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Synthesis, Characterization, and Deblocking of Poly(4-*tert*-butoxystyrene) and Poly(4-*tert*-butoxy-α-methylstyrene)

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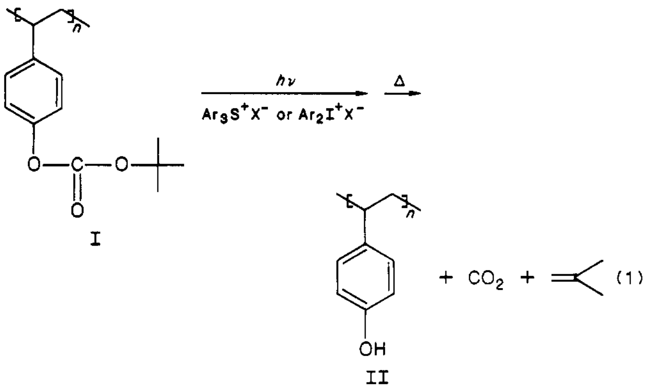
ABSTRACT: The monomers 4-*tert*-butoxystyrene and 4-*tert*-butoxy-α-methylstyrene were prepared by reaction of the corresponding 4-styryl and 4-α-methylstyryl Grignard reagents with *tert*-butyl peroxybenzoate. While 4-*tert*-butoxystyrene was polymerized by both free radical and ionic methods, the corresponding 4-*tert*-butoxy-α-methylstyrene could be polymerized only by cationic techniques. Model reactions employing 4-*tert*-butoxytoluene and various photosensitive diaryliodonium salts showed that deblocking the phenolic group takes place readily and requires a short thermolysis after irradiation. Poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene) were successfully deblocked by using various acids to yield the corresponding poly(4-hydroxystyrene) and poly(4-hydroxy-α-methylstyrene).

Introduction

The growing applications of polymers in the field of microelectronics represents one of the newest, most exciting, and challenging areas of research in polymer synthesis today. Currently, a particularly active field lies in the area of the design and synthesis of imageable polymeric materials which can serve as photoresists. The chief requirement of a photoresist is that on exposure to light or radiation, the irradiated portions of the photoresist undergo some chemical transformation which allows them to be distinguished, usually on the basis of solubility, from the nonirradiated portions of the photoresist. If the solubility in a given solvent of the irradiated areas is enhanced relative to the nonirradiated ones, the photoresist is said to have positive tone. Conversely, a negative tone results from decreased solubility of the photoresist on irradiation.

In this laboratory in recent years, we have been exploring a number of applications of photosensitive onium salts including those involving imaging.[1] The discovery that certain onium salts such as diaryliodonium and triarylsulfonium salts produce strong Brønsted acids on photolysis presented a unique opportunity to design novel imaging systems which rely on various acid-catalyzed processes for their action. One such approach to the design of a new photoresist has been described recently by Willson and his co-workers[2-5] and is shown in eq 1. Poly(4-(*tert*-butoxycarbonyloxy)styrene) (I) is insoluble in aqueous base; however, when it is irradiated in the presence of a photosensitive onium salt, the acid which is produced catalytically removes the (*tert*-butoxycarbonyl)oxy groups yielding poly(4-vinylphenol) (II), carbon dioxide, and isobutylene. Discrimination between the irradiated and nonirradiated portions of the resist to produce fine patterns in a positive tone can now be made since poly(4-hydroxystyrene) is very soluble in dilute aqueous base. Negative tone images can be made by using chlorinated solvents in which poly(4-(*tert*-butoxycarbonyloxy)styrene) is preferentially removed by dissolution. Similarly, the corresponding poly(4-(*tert*-butoxycarbonyloxy)-α-methylstyrene) could also be employed as a photoresist. Since the deblocking reaction shown in eq 1 is catalytic, a kind of photomultiplication effect is observed in which the overall quantum yield for deblocking is very large and of the order of magnitude of 1000. This photomultiplication effect has been termed "chemical amplification". Consequently, such resists have an inherently high photosensitivity.



It occurred to us that it should be possible to design other photoresist systems based on analogous chemistry. Along with good sensitivity to UV irradiation and excellent

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Table I
Preparation and Characterization of Various *tert*-Butoxy-Substituted Polymers

monomer	solv	temp (°C) time (h)	yield (%)	initiator (%)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	T_g (°C)
4-*tert*-butoxystyrene	bulk	70 16	95	AIBN (0.6)	181 500	437 000	103
4-*tert*-butoxystyrene	bulk	70 16	96	AIBN (2.4)	50 400	132 000	
4-*tert*-butoxystyrene	THF	−70 2	94	*n*-BuLi	41 400	58 800	
3-*tert*-butoxystyrene	bulk	70 16	96	AIBN (0.6)	35 600	106 300	62
4-*tert*-butoxy-α-methylstyrene	CH_2Cl_2	−78 1.5	90	$BF_3\cdot Et_2O$	157 600	210 200	160

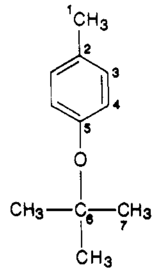
resolution, an additional major requisite for polymers used in photoresists is that they be capable of being developed after exposure in aqueous media. This latter criterion is imposed by environmental concerns associated with disposal of the developing solutions. For this reason, most organic photoresists employed today use as matrix materials or film formers phenolic resins which can be developed by dissolution in aqueous bases.[6] The first goal of our work was, therefore, to prepare polymers containing incipient pendant phenolic groups which are blocked by acid labile protecting groups. Secondly, we desired blocking groups which are sufficiently thermally stable so that the photoresist can be applied from solution and the solvent be removed by the usual baking procedures. Lastly, it was desirable that the blocked polymer have a sufficiently high T_g so that the lithographic features are not distorted during subsequent postirradiation thermal processing steps such as baking and plasma etching.

Experimental Section

Materials. The diaryliodonium and triarylsulfonium salts employed in this work were prepared as described in earlier publications.[7,8] *tert*-Butyl peroxybenzoate, 4-bromostyrene, 4-bromoacetophenone, 4-chloro-α-methylstyrene, and 2,2-azobis(isobutyronitrile) (AIBN) were used as purchased from the Aldrich Chemical Co.

Measurements. All molecular weights were determined in chloroform by using a Waters 244 gel permeation chromatograph (GPC) and are based on polystyrene standards. Glass transition temperatures were determined on a Perkin-Elmer DSC-2 differential scanning calorimeter. Proton magnetic spectra were obtained on a Varian EM 390 90-MHz spectrometer while the ^{13}C NMR spectra were measured on a Varian XL 200-MHz spectrometer. A VG Analytical ZAB-2F GC–mass spectrometer equipped with 30-m DB1 polydimethylsiloxane capillary columns was used for the identification of the deblocking products of 4-*tert*-butoxytoluene by various photosensitive onium salts.

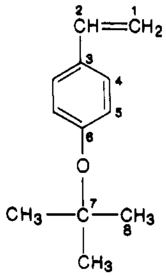
Preparation of a Model Compound: 4-*tert*-Butoxytoluene. There were placed in a 2000-mL three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, dropping funnel, and nitrogen inlet 17.25 g (0.71 mol) of magnesium turnings and about 50 mL of tetrahydrofuran (THF). To this mixture under an atmosphere of nitrogen was added dropwise with stirring 118.4 g (0.69 mol) of 4-bromotoluene in 380 mL of dry THF. When addition was finished, the reaction mixture was heated at 65–70 °C for 2 h. To the above reaction mixture cooled to 0 °C was added dropwise 83.2 g (0.166 mol) of *tert*-butyl peroxybenzoate in 150 mL of anhydrous ether at such a rate to maintain the temperature between 0 and 5 °C. The addition required 1.25 h, and then the reaction mixture was stirred for an additional 2 h. After the reaction mixture was filtered to remove the precipitated magnesium benzoate, the ether was removed on a rotary evaporator and the remaining liquid poured into 1000 mL of aqueous 3% HCl. The organic layer was separated and the aqueous layer washed with two 200-mL portions of ether. Next, the aqueous layer was discarded, and the organic solutions were combined and washed twice with 10% NaOH followed by washing with water until the washings were neutral. After the resulting organic layer was dried over Na_2SO_4, the ether was removed by using a rotary evaporator and the resulting liquid fractionally vacuum distilled to give 44.6 g (63% yield) of 4-*tert*-butoxytoluene (bp 56–57 °C (0.5 mm)). ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.22 (s, 9 H, *t*-Bu), 2.17 (s, 3 H, Me), 6.88 (A_2B_2, 4 H, Ar–H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 21.3 (C_1), 133.1 (C_2), 129.8 (C_3), 124.8 (C_4), 153.3 (C_5), 78.5 (C_6), 29.4 ppm (C_7).



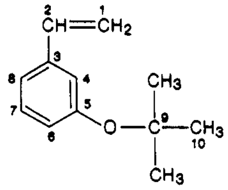
Model Deblocking Studies. Prior to the model deblocking studies, the photolysis of several diaryliodonium salts and triarylsulfonium salts was carried out in the presence of 4-*tert*-butoxytoluene and the products were determined by means of GC–mass spectroscopy. Definitive assignments could be made on the basis of the parent peaks, the fragmentation patterns, and a comparison of the GC retention times with those of authentic compounds.

Deblocking studies were then carried out on solutions prepared from 0.01 mol of 4-*tert*-butoxytoluene, 0.0005 mol of the desired (4-methoxyphenyl)phenyliodonium salt, and 0.01 mol of 1,1,2,2-tetrachloroethane as solvent and internal standard. Aliquots of the above solutions were transferred to quartz NMR tubes and the samples mounted in a merry-go-round holder and irradiated for 1 min by using an unfiltered Hanovia 450-W medium-pressure mercury arc lamp fitted with a water-cooled quartz well. After irradiation, the sample tubes were heated for 5 min in a water bath at 100 °C. The course of the deblocking reaction and the product ratios were followed at the start of the reaction and throughout by means of gas chromatography using a Hewlett-Packard 5840A gas chromatograph equipped with 6 ft × $^1/_8$ in. OV-101 polydimethylsiloxane columns.

Preparation of 4-*tert*-Butoxystyrene (3-*tert*-Butoxystyrene). To a 2000-mL three-necked round-bottom flask equipped with a dropping funnel, thermometer, reflux condenser, paddle stirrer and nitrogen inlet were placed 19.4 g (0.80 mol) of magnesium turnings and enough freshly dried and distilled tetrahydrofuran (THF) to cover the turnings. There were then added dropwise with stirring a solution of 143.3 g (0.78 mol) of freshly distilled 4-bromostyrene (bp 46–47 °C (0.03 mm)) in 500 mL of THF. After 20 mL of the 4-bromostyrene had been added, an exothermic reaction set in and was maintained between 25 and 35 °C by adjusting the rate of addition of the bromo compound and with the aid of an ice bath. After the addition had been completed, the reaction mixture was heated to 60 °C for 0.5 h. Using a NaCl–ice bath, the mixture was cooled to 0 °C and a solution of 100.88 g (0.52 mol) of *tert*-butyl peroxybenzoate in 200 mL of THF was added via the dropping funnel at such a rate that the reaction temperature was maintained between 0 and 5 °C. After completion of the addition, the reaction mixture was stirred at 25 °C for 2 h. The organic layer was separated from the solid magnesium benzoate by decantation and the volume of the solution reduced on a rotary evaporator. The yellow oil that remained was washed with 1000 mL of 3% aqueous HCl solution and the organic layer separated. The aqueous layer was washed with two 200-mL portions of ether, and the ether and organic layers were combined and together washed with two 75-mL portions of a 10% NaOH solution followed by washing with water until the aqueous washings were neutral. After the solution was dried over Na_2SO_4 and the ether was removed via a rotary evaporator, the remaining pale yellow oil was purified by fractional distillation in the presence of a few milligrams of ionol (2,6-di-*tert*-butyl-4-methylphenol) as an inhibitor. There were obtained 46 g (50% yield, bp 45 °C (0.02 mm)) of 4-(*tert*-butyloxy)styrene having the following elemental analysis. Calcd for $C_{12}H_{16}O$: C, 81.82; H, 9.09. Found: C, 81.64; H, 8.89. ^1H NMR (90 MHz, $CDCl_3$): δ 1.2 (s, 9 H, *t*-Bu), 5.5, (q, 1 H, $CH{=}CH_2$, trans, A), 5.0, (q, 1 H, cis, B), 6.55 (q, 1 H, $CH{=}CH_2$, X) (J_{AB} = 1 Hz, J_{AX} = 15 Hz, J_{BX} = 9 Hz), 6.99 (A_2B_2, 4 H, Ar–H). ^{13}C NMR (50.3 MHz, $CDCl_3$) 4-*tert*-butoxystyrene: δ 112.3 (C_1), 136.1 (C_2), 132.6 (C_3), 126.5 (C_4), 123.9 (C_5), 155.0 (C_6), 78.4 (C_7), 28.8 ppm (C_8).



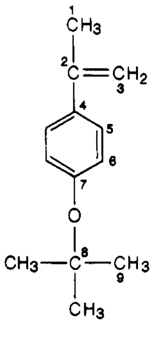
Using an identical procedure and staring with 3-bromostyrene, there were prepared in 56% yield, 3-*tert*-butoxystyrene having a boiling point of 50–52 °C (0.05 mm). ^1H NMR (200 MHz, $CDCl_3$): δ 1.33 (s, 9 H, *t*-Bu), 5.7, (d, 1 H, $CH{=}CH_2$, trans, A), 5.2, (d, 1 H, cis, B), δ 6.6 (q, 1 H, $CH{=}CH_2$, X), $J_{AB} \sim 0$ Hz, J_{AX} = 17.39 Hz, J_{BX} = 10.99 Hz, 6.85–7.22 ppm (m, 4 H, Ar–H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 113.6 (C_1), 136.5 (C_2), 138.3 (C_3), 121.6 (C_4), 155.4 (C_5), 121.1 (C_6), 128.6 (C_7), 123.3 (C_8), 78.1 (C_9), 28.6 (C_{10}).



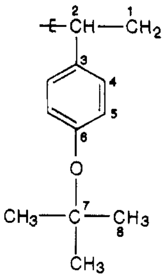
Preparation of 4-*tert*-Butoxy-α-methylstyrene. Procedure A. Placed in a 1000-mL three-necked round-bottom flask equipped as above were 16.9 g (0.70 mol) of magnesium turnings and 50 mL of THF. A portion of a solution composed of 100 g (0.66 mol) of 4-chloro-α-methylstyrene in 200 mL of THF was added. There were added 5 drops of methyl iodide followed by the remainder of the solution of the aryl chloride, and the reaction mixture was heated to reflux and maintained at this temperature for 16 h. The dark solution was cooled to 0 °C by using a dry ice–acetone bath and a solution consisting of 85 g (0.44 mol) of *tert*-butyl peroxybenzoate in 300 mL of ether was added dropwise maintaining the temperature between 5 and 10 °C. The reaction mixture was stirred at 0–5 °C for 0.5 h following completion of the addition then allowed to warm to room temperature. Next, the liquid portion of the reaction mixture was decanted onto 2000 mL of ice and 40 mL of concentrated HCl. The organic layer was separated, the aqueous layer extracted with ether, and the ether extract combined with the organic layer. The organic phase was washed with dilute NaOH, followed by dilute sodium bisulfite and water then finally dried over anhydrous sodium sulfate. After the solvents were removed under reduced pressure, there remained a mixture of a crystalline material which was identified as the coupling product 4,4′-diisopropenylbiphenyl and an oil. After the crystalline byproduct was filtered off, the oil was subjected to fractional vacuum distillation in the presence of NaOH as an inhibitor to give 58 g (69%) of 4-*tert*-butoxy-α-methylstyrene (bp 65–68 °C (0.03 mm)).

Procedure B. To a cold (~−10 °C) solution of methyl magnesium bromide (187 mL, 3.0 M, 0.56 mol) in ether was added 97 g (0.51 mol) of 4-bromoacetophenone in 300 mL of ether. The cloudy, turbid reaction mixture was allowed to stir for 1 h following completion of the addition at −10 °C and then quenched by pouring the reaction into a mixture of ice and saturated aqueous ammonium chloride solution. The quenched reaction mixture was transferred to a separatory funnel, and the aqueous and organic layers were separated. The aqueous portion was extracted with two portions of ether, and these combined with the organic layer. The combined organics were washed with water, saturated sodium bicarbonate, and brine and then dried over anhydrous potassium carbonate. Concentration under reduced pressure yielded a yellow oil to which was added a small amount of iodine crystals. The mixture was heated to 70–75 °C for 3.5 h after which it was cooled to room temperature and diluted with ether. The mixture was transferred to a separatory funnel where it was washed with saturated sodium bisulfite. Drying over anhydrous potassium carbonate and then concentration under reduced pressure yielded approximately 100 g of crude 4-bromo-α-methylstyrene which was used without purification in the next step.

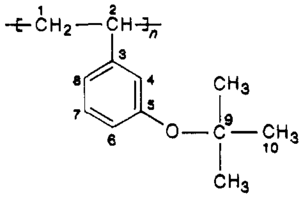
Into a three-necked round-bottom flask equipped with a mechanical stirrer, a dropping funnel, thermometer, and reflux condenser were placed 13.6 g (0.65 mol) of magnesium and 110 mL of THF. To this was added the crude 4-bromo-α-methylstyrene dissolved in 280 mL of THF. The bromide was added slowly at first, and some heating was required to initiate reaction. Once begun, the addition of the aryl bromide was controlled such that the reaction temperature remained at approximately 55 °C. After the addition was complete, the reaction mixture was allowed to cool to room temperature and then further cooled to −10 °C. At this point a solution consisting of 67.5 mL (0.36 mol) of *tert*-butyl peroxybenzoate in 110 mL of THF was added at such a rate that the reaction temperature remained at ≤5 °C. The cold bath was removed, and the turbid solution was warmed to room temperature and allowed to stand overnight. The reaction mixture was filtered and the filtrate concentrated under reduced pressure. The resulting yellow oil was treated with cold 2% HCl and extracted with ether, and then the ether solution was washed with 10% NaOH, saturated sodium bisulfite, and water. After concentration under reduced pressure, the product was distilled over KOH yielding 38.4 g (0.2 mol, 56%) of 4-*tert*-butoxy-α-methylstyrene (bp 84–88 °C (0.2 mm)) as a colorless oil. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.13; H, 9.21. ^1H NMR (90 MHz, $CDCl_3$): δ 1.3 (s, 9 H, *t*-Bu), 2.09 (s, 3 H, Me), 4.8–5.3 (m, 2 H, $C{=}CH_2$), 6.75–7.45 (m, 4 H, Ar–H). ^{13}C NMR (50.3 MHz, $CDCl_3$) 4-*tert*-butoxy-α-methylstyrene: δ 21.8 (C_1), 142.4 (C_2), 111.2 (C_3), 135.9 (C_4), 125.8 (C_5), 123.6 (C_6), 154.7 (C_7), 78.3 (C_8), 28.8 (C_9).



Free Radical Polymerization of 4-*tert*-Butoxystyrene. A solution of 5.0 g of 4-*tert*-butoxystyrene and 0.03 g of 2,2-azobis(isobutyronitrile) (AIBN) was placed in a cleaned and dried screw cap vial. The mixture was flushed with nitrogen for several minutes and then sealed and placed in a constant temperature bath at 70 °C for 16 h. A solid plug of polymer was obtained which was dissolved in dichloromethane and precipitated into methanol. The polymer was washed thoroughly with methanol and then dried in a vacuum oven at 80 °C. There were obtained 4.76 g (95% yield) of poly(4-*tert*-butoxystyrene) having a M_n = 181 500 g/mol, M_w = 437 000 g/mol, and a dispersity M_w/M_n = 2.4. ^{13}C NMR (50.3 MHz, $CDCl_3$) poly(4-*tert*-butoxystyrene): δ 31.9 (C_1), 44.4 (C_2), 140.1 (C_3), 127.5 (C_4), 123.6 (C_5), 152.9 (C_6), 77.8 (C_7), 29.1 ppm (C_8).



In an identical manner, 3-*tert*-butoxystyrene was polymerized by free radical means giving a 96% conversion to polymer having a GPC determined M_n = 35 600 g/mol, M_w = 106 300 g/mol, and M_w/M_n = 2.99. ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 40.1 (C$_1$), 44.1 (C$_2$), 146.2 (C$_3$), 122.3 (C$_4$), 154.9 (C$_5$), 121.3 (C$_6$), 128.1 (C$_7$), 123.3 (C$_8$), 77.6 (C$_9$), 28.9 (C$_{10}$).



Anionic Polymerization of 4-*tert*-Butoxystyrene. Into a dried 25-mL two-necked round-bottom flask filled with an atmosphere of argon and equipped with a small magnetic stirrer and rubber septa were placed 7.32 g of 4-*tert*-butoxystyrene and 8 mL of THF. The reaction mixture was flushed with argon and cooled in a dry ice–acetone bath to −70 °C. To the cooled solution was added by means of a syringe 0.5 mL of *n*-butyllithium (2.5 M solution in hexane). The initial deep blue-green color rapidly changed to orange, and the solution became very viscous. Polymerization was continued for an additional 2 h at −70 °C and was then quenched by the addition of methanol prior to allowing the reaction mixture to warm to room temperature. The quenched polymer was dissolved in dichloromethane and precipitated into methanol. After the polymer was thoroughly washed with methanol, it was broken into small pieces and dried at 40 °C overnight in vacuo. There were obtained 6.9 g (94.3% yield) of poly(4-*tert*-butoxystyrene) having a M_n = 41 400 g/mol, M_w = 58 800 g/mol, and M_w/M_n = 1.4 as determined by GPC.

Cationic Polymerization of 4-*tert*-Butoxy-α-methylstyrene. To a solution of 10 g (53 mmol) of 4-*tert*-butoxy-α-methylstyrene in 24 mL of dichloromethane at −40 °C was added 1.75 mL (2.7 mmol) of a 10% solution of boron trifluoride etherate in ether (prepared by diluting 0.5 mL of boron trifluoride etherate to 5 mL with anhydrous ether) all at once. The solution turned orange immediately, but the color faded to yellow within 10–15 s. The mixture was allowed to stir an additional 1.25 h at this temperature, and then it was quenched at −40 °C with a solution of NH$_4$OH in methanol. The solution was allowed to warm to room temperature and then poured into 550 mL of methanol containing a small amount of NH$_4$OH. The resulting powdery solid was collected by suction filtration and dried in a vacuum oven at 60 °C. There were obtained 8.7 g of polymer having a M_n = 5200 g/mol, M_w = 18 100 g/mol, and M_w/M_n = 3.5.

The polymerization was repeated by using 0.88 mL of a 10% solution of boron trifluoride in ether. In this case, the yield was 8.8 g and the GPC indicated a M_n = 7800 g/mol, M_w = 21 900 g/mol, and M_w/M_n = 2.8.

The polymerization was repeated once again holding the catalyst level constant at 0.88 mL but lowering the temperature to −60 °C. This resulted in a yield of polymer of 8.7 g with a M_n = 15 100 g/mol, M_w = 45 700 g/mol, and M_w/M_n = 3.0. At −78 °C, a yield of 90% polymer was obtained having a M_n = 157 600 g/mol, M_w = 210 200 g/mol, and M_w/M_n = 1.3. The T_g of this polymer was 160 °C.

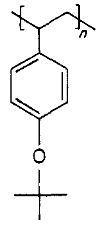
Deblocking Studies of Poly(4-*tert*-butoxystyrene) and Poly(4-*tert*-butoxy-α-methylstyrene). Acid-Catalyzed Deblocking. To 0.2 g of poly(4-*tert*-butoxystyrene) in 3 mL of 1,1,1-trifluoroethanol were added at −5 °C two drops of trifluoromethanesulfonic acid with stirring. A white precipitate of the deblocked polymer formed immediately. After 15 min, stirring was stopped and the precipitated polymer was filtered, washed with fresh solvent, and then dried overnight at 60 °C in vacuo. There were obtained 0.15 g of polymer which on analysis by ^{1}H NMR showed the complete absence of a signal for the methyls of the *tert*-butoxy groups at 1.20–1.30 ppm. Comparison of the ^{1}H NMR spectrum of this polymer with that of authentic poly(4-hydroxystyrene) obtained from the Maruzen Oil Co. showed that the two polymers were identical. The same procedure was used for the deblocking of poly(4-*tert*-butoxy-α-methylstyrene), except that the deblocked polymer was recovered by precipitation into water followed by filtering and drying as described above.

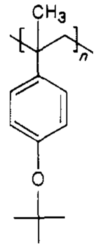
Photochemical Deblocking. Solutions containing 0.25 g of polymer poly(4-*tert*-butoxystyrene) or poly(4-*tert*-butoxy-α-methylstyrene) and 0.025 g of bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate in 3.5 mL of 1-methoxy-2-propyl acetate were prepared. The solutions were spin coated onto 50-mm diameter quartz disks by using a Headway spin coater. The quartz disks were baked in a forced air oven at 80 °C for 30 min, and the UV spectrum was then recorded on a Shimadzu UV-240 UV–visible spectrophotometer. Next, the disks were irradiated for 10 s at a distance of 6 in. from a General Electric H3T7 medium-pressure mercury arc lamp ballasted at 800 W. Again, the UV spectra were recorded. The disks were then heated at 100 °C for 5 min in a forced air oven, and the UV spectra were once again recorded.

Photoimaging of Poly(4-*tert*-butoxystyrene). A solution of 0.5 g of poly(4-*tert*-butoxystyrene) (M_n = 50 400 g/mol), 0.1 g of bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate, and 7 mL of glyme was spun onto silicon wafers and baked for 30 min at 90 °C. A metal contact mask was placed on the wafers, and they were then irradiated by using a General Electric H3T7 medium-pressure arc lamp for various times. After irradiation, the wafers were baked at 100 °C in a forced air oven for 5–15 s and then developed by immersion in either a 1.6 N aqueous NaOH solution or dichloromethane for 1 min.

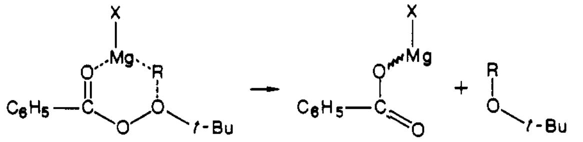
Results and Discussion

Monomer Synthesis. An excellent phenolic blocking group that meets the criteria of good thermal stability and yet is easily removed under conditions of acid catalysis is the *tert*-butyl ether group.[9-14] Thus, if polymers III and IV could be prepared, it should be possible to use the acids produced by the photolysis of onium salts to deblock them to generate the corresponding poly(4-vinylphenol) (II) and the corresponding poly(4-isopropenylphenol). While *tert*-butoxy groups are of great potential interest as acid labile blocking groups for phenols, they have been little utilized due to the general difficulty of their preparation and the low yields obtained in their synthesis.[15-17] Other methods, such as the condensation of phenols with isobutylene,[13] take place under very strongly acidic conditions and are, therefore, imcompatable with the preparation of the styrenic and α-methylstyrenic monomer precursors of polymers III and IV. For the synthesis of these substrates, a mild, relatively high yield method was required. Such a method is that described by Lawesson and Yang[18] involving the reactions of aryl and alkyl Grignard reagents with *tert*-butyl peroxybenzoate. This reaction is specific to organomagnesium compounds and fails in the case of other organometallic agents such as alkyl- or aryllithium compounds. Apparently, the ability of the magnesium atom to participate by coordination in a six-member-ring


III

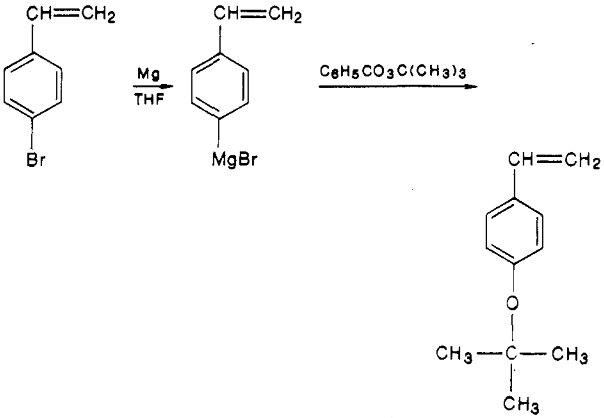

IV

transition state as shown in eq 2 is necessary for the success of this reaction.



(2)

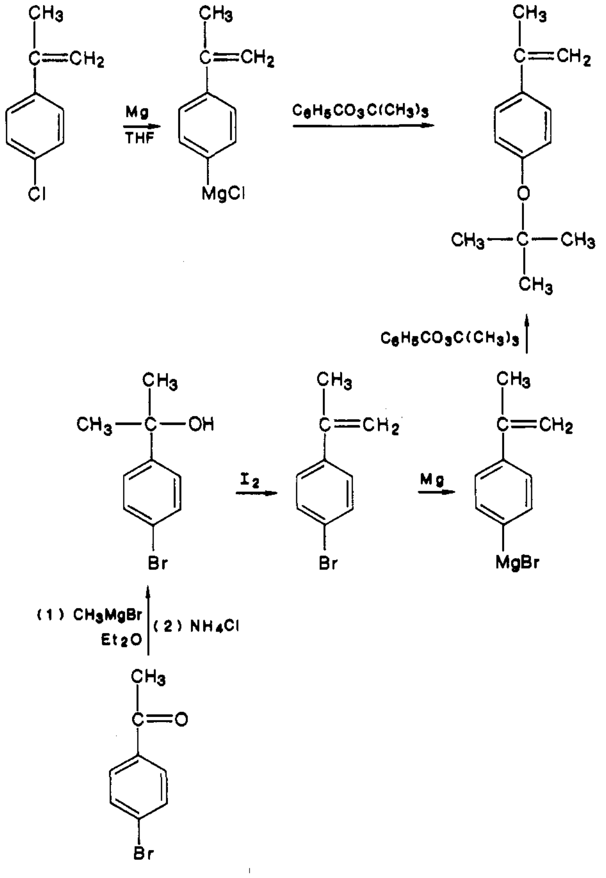
The synthetic pathway used for the preparation of 4-*tert*-butoxystyrene is shown in eq 3. Starting with 4-



(3)

bromostyrene, the corresponding styryl Grignard reagent was prepared.[19,20] Subsequently, the Grignard compound was converted in the presence of *tert*-butyl peroxybenzoate to the desired monomer in 50% overall yield. ^{13}C NMR was the method of choice of characterization for this new monomer, and the other monomers prepared during the course of this work and the peak assignments are given in Experimental Section. Analogously, 3-*tert*-butoxystyrene was prepared in 56% yield by the same synthetic route.

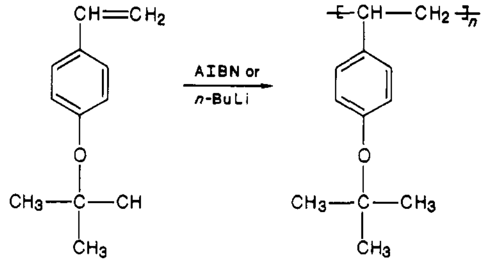
The corresponding 4-*tert*-butoxy-α-methylstyrene was prepared by the two routes shown in eq 4 and 5. Both of these methods employ the Lawesson reaction for the final introduction of the *tert*-butoxy group.



(4)

(5)

Polymer Synthesis. The polymerization of 4-*tert*-butoxystyrene can be carried out under either free radical or anionic conditions as depicted in eq 6.

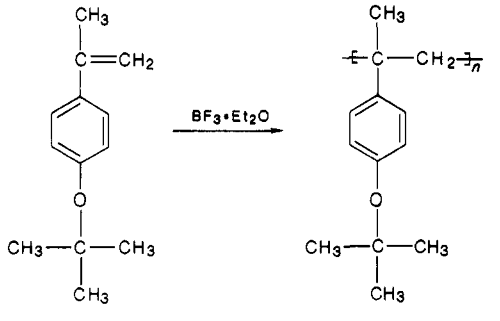


(6)

Table I contains the results of preliminary investigations of the polymerization of this monomer using various initiators and conditions. Again, ^{13}C NMR was found useful to definitively characterize the polymer and the peak assignments are given in the Experimental Section. It is interesting to note that contrary to the usual T_g lowering effect noted when alkoxy substituents are placed in the 4-position of polystyrene (T_g = 98 °C), introduction of the bulky 4-*tert*-butoxy group raises the T_g to 103 °C. 3-*tert*-Butoxystyrene can also be readily polymerized under free radical conditions giving the corresponding poly(3-*tert*-butoxystyrene) having a T_g of 62 °C. In this case, placing the *tert*-butoxy group in an unsymmetrical position results in a marked lowering of the glass transition temperature.

The application of organic polymers to photoresist applications requires rigid control over the molecular weight. Accordingly, the free radical polymerization of 4-*tert*-butoxystyrene was carried out in solution and in bulk by using both the solvent 1,2-dichloroethane and/or 1-dodecanethiol as chain-transfer agents. The results are given in Table II and demonstrate that the use of chain transfer agents allows the controlled synthesis of poly(4-*tert*-butoxystyrene) of nearly any desired molecular weight. Particularly useful is the solution polymerization in 1,2-dichloroethane which gives good molecular weight control with comparatively narrow molecular weight distributions.

Unlike 4-*tert*-butoxystyrene, 4-*tert*-butoxy-α-methylstyrene does not polymerize either under free radical or anionic conditions. Instead, cationic initiators such as $BF_3 \cdot Et_2O$ complex are effective for the polymerization of this monomer (eq 7). Initially, there was some concern



(7)

that under the acidic conditions of the polymerization, the phenol would be deblocked with the loss of the *tert*-butoxy groups. As shown in the ^{13}C NMR of Figure 1, cationic polymerization at −40 to −60 °C followed by quenching with base at that temperature produced the desired polymer with the *tert*-butoxy groups (CH_3, 28.8 ppm; quaternary C, 77.5 ppm) still intact. Further evidence was provided by the absence of phenolic OH stretching frequencies between 3644 and 3605 cm^{-1} in the IR as well as the fact that the polymer was soluble in chlorinated solvents and insoluble in aqueous base while the corresponding hydrolyzed polymer poly(4-hydroxy-α-methyl-

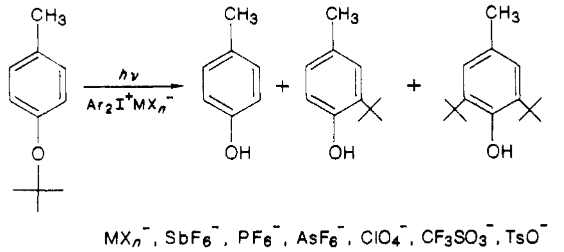
Table II
Study of the Polymerization of 4-*tert*-Butoxystyrene in the Presence of Chain Transfer (CT) Agents

polym conditns[a]	amt of CT agent	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n/\bar{M}_w$
bulk polymerizatn with $C_{12}H_{25}SH$	0	70200	237800	3.3
	15 μL	35200	212200	6.2
	25 μL	40100	245100	6.1
	50 μL	24500	180000	7.4
	75 μL	26900	186000	6.9
soln polymerizatn in $ClCH_2CH_2Cl$	0	76400	266600	3.5
	0.5 mL	25200	52400	2.1
	1.0 mL	15600	33400	2.1
	1.5 mL	12900	27900	2.2
	2.0 mL	10000	21200	2.1
soln polymerizatn with $C_{12}H_{25}SH$ in 2:1 monomer/$ClCH_2CH_2Cl$	0	18900	35700	1.9
	6 μL	11300	26400	2.3
	12 μL	11400	28500	2.5
	24 μL	10100	28600	2.8
	36 μL	6300	22000	3.5

[a] Polymerizations run by using 2.0 g of monomer and 0.056 g (2.8%) of AIBN.

styrene) is insoluble in chlorinated solvents but soluble in aqueous base. High molecular weight (M_n = 157600 g/mol) poly(4-*tert*-butoxy-α-methylstyrene) prepared at −78 °C has a T_g = 160 °C as determined by DSC.

Model Deblocking Studies. Other than a few cursory studies that appear in the literature,[21,22] there has been no thorough study of the acid-catalyzed deblocking reaction of *tert*-butyl aryl ethers. For that reason, it was decided to undertake such a study with particular emphasis on the effects of the acid strength on the deblocking reaction. For this study, a model compound, 4-*tert*-butoxytoluene, was chosen which structurally resembles both poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene). Protonic acids of various acid strengths were conveniently generated by the irradiation of a series of diaryliodonium salts having the (4-methoxyphenyl)phenyliodonium cation and bearing various anions. Identification of the cleavage products was made by GC–mass spectroscopy and by comparison with the authentic compounds. After this initial identification was made, the reaction was conveniently followed by means of gas chromatography. It was observed that deblocking of the phenolic group does not occur spontaneously on irradiation of 4-*tert*-butoxytoluene in the presence of any photosensitive onium salt at 25 °C. However, when the irradiated sample was heated at 100 °C, rapid, quantitative deblocking of the phenolic group took place in all cases. In eq 8 are shown the major products of the acid-catalyzed deblocking of 4-*tert*-butoxytoluene which were identified as described above. Along with those shown, a number of other very minor products were found which, by reason of their masses and gas chromatographic retention times, were assumed to be positional isomers of the main products.



(8)

4-Methylphenol is formed by deblocking of the starting compound by loss of isobutylene. In many cases, during the thermal treatment of the sample after irradiation, outgassing of the sample was observed and was presumed due to the release of isobutylene. Two *tert*-butylated compounds, 2-*tert*-butyl-4-methylphenol and 2,6-di-*tert*-butyl-4-methylphenol, were also identified among the products. These compounds appear respectively to arise by deblocking of the 4-*tert*-butoxytoluene followed by the intra- and intermolecular alkylation of 4-methylphenol and 2-*tert*-butyl-4-methylphenol by the liberated isobutylene under the highly acidic conditions of the reaction. In Table III are shown the effects of various anions of the photosensitive diaryliodonium salt employed for the deblocking of the model compound. As can be seen, there is a marked effect on the relative proportions of products depending on the anion which was employed. Since it has already been shown[7] that the quantum yields of photolysis of various diaryliodonium salts are dependent only on the structure of the cationic portion of the molecule and independent of the character of the anion, one should expect identical amounts of the corresponding protonic acids to be produced per given unit irradiation intensity and time. Thus, the differences in the relative proportion of products shown in Table III must occur only as a consequence of the nature and acidity of those acids which are produced. Those diaryliodonium salts bearing the tosylate and perchlorate anions which generate the weakest acids favor the loss of isobutylene to give mainly 4-methylphenol. On the other hand, anions such as SbF_6^-, AsF_6^-, and $CF_3SO_3^-$ derived from very strong acids promote the realkylation of 4-methylphenol with isobutylene to give 2-*tert*-butyl-4-methylphenol. The situation with the PF_6^- anion is anomalous since the corresponding protonic acid HPF_6 is very strong and, yet, mainly 4-methylphenol is produced. The reasons for this behavior are not understood. In all cases, the amount of the dialkylation product 2,6-di-*tert*-butyl-4-methylphenol observed was small, presumably due to the difficulty of introducing a second *tert*-butyl group

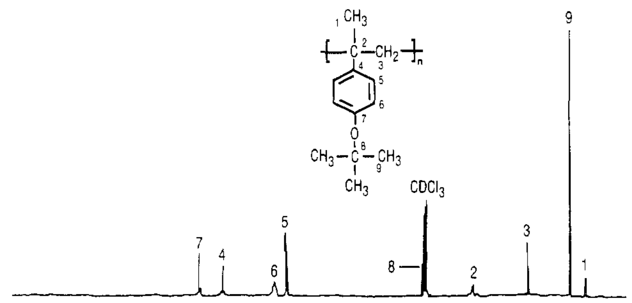
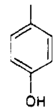
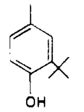
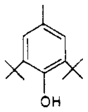


Figure 1. ^{13}C NMR (50.3 MHz, $CDCl_3$) poly(4-*tert*-butoxy-α-methylstyrene): δ 23.6 (C_1), 61.0 (C_2), 42.6 (C_3), 144.4 (C_4), 122.9 (C_5), 126.8 (C_6), 152.2 (C_7), 77.5 (C_8), 28.8 (C_9).

Table III
Study of the Deblocking of 4-*tert*-Butoxytoluene with (4-Methoxyphenyl)phenyliodonium Salts as a Function of the Anion[a]

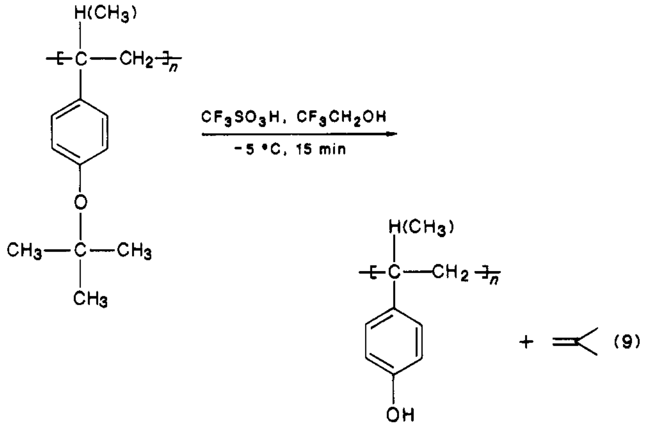
	products (%)		
anion			
TsO^-	79	13	3
ClO_4^-	85	8	<1
PF_6^-	61	25	4
SbF_6^-	39	57	3
AsF_6^-	46	48	5
$CF_3SO_3^-$	30	65	4

[a] Solution 0.01 mol of 4-*tert*-butyltoluene in 0.01 mol of 1,1,2,2-tetrachloroethane containing 5 × 10^{-4} mol of (4-methoxyphenyl)phenyliodonium salts; irradiated 1 min and then heated 5 min at 100 °C.

into the already sterically hindered 6-position of 2-*tert*-butyl-4-methylphenol.

Additional model deblocking studies were carried out with 4-*tert*-butoxytoluene. It was found that a wide variety of photosensitive diaryliodonium and triarylsulfonium salts could be used to carry out the deblocking reaction. Usually, an irradiation time of 15 s using a Hanovia 450-W medium-pressure mercury arc lamp followed by a brief heating at 100 °C was sufficient to fully deblock the phenolic group.

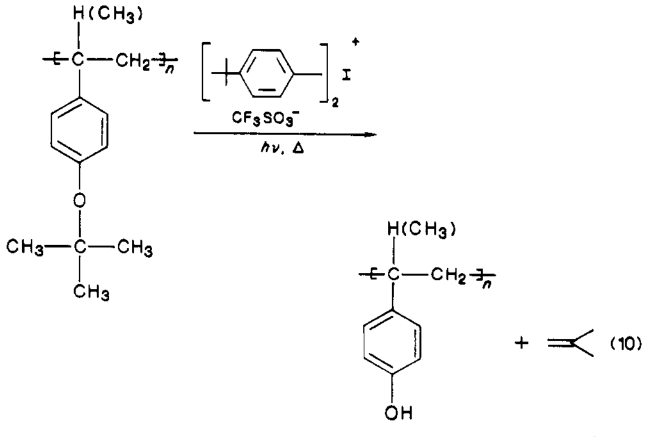
Deblocking Studies of Polymers Bearing *tert*-Butoxy Groups. With the model compound deblocking studies in hand as a guide, studies were conducted on the polymers poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene) using strong acids as well as photosensitive diaryliodonium salts to carry out the photochemical deblocking of the phenolic groups. As shown in eq 9, it was found that the polymers could be fully deblocked within 15 min by treatment with a catalytic amount of trifluoromethanesulfonic acid using 1,1,1-trifluoroethanol as a solvent.



(9)

Examination of the polymers using ^{1}H NMR showed that the band at 1.2–1.3 ppm ascribed to the methyls of the *tert*-butoxy groups had completely disappeared, indicating that the polymers had undergone quantitative deblocking of the phenolic groups. Comparison of the ^{1}H NMR of the deblocked poly(4-*tert*-butoxystyrene) with authentic poly(4-hydroxystyrene) showed that the two materials were identical. Whereas the initial *tert*-butoxy-substituted polymers were insoluble in methanol, the deblocked polymers were completely soluble in this solvent.

Alternatively, as depicted in eq 10, photosensitive onium salts could be used to smoothly deblock the polymers with the loss of isobutylene to give the corresponding macromolecules containing phenolic groups.



(10)

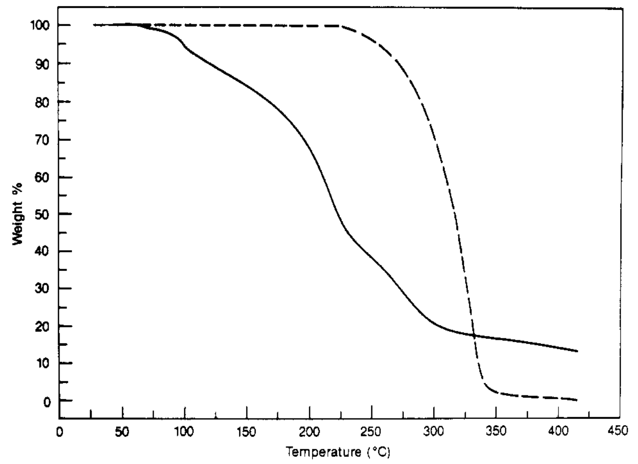


Figure 2. Thermogravimetric analysis study of the thermal decomposition of poly(4-*tert*-butoxy-α-methylstyrene) (---) and after 10-s UV irradiation in the presence of 10% by weight bis(4-*tert*-butylphenyl)iodonium hexafluoroantimonate (—).

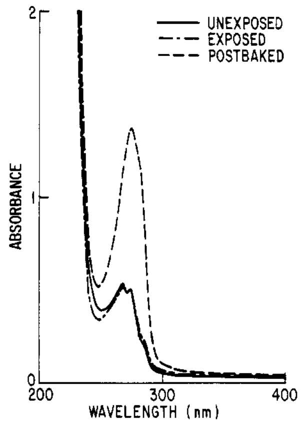


Figure 3. UV study of the deblocking of poly(4-*tert*-butoxystyrene) by bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate before irradiation (unexposed), after 10-s irradiation (exposed), and after heating (postbaked) at 100 °C for 5 min.

Figure 2 shows a thermogravimetric analysis study of a film of pure poly(4-*tert*-butoxy-α-methylstyrene) as well as a curve of a film containing the photoiniator bis(4-*tert*-butylphenyl)iodonium hexafluoroantimonate after irradiation. Poly(4-*tert*-butoxy-α-methylstyrene) is quite thermally stable and undergoes gradual weight loss by depolymerization losing 45% of its weight at 340 °C. In contrast, polymers containing pendant (*tert*-butoxycarbonyl)oxy groups are considerably less thermally stable. For example, poly(4-(*tert*-butoxycarbonyloxy)styrene) loses 45% of its weight at 191 °C.[4] After irradiation, the acid generated by photolysis of the iodonium salt catalyzes the facile loss of isobutylene which is indicated by the rapid loss in weight of the polymer. Here, as in the case of the model compound, deblocking of the phenolic groups only occurs upon heating after irradiation of the polymer films containing the photoinitiator. This is shown in Figure 3 where the UV band at 278 nm assigned to the presence of phenolic groups in a film of poly(4-*tert*-butoxystyrene) develops only after postbaking the irradiated polymer. Identical results were obtained by using films of poly(4-*tert*-butoxy-α-methylstyrene). It is interesting to note that in contrast to the model compound where substantial realkylation by isobutylene to give ring substituted *tert*-butylated products occur that realkylation in the polymers takes place to very much less degree as indicated by ^{1}H NMR. The reason for this may be due to the presence of steric hindrance at the open ortho and meta ring positions by the neighboring pendant aromatic groups in the polymer which are absent in the model compound. Consequently, poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene) can serve as convenient masked sources of the corresponding poly(4-hydroxystyrene) and poly(4-hydroxy-α-methylstyrene) which are difficult to obtain using alternate routes.

Preliminary lithographic evaluations were carried out on poly(4-*tert*-butoxystyrene) and poly(4-*tert*-butoxy-α-methylstyrene) employing bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate as the photosensitive acid precursor to determine whether it was possible to employ such polymers as useful photoresists. Indeed, it was observed that a short 2–3-s irradiation through a mask followed by heating the exposed photoresist films for 5 s at 100 °C gave a visible latent image in the polymer films. Microscopic examination of the latent image shows that it is due to the differences in film thickness which arise from the loss of isobutylene in the irradiated portions of the photoresist film. The irradiated portions of the photoresist could be preferentially removed by dissolution in 1.6 N aqueous NaOH. Positive images with good resolution resulted. Conversely, treatment of the exposed and postbaked photoresist with dichloromethane removed the unexposed portions of the pattern leaving a negative image of the mask. The above successful imaging experiments were carried out by using a photoinitiator which absorbs at 237 nm in the region classified as the "deep UV". Conventional novolac-based resins cannot be used in the "deep UV" because these polymers have too great an optical density at these wavelengths.[6] As may be noted in Figure 3, the absorption in the UV spectrum of poly(4-*tert*-butoxy-α-methylstyrene) and the analogous poly(4-*tert*-butoxystyrene) are negligible in the region above 280 nm. These polymers are, therefore, most useful for the design of photoresists which function in the "mid" and long wavelength regions of the UV spectrum. Finally, these *tert*-butoxylated polymers provide another example of photoresist materials whose inherent high photosensitivities are a consequence of a chemical amplification or photomultiplication effect which is due to the catalytic nature of the deblocking reaction. The lithographic performance of these materials was further studied and will be reported elsewhere.

Conclusions

Styrenic and α-methylstyrenic polymers bearing *tert*-butoxy groups on the pendant aromatic moieties are easily converted to the corresponding hydroxyl functional polymers by removal of the *tert*-butoxy groups under conditions of acid catalysis. In this study, it has been shown that the required vinyl aromatic monomer precursors of these polymers can be prepared by the reaction of the appropriate vinyl aromatic Grignard reagent with *tert*-butyl peroxybenzoate. These monomers can be readily polymerized by conventional free radical, anionic, and cationic techniques to yield the desired *tert*-butoxy-substituted polymers. The polymers can be employed together with photosensitive onium salts to give very sensitive photoresists with potential microelectronic applications.

Acknowledgment. We thank E. A. Williams for her help in obtaining the ^{13}C NMR data, N. Marotta for the TGA curves, and R. May for his assistance in obtaining and interpreting the mass spectroscopy data.

Registry No. Poly(4-*tert*-butoxystyrene), 95418-60-3; poly(4-*tert*-butoxy-α-methylstyrene), 105649-66-9; 4-*tert*-butoxytoluene, 15359-98-5; 4-*tert*-butoxystyrene, 95418-58-9; 3-*tert*-butoxystyrene, 105612-79-1; 4-*tert*-butoxy-α-methylstyrene, 105612-78-0; trifluoromethanesulfonic acid, 1493-13-6; bis(*tert*-butylphenyl)iodonium trifluoromethanesulfonate, 84563-54-2; bis(4-*tert*-butylphenyl)iodonium hexafluoroantimonate, 61358-23-4; dodecylthiol, 112-55-0; (4-methoxyphenyl)phenyliodonium tosylate, 27126-77-8; (4-methoxyphenyl)phenyliodonium perchlorate, 116970-48-0; (4-methoxyphenyl)phenyliodonium hexafluorophosphate, 80134-77-6; (4-methoxyphenyl)phenyliodonium antimonate, 87709-41-9; (4-methoxyphenyl)phenyliodonium arsenate, 116970-49-1; (4-methoxyphenyl)phenyliodonium trifluoromethanesulfonate, 115298-63-0.

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