBN (0.81 g, 0.005 mol) and 10 mL of toluene was syringed into the reactor, and the injection port was washed with an additional 15 mL of toluene. The SO_2 was distilled under vacuum into a graduated flask (−78 °C) and degassed by a freeze/thaw method. The measured SO_2 (0.5517 mol, 22 mL at −78 °C) was then distilled into the reactor, which was sealed off. The reactor was placed into a 65 °C bath. The reaction was quenched after 4 h by cooling (0 °C) and by the addition of acetone (~100 mL). The polymer was precipitated from the reaction liquid by adding it dropwise into 4 L of 2-propanol/methanol (1:1 v/v). The polymer was purified by redissolution into acetone and precipitated from the 2-propanol/methanol two times, followed by drying in a vacuum oven at room temperature. The average yield was 60%.

(2) Preparation of Poly[acetoxystyrene(*tert*-butoxycarbonyloxy)styrene) (PATBS). The procedure was similar to that for the preparation of PATBSS except for the elimination of the SO_2.

Dissolution of the Polymer in Aqueous Base. Solutions containing the polymer (15 wt %) and an acid generator (10% by weight of polymer) were prepared in 2-methoxy ethyl ether and spin-coated onto 4-in. silicon substrates. If a photoacid generator was used, the wafers were preexposure baked at 105 °C for 1 min and then given an exposure of 30 mJ/cm^2 prior to a postexposure bake (PEB) of 125 °C for 1 min. Exposures were carried out using either a Süss Model MA56A contact aligner equipped with a Lambda Physik excimer laser operating at 248 nm or a GCA prototype Laser Step deep-UV exposure tool operating at 248 nm. Films prepared from polymers containing a thermal acid generator (2-nitrobenzyl tosylate[7]) were baked at 80 °C for 30 s to mimic the preexposure bake step and then heated to 125 °C for 3 min to liberate acid as in the PEB step. After acid generation, the polymer was removed from the substrate with 1.5 mL of aqueous tetramethylammonium hydroxide (TMAH, 1 part of TMAH (25 wt % in water) to 4 parts of water). Dissolution was complete after 1 min. The base solution of polymer was neutralized with 0.5 mL of acetic acid, diluted with 5 mL of water, and shaken with 5 mL of pentane. This procedure extracted the neutralized polymer into a pentane–water emulsion which was filtered to recover the polymer. The polymer was then washed with several aliquots of water and dried under vacuum overnight. This process was carried out on 15 substrates to obtain 30 mg of polymer. To ensure that acetic acid was not responsible for the experimental results, the base solution was diluted with water and shaken with pentane. This did not prove effective in extracting the polymer. It was, therefore, necessary to allow the water/pentane to evaporate overnight in order to study the polymer.

Resist Formulation. Solutions were prepared by dissolving the photoacid generator[5] into ethyl 3-ethoxypropionate (EEP), and then the matrix polymer (15 wt/vol %) was added to the EEP–photoacid generator solution. The solutions were then filtered through a series of 1.0-, 0.5-, and 0.2-μm Teflon membrane filters, spin-coated onto silicon substrates, and baked at 105 °C for 2 min. The resist-coated substrates were then exposed by using a GCA Laser Step deep-UV exposure tool operating at 248 nm. After exposure, the substrates were postexposure baked at 115 °C for 20–60 s on a hot plate equipped with a vacuum hold-down chuck. The exposed and baked films were then developed in 0.17–0.5 N TMAH for 2 min. Resolution and image quality were determined by examining developed patterns with a JEOL Model 35CSF scanning electron microscope (SEM).

Materials Characterization. Size exclusion chromatography (SEC) was used for determination of the molecular weight (M_w) and molecular weight distribution (MWD) of PTBSS and PATBSS. The eluting solvent was tetrahydrofuran (THF) at 35 °C (flow rate 1 mL/min). A Waters Model 510 pump (column pressure = 1000 psi) was used in conjunction with a Waters Model 410 differential refractometer detector and a Viscotek Model 100 differential viscometer detector. A set of Polymer Laboratories DL-gel, 5-mm particle size MIXC pore type columns was employed. A universal calibration curve was obtained using a set of narrow MWD linear polystyrene standards supplied by Polymer Laboratories, Ltd. Data acquisition and analysis were performed by an AT&T 6312 microcomputer equipped with a 12-bit A/D card and an ASYST Unical 3.14 software system supplied with the Viscotek instrument.

Thermal analysis data were obtained using a Perkin-Elmer TGA-7 thermogravimetric analyzer interfaced with a TAC-7 thermal analysis controller and a PE-7700 data station. TGA samples were heated at a rate of 10 °C/min with a purified N_2 gas flow of 20 cm^3/min. TGA was used to characterize polymers with respect to composition, degree of *t*-BOC loss, temperature of *t*-BOC loss, and decomposition temperature.

Sulfur concentrations were determined by X-ray fluorescence (XRF), employing the sulfur Kα X-ray line (2.308 keV). The X-ray fluorescence measurements were made on an AT&T Bell Laboratories X-ray milliprobe spectrometer[2] with an accuracy of 5%.

The elemental analyses (C, H, S) of the sulfur-containing polymers were determined by Galbraith Laboratories, Knoxville, TN, and Schwarzkopf Microanalytical Laboratory, Woodside, NY. Oxygen was determined by difference.

Fourier transform infrared spectrometry (FTIR) was performed on a Mattson Instruments Galaxy Series 8020 FTIR spectrometer in dual-beam mode. FTIR was used to monitor the extent of deprotection of TBS in the polymers. With deprotection, the carbonyl band at 1760 cm^{-1} decreased in intensity and a hydroxyl stretch at 3500 cm^{-1} appeared.

The ^{13}C NMR spectra were recorded at 50 °C on a JEOL GX-500 spectrometer at a resonance frequency of 125 MHz. Quantitative spectra were obtained with gated decoupling without the nuclear Overhauser effect with 20 wt % samples in chloroform-*d*. The base-developed polymer extracted from the silicon wafers was run at 2 wt % in dimethylformamide-d_7: a pulse delay of 12 s and 10 000 scans were required to achieve adequate signal to noise. When base development was carried out directly in an NMR tube, poly(acetoxystyrene hydroxystyrene sulfone) (100 mg) was dissolved in 3 mL of a 20 vol % solution of TMAH (20 wt % in methanol) in D_2O. Additional TMAH was added (0.6 mL) for complete acetoxy cleavage.

^{1}H NMR experiments were done on a General Electric QE 300 FT NMR spectrometer. Samples (2 mg) of poly(acetoxystyrene hydroxystyrene sulfone) and samples of base-developed polymers from both the irradiation experiments with a substituted nitrobenzyl benzenesulfonate ester and the thermolysis experiments with 2-nitrobenzyl tosylate were dissolved in DMF-d_7.

Results and Discussion

Materials Synthesis and Characterization. Polymer characteristics such as molecular weight, molecular weight distribution, and composition are known factors that must be controlled to achieve reproducible lithographic performance in a given material.[9] Thus, the effects of PATBSS and PATBS polymer composition and M_w due to various reaction conditions such as temperature, monomer feed ratio, and monomer and initiator concentration were studied using bulk and solution polymerizations. The M_w of the terpolymer varied inversely with the reaction temperature, as shown in Table I. Increasing the reaction temperature from 55 to 65 °C changes the M_w from 198K to 100K, indicating the need to have good temperature control throughout the reaction to obtain a given M_w. Table I shows that the incorporation of SO_2 into the polymer backbone is also temperature dependent: the lower the temperature, the higher the SO_2 incorporation. These results are similar to those obtained from PTBSS[1] and indicate that the polymerization mechanism is similar. The styrene monomer ratio in PATBSS is largely identical to that in the original feed. This result is in contrast to what is found for the non-SO_2-containing copolymer, PATBS, where feed ratios ranging from 30/70 to 48/52 TBS/acetoxystyrene afford approximately 1:1 copolymers (Table II). As expected, the ratio of the initiator, AIBN, to styrene monomers influ-

Table I
Characterization of Poly[4-acetoxystyrene 4-(*tert*-butoxycarbonyloxy)styrene sulfone] (PATBSS)

sample	TBS/AS[a] feed	comp	reacn temp (°C)	MW	styrene:SO_2	T_g (°C)
			Reproducibility			
1	50/50	48/52	65	100K	2.8:1	148
2	50/50	50/50	65	98K	2.8:1	147
3[b]	50/50	50/50	65	100K	3.0:1	140
			Temperature			
4	50/50	50/50	55	198K	2.4:1	151
5[c]	50/50	50/50	55	171K	2.3:1	149
6	50/50	50/50	40	220K	2.1:1	154
			Feed			
7	0/100	0/100	65	87K	2.7:1	128
8	40/60	45/55	65	114K	2.7:1	146
1	50/50	48/52	65	100K	2.8:1	148
9	60/40	60/40	65	104K	2.8:1	144
10	70/30	70/30	65	86K	2.7:1	143
			Bulk vs Solution Polymerization			
11[d]	50/50	47/53	65	185K	2.6:1	148
1	50/50	48/52	65	100K	2.8:1	148

[a] AS is defined as 4-acetoxystyrene. [b] This synthesis utilized AS as received from the supplier. [c] Increased SO_2 feed. [d] Bulk.

Table II
Characterization of Poly[4-acetoxystyrene 4-(*tert*-butoxycarbonyloxy)styrene] (PATBS)

sample	TBS/AS feed	comp	reacn temp (°C)	MW
1	48/52	48/52	50	7200K
2	30/70	45/55	65	140K
3	20/80	0/100	65	65K

ences the M_w of the polymer. The higher the concentration of initiator, the lower the M_w.

Individual markers for each component of PATBSS in the ^{13}C NMR spectra are integrated to obtain the overall polymer composition of TBS and AS in the polymer along with the sulfone content and the triad sequence distributions. The carbonyl (168.90 ppm) and methyl (21.12 ppm) resonances of the acetoxy functional group and the quaternary (83.53 ppm) and methyl (28.07 ppm) resonances of the *t*-BOC group are well-resolved resonances that serve as internal markers for calculating composition (Figure 1). The chemical shifts of the α and β backbone carbons in the aliphatic spectral region do not change with the addition of the acetoxy functional group compared to the PTBSS polymers.[2]

The thermal characteristics of PATBSS are comparable to those of the PTBSS analog. Onset of thermal *t*-BOC removal occurs at 188 °C for PATBSS versus 178 °C for PTBSS. Response of the polymer to subsequent heating is similar, confirming the thermal stability of the acetoxy appendage. The glass transition of the acetoxystyrene-containing polymers is also comparable to those obtained for the TBS–sulfone copolymers (Table I).

The resist materials formulated with PATBSS as the matrix and a nitrobenzyl benzenesulfonate based PAG exhibit significantly improved adhesion and decreased weight loss in the exposed areas in comparison to PTBSS-based systems. Incorporation of 50 wt % acetoxystyrene (based upon total styrene content in the polymer) decreases the wt % volatiles from the resist from ~40% for the parent PTBSS to ~18% for the acetoxy analog. Incorporation of the acetoxy monomer additionally increases the polarity of the polymer, thus affecting adhesion to typical semiconductor device substrates. The purely styrenic copolymer (no SO_2) similarly exhibits reduced weight loss and improved adhesion compared to its *t*-BOC counterpart but does not image upon aqueous base treatment. Using the process outlined in the Experimental Section, images as small as 0.25 μm (Figure 2) can be defined in 0.8-μm-thick PATBSS-based resist films using a GCA Laser Step 248-nm exposure tool fitted with a 0.48 NA lens and an exposure dose of 50–60 mJ/cm.[2,10]

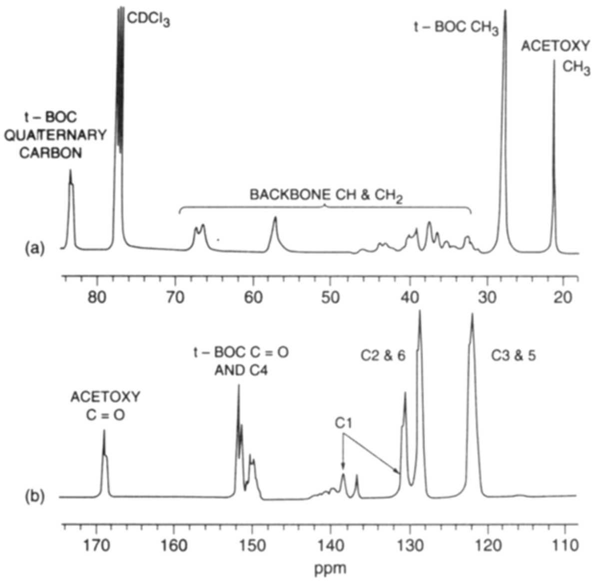


Figure 1. ^{13}C NMR spectrum at 50 °C of (a) the aliphatic region and (b) the aromatic region for PATBSS in $CDCl_3$. The individual assignments are made on the spectrum. The numbering sequence for the aromatic carbons is given on Scheme I.

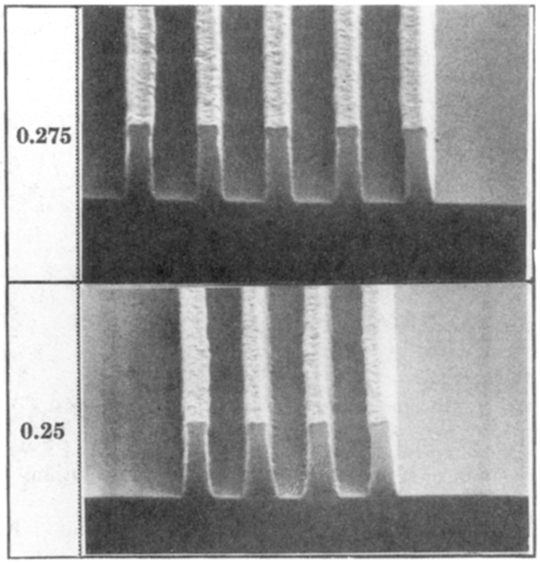


Figure 2. SEM micrograph depicting nominal 0.275- and 0.25-μm equal line/space images obtained in PATBSS–PAG resist films.

Mechanism of Aqueous Base Cleavage. Two IR spectra of PATBSS/nitrobenzyl ester film are shown in Figure 3. In Figure 3b, the film was exposed to 100 mJ/cm^2 of 248-nm light, baked at 120 °C for 1 min, and developed in a weak base (1 part of TMAH to 15 parts of H_2O) to solubilze slightly more than one-half of the original film thickness. Figure 3a is the spectrum of the same resist prior to any exposure. Two points are evident from these spectra. First, the absence of the carboxylate absorption of TBS at 1151 cm^{-1} in Figure 3b indicates that the *t*-BOC group has been cleaved. The loss of this group is also responsible for the decrease in the band at 1764 cm^{-1}, which can be attributed to the carbonyl stretches of acetoxystyrene and TBS. The fact that there is significant absorption at 1764 cm^{-1} allows us to conclude that the acetoxy group has not been cleaved by acid during the

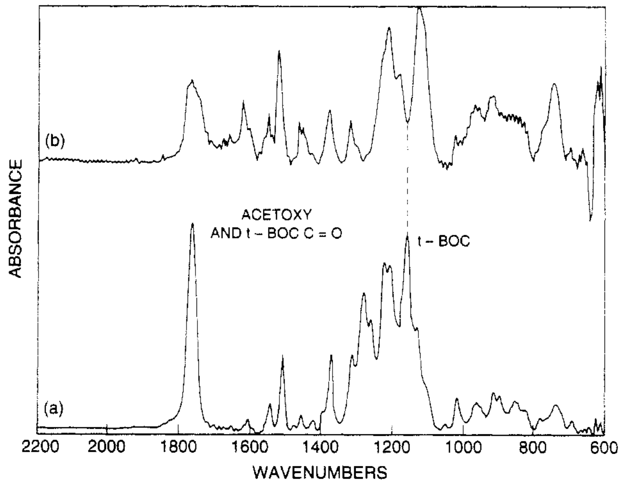


Figure 3. IR spectra of PATBSS–PAG films (a) before exposure and (b) after a 100 mJ/cm^2 exposure and partial dissolution in a 1:15 TMAH:H_2O solution.

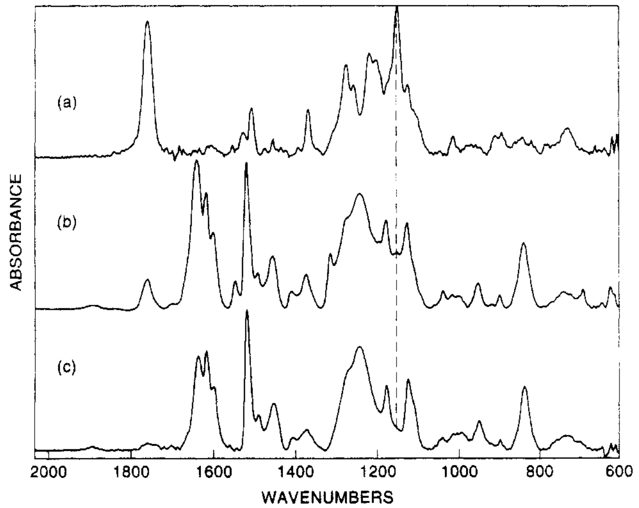


Figure 4. IR spectra comparing (a) an unexposed PATBSS–PAG film, (b) an exposed, post-exposure-baked, base-treated, and recovered PATBSS–PAG film, and (c) a PATBSS–thermal acid generator film after recovery from base solution.

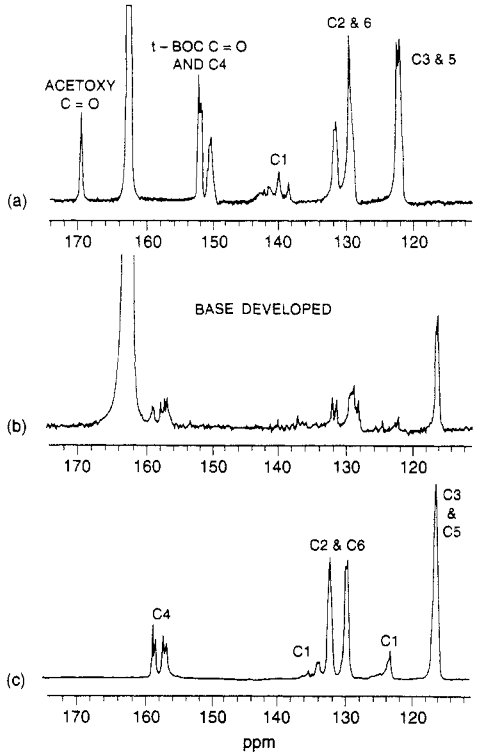


Figure 5. ^{13}C NMR spectra of (a) the parent PATBSS, (b) the isolated base-treated polymer dissolved in DMF-d_7 (162.7 ppm), and (c) poly(hydroxystyrene sulfone) dissolved in 1,4-dioxane-d_8.

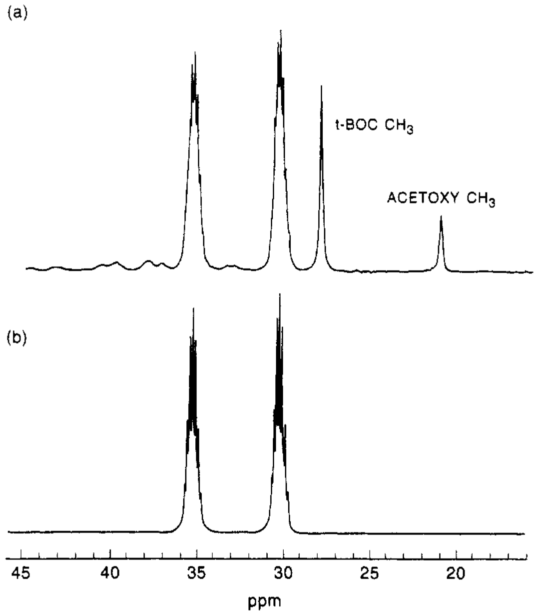


Figure 6. Upfield carbon spectra showing the methyl resonances of (a) PATBSS and (b) the base-treated polymer dissolved in DMF-d_7 (30.1 and 35.2 ppm).

exposure process. Similar results are obtained when the copolymer PATBS is utilized.

Spectra a and c in Figure 4 depict the IR spectra of a thin film of PATBSS containing the thermal acid generator (2-nitrobenzyl tosylate)[7] before acid generation and after thermal *t*-BOC deprotection followed by dissolution in aqueous base and subsequent recovery of the polymer. Note that in the spectrum of the polymer after it had been recovered from base (Figure 4c), there is no carbonyl absorption at 1764 cm^{-1}, which strongly suggests that the acetoxy group was removed from the polymer during the dissolution process. The same conclusion can be drawn from the IR spectrum in Figure 4b, which depicts the spectrum obtained from PATBSS containing a photoacid generator after exposure to 100 mJ/cm^2 of 248-nm radiation followed by aqueous base dissolution and recovery of the polymer. It is evident in Figure 4 that the carbonyl absorption peak is greatly reduced in both cases relative to other peaks. The small carbonyl peak at 1764 cm^{-1} in the photoacid spectrum of Figure 4b is probably due to small amounts of *t*-BOC, since some absorption from *t*-BOC is apparent at 1151 cm^{-1}.

NMR analysis was used to further elucidate the chemical changes taking place within the PATBSS polymer film during base dissolution. Two regions of the ^{13}C NMR spectra are of interest. The downfield region (110–181 ppm) includes the aromatic ring carbons and the carbonyl resonances of the TBS and acetoxystyrene monomer units. Figure 5 shows the assignments for the parent polymer. The spectrum of the base-developed polymer obtained after a thermal acid treatment of PATBSS is quite different (Figure 5b). The acetoxy carbonyl resonance at 169.27 ppm is absent. This polymer is identified as the totally deprotected product, poly(hydroxystyrene sulfone) (Figure 5c).

The upfield spectral region (20–40 ppm) monitors the methyls comprising the *t*-BOC (27.70 ppm) and acetoxy (20.95 ppm) functional groups (Figure 6a). The methyl resonances are absent in the polymer recovered after base dissolution (Figure 6b), confirming that both functional groups are removed after acid and subsequent aqueous

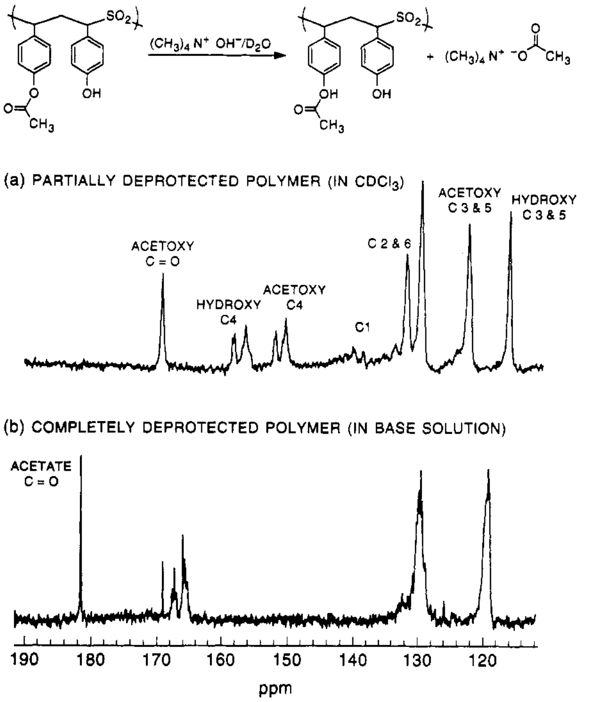


Figure 7. ^{13}C NMR spectra of (a) partially deprotected PATBSS dissolved in chloroform-*d* and (b) the completely deprotected polymer in TMAH and D_2O. The sharp resonance at 169 ppm is due to absorbed CO_2 in the aqueous base solution.

base treatment. This conclusion was further supported by the ^{1}H NMR spectrum (not shown). The spectrum of poly(acetoxystyrene hydroxystyrene sulfone) had a singlet resonance at 2.18 ppm attributed to the acetoxy methyl group. This singlet was absent from samples of material recovered from base dissolution of films obtained from either the irradiation or thermolysis experiments.

Since it was shown by the earlier IR experiments that only the *t*-BOC group was removed with the photoacid generator, an experiment was designed to mimic the base development step directly in the NMR tube. Poly(acetoxystyrene hydroxystyrene sulfone) (Figure 7a), prepared by thermally removing the *t*-BOC group, was dissolved in a solution of TMAH in water. The progress of the polymer reaction with the base was monitored by ^{13}C NMR (Figure 7). The base reacts with the acetoxy group, which can be seen by the elimination of the acetoxy carbonyl (169.27 ppm) and subsequent formation of ammonium acetate through the growth of its carbonyl at 181.64 ppm (Figure 7b) (note that the chemical shifts of the product, poly(hydroxystyrene sulfone), are affected by the aqueous base when compared to the shifts obtained for the same polymer in an organic solvent). This result conclusively proves that the cleavage of the acetoxy group is accomplished in the sulfone terpolymer by base and is not an artifact of how the base-treated polymer was isolated from the substrate.

To understand the role that sulfone plays in the PATBSS copolymer, we also studied copolymers of acetoxystyrene and (*tert*-butoxycarbonyloxy)styrene (PATBS). PATBS–acid generator films exhibited *t*-BOC acidolysis as evidenced by the disappearance of the IR absorption at 1151 cm^{-1} (Figure 8). This shows that TBS is serving its role as the imaging monomer. The films are, however, not soluble in aqueous base solution, indicating that the acetoxystyrene monomer is not undergoing base cleavage as occurred in PATBSS. Insight as to why sulfone is required for the base cleavage of the acetoxy group may be found in IR studies. Figure 9 compares the carbonyl region of films of PATBSS and an acid generator before (a) and after exposure (b) to that of PATBS films with an acid generator after exposure (c). In both copolymers the carbonyl region is significantly broader after acidolysis of the *t*-BOC group than it is before exposure. This broadening is, however, much more pronounced in the copolymer without sulfone. By comparison with the literature,[11] we can attribute this broadening to formation of hydrogen bonds between the carbonyl of the acetoxy group and the hydroxy of the hydroxystyrene, formed by acidolysis of *t*-BOC. It is plausible that the polar sulfone monomer provides an environment in which hydrogen bond formation is less likely. It is also possible that sulfone, which is known to increase the rigidity of the polymer backbone, contributes a steric impediment to hydrogen bond formation. Regardless of the exact explanation, these data prove that sulfone interferes with hydrogen bond formation. We can further speculate that the strong hydrogen bond formation in the exposed PATBS makes it difficult for the aqueous base to penetrate the PATBS–PAG film in high enough concentration to allow for base cleavage of the acetoxy group. This hypothesis is supported by two additional facts. First, the exposed film of PATBS can be dissolved by solvents such as acetone which can interrupt hydrogen bonds. Spectroscopic analysis of the polymer dissolved in acetone indicates that no reactions other than *t*-BOC acidolysis have occurred. Second, hydrolysis of the acetoxy group in PATBS can be achieved quite readily once the polymer is dissolved. Note the

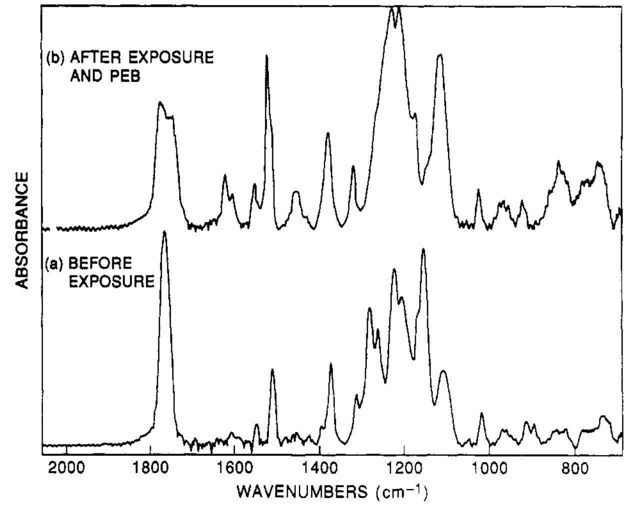


Figure 8. IR spectra of PATBS–PAG film (a) before exposure and (b) after exposure and PEB.

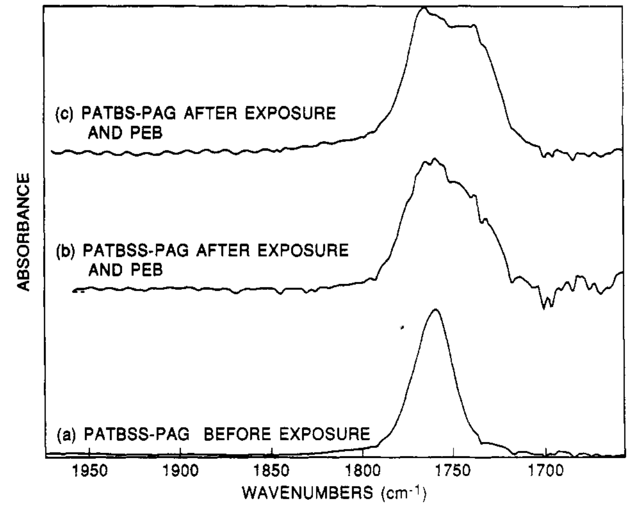


Figure 9. IR spectra of the carbonyl region of a PATBSS–PAG film (a) before exposure and (b) after exposure and PEB. These are compared to the IR spectrum of the carbonyl region of a PATBS–PAG film after exposure and PEB (c).

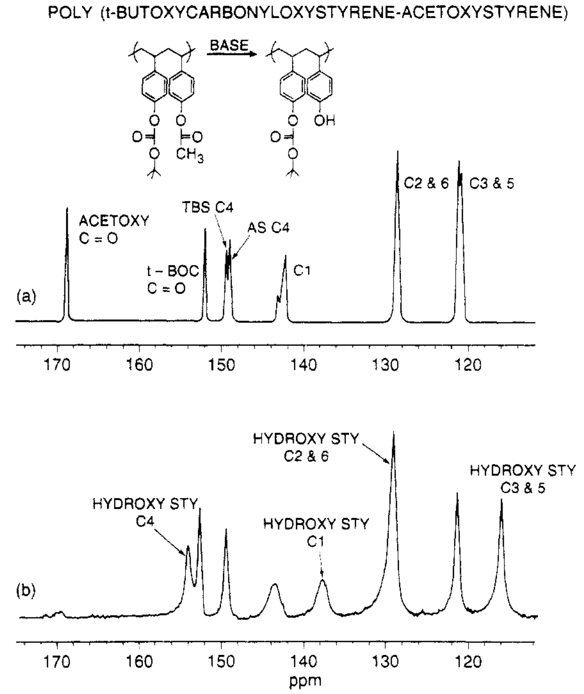
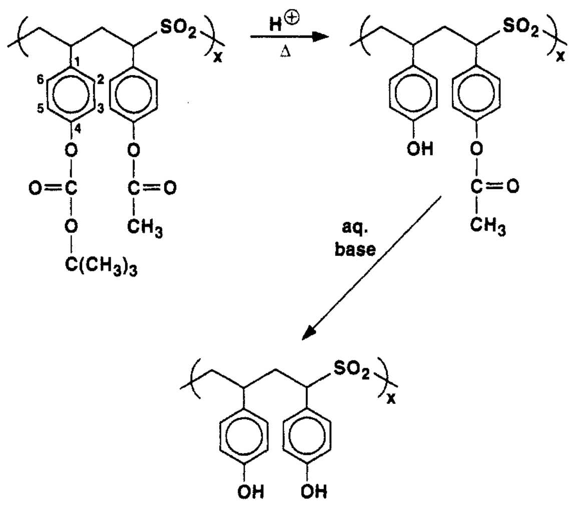


Figure 10. ^{13}C NMR spectra of (a) PATBS and (b) the solution base deprotected polymer in $CDCl_3$ at 50 °C.

Scheme I



disappearance of the acetoxy carbonyl and C4 peaks in the ^{13}C NMR spectrum after base treatment of the solubilized polymer (Figure 10).

In view of the results obtained above, the following mechanism accounting for the transformations taking place in PATBSS films formulated with acid generators is proposed (Scheme I). Upon exposure to acid, acid-catalyzed deprotection of the *t*-BOC group affords poly(acetoxystyrene hydroxystyrene sulfone). In marked contrast to poly(acetoxystyrene hydroxystyrene), the sulfone terpolymer allows penetration of aqueous base into the surface of the material. Penetration of the base into the film surface then allows the base-sensitive acetoxy group to be hydrolyzed, affording poly(hydroxystyrene sulfone). This product is equivalent to that obtained upon acid-catalyzed deprotection of PTBSS and is very soluble in aqueous base. No hydrolysis of the acetoxy group is observed in the hydrophobic, unexposed, *t*-BOC-containing regions of the film, i.e., regions where no *t*-BOC deprotection has occurred. This combined process of acid-catalyzed deprotection followed by base hydrolysis constitutes a novel idea in photoresist chemistry. The number of acid-sensitive groups can be kept to a minimum by enhancing base solubility through the incorporation of groups which will be cleaved only in exposed areas by the final processing step, base development.

Summary

This paper describes the synthesis of a novel polymer, PATBSS, in which each monomer performs a different function in the lithographic capabilities of the polymer. The chemistry occurring in PATBSS–acid generator films was elucidated by IR and NMR techniques. Spectroscopic evidence has shown that acid-catalyzed cleavage of the *t*-BOC group occurs readily upon mild heating and that subsequent treatment with aqueous base effects hydrolysis of the acetoxy groups. This hydrolysis takes place exclusively in regions of the film which have an increased hydrophilicity due to *t*-BOC loss. The sulfone monomer is essential for base hydrolysis of the acetoxy group in solid polymer films. The presence of the sulfone monomer decreases the formation of hydrogen bonds between the carbonyl of acetoxystyrene and the hydroxystyrene formed upon *t*-BOC removal. This decrease in hydrogen bonding may be explained by increased polarity and/or by steric interference caused by increased chain rigidity in the sulfone-containing copolymer. In addition to decreasing the number of hydrogen bonds, sulfone also contributes to the polarity of the polymer, thereby increasing the ability of the base to penetrate the polymer film and effect acetoxy cleavage. While we do not know the exact importance of each of these explanations, we do know that sulfone is an essential comonomer in this polymer. By combining the three monomers, we have designed a novel imaging system based upon integrated chemistry.

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