Formation of Polymers Containing 4-Hydroxystyrene via Hydrolysis of 4-((Trimethylsilyl)oxy)styrene

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ABSTRACT: A novel strategy for the incorporation of hydroxystyrene into styrenic polymers has been developed. Utilization of the trimethylsilyl protective group allows facile incorporation of ((trimethylsilyl)oxy)styrene into a variety of styrene and styrene–sulfone polymer materials. The method involves a radical polymerization to give pure, high molecular weight polymers. The silylated material is readily converted to its hydroxy equivalent under mildly acidic conditions. Specifically, the synthesis and characterization of copolymers of 4-hydroxystyrene, ((*tert*-butoxycarbonyl)oxy)styrene, and/or sulfur dioxide are presented.

Introduction

Poly(*p*-hydroxystyrene) has attracted much attention due to the potential use and versatility of the material. The high chemical and thermal resistance of poly(hydroxystyrene) has led to its application as a curing agent for epoxy resins,[1] as a polymeric adsorbent for the removal of organic material from aqueous waste,[2] and as a matrix resin for a photoresist system.[3] Modified forms of poly(hydroxystyrene) are used in the formulation of fire-retardant polymer blends, electrical insulators, gas-separating membranes,[4] and water- or oil-repellent finishes for textiles.[5] In addition, many derivatives have been prepared with hindered phenolic functionalities[6] for use as radical scavengers and antioxidants.

The preparation of poly(hydroxystyrene) has been extensively studied, yet it remains difficult to obtain pure, high molecular weight polymers containing the hydroxystyrene monomer. Much of this difficulty is due to the synthesis of the hydroxystyrene. Many procedures exist for the preparation of 4-hydroxystyrene (1). Sovish[7] described a procedure in which 1 is distilled directly from a mixture of *p*-hydroxycinnamic acid, quinoline, and copper powder. However, the product was found to polymerize spontaneously at temperatures as low as 0 °C. The presence of acidic impurities remaining after isolation may have initiated the self-polymerization. Overberger[8] developed a similar synthesis in which *p*-hydroxycinnamic acid was sublimed to give a mixture of starting material and the product, 1, which is isolated in increased yields. Overberger also reported self-polymerization of the monomer at room temperature in the solid state. Tachibana et al.[9] dehydrogenated *p*-ethylphenol over a tin oxide catalyst at high temperatures to give the hydroxy-containing monomer, 1. Another method involves the thermal decomposition of 4,4′-ethylidenebis[phenol] in the presence of either an iron oxide–chromium oxide catalyst[10] or sulfuric acid.[11] The difficult aspect of the various syntheses of 4-hydroxystyrene is purification. The isolated monomer 1 is an unstable compound and will polymerize to yield low molecular weight polymers even under refrigeration.

We have been interested in polymers which can undergo facile side-chain transformations that modify the overall polarity or solubility of the macromolecules for use in microlithography. The *tert*-butoxycarbonyl (BOC) protected phenolic systems have been extensively investigated for resist applications because the BOC group can be selectively eliminated to produce a hydroxy moiety in the presence of a photoacid generator (PAG) upon exposure to UV radiation followed by postexposure bake (PEB).[12–15] Poly(((*tert*-butoxycarbonyl)oxy)styrene-*co*-sulfone) (PTBSS) in particular has proven to be an important component of sensitive deep-UV photoresists operating at 248 nm.[15,16] However, deprotection of the unexposed region occurs during processing, leading to a loss of linewidth control. Thus, it is desirable to decrease the relative amount of BOC groups that are incorporated into the polymer. The incorporation of hydroxystyrene into polymers with ((*tert*-butoxycarbonyl)oxy)styrene (TBS) has been proposed to address this issue.

Several groups have synthesized polymers containing hydroxystyrene for use as resist materials using two general approaches. One method involves chemical modification of poly(4-hydroxystyrene) to yield the desired copolymer. Polymer modification in general is difficult to control, particularly when polymers with specific compositions are desired. Murata,[17] Yamaoka,[18] and Cunningham[19] have partially silylated poly(4-hydroxystyrene) to give a copolymer of 4-hydroxystyrene and 4-((trimethylsilyl)oxy)styrene which gives reasonably good lithographic results. However, the polymer is nonhomogeneous, as some regions are rich in hydroxystyrene while others are rich in (silyloxy)styrene.

In another method, the phenolic group of the 4-hydroxystyrene monomer is protected prior to polymerization. This procedure has been used to deprotect poly(((*tert*-butoxycarbonyl)oxy)styrene) (PTBS) by chemical means[12,13] to afford poly(hydroxystyrene). PTBS can also be partially deprotected thermally[1,20] or by acidolysis[1,21] to yield a copolymer of hydroxystyrene and TBS. Copolymers of 4-acetoxystyrene and allyl esters can be selectively hydrolyzed in the presence of acid or base to afford a hydroxystyrene–allyl ester copolymer.[22] Similarly, the acetyl side groups of poly(*p*-acetoxystyrene) can be removed, although problems are encountered when other reactive monomers are present.[23] Our approach to the synthesis of polymers containing hydroxystyrene is similar to the latter method which involves the polymerization of monomers with the hydroxyl group protected, followed by removal of the protecting group after polymer synthesis to generate the free, phenolic material. Previous work has shown that 4-((trimethylsilyl)oxy)styrene (TMSS) can be readily polymerized with other substituted styrene monomers in a random fashion.[24] These polymers are readily converted to their hydroxystyrene counterparts upon mild acid-catalyzed hydrolysis. The use of the

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silyloxy protecting group has many advantages: the (silyloxy)styrene monomer is simple to synthesize and easy to handle, cleavage of the silyloxy protecting group is facile in the presence of many reagent-sensitive groups such as the BOC moiety, and the (silyloxy)styrene polymer can be readily characterized prior to deprotection. This paper reports the synthesis and characterization of homo-, co-, and terpolymers of 4-hydroxystyrene (HS), TBS, and sulfone constructed from the (silyloxy)styrene precursor.

Experimental Section

Reagents. 4-Vinylphenyl acetate was obtained from Hoechst-Celanese. 4-((*tert*-Butoxycarbonyl)oxy)styrene was obtained from Kodak and used as received. Anhydrous sulfur dioxide (SO_2) was obtained from Matheson Gas Products. The azobisisobutyronitrile (AIBN) was obtained from Alfa. The syntheses of 4-vinylphenol[22] and 4-((trimethylsilyl)oxy)styrene were described elsewhere.[24] All other chemicals were obtained from Aldrich.

General Directions. All manipulations involved with the synthesis of polymers were performed on a vacuum line (0.05 mmHg). The polymerizations were carried out in a heavy-walled Kjeldahl flask modified with a vacuum/pressure stopcock allowing for the addition of monomer under vacuum and transfer and distillation of SO_2 on the vacuum line. The initiator to styrene monomer mole ratio was 1:50. The volume of toluene (Aldrich Sure-Seal) used was equivalent to the styrene monomer volume, except for polymers containing sulfone. For these, the styrene monomer volume was equivalent to the total volume of SO_2 and toluene. The molar feed ratio of styrene monomer to SO_2 was 1:1.25.

Characterization. ^1H NMR spectra were recorded on a Bruker AM360 spectrometer on solutions in $CDCl_3$ or CD_3OD using the solvent proton signal as reference. Fourier transform infrared spectrometry (FTIR) was performed on a Mattson Instruments Galaxy Series 8020 FTIR spectrometer in dual-beam mode using double-polished silicon wafers or KBr disks. Ultraviolet spectroscopy was performed on a Hewlett-Packard 8452A diode array spectrophotometer on thin films of the polymers in EEP (15 wt %) spun onto quartz disks. The coated substrates were dried on a hot plate at 105 °C for 4 min. The film thicknesses of the UV samples were measured by a Sloan Dektak 3030 surface measuring system.

Analytical TLC was performed on commerical Merck plates coated with silica gel GF254 (0.25 mm thick). Size exclusion chromatography (SEC) was performed with a Waters Model 510 pump 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 μm particle size MIXC pore-type columns were used with tetrahydrofuran as the eluting solvent. Data acquisition and analysis were performed by an AT&T 6312 microcomputer equipped with an ASYST Unical software system. The molecular weight data are reported relative to a universal calibration curve generated from narrow molecular weight, linear polystyrene standards (Polymer Laboratories).

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. DSC samples were heated at a rate of 10 °C/min.

Elemental analyses (C, H, S, and Si) were determined by Robertson Microlit Laboratories Inc., Madison, NJ.

General Procedure for the Synthesis of Polymers. A mixture of AIBN and toluene in a modified Kjeldahl reactor flask was placed in a −75 °C bath and the flask evacuated. The degassed styrene monomers were transferred under vacuum into the reactor flask. If used in the polymerization, the SO_2 was distilled into a graduated flask at −75 °C, degassed by a freeze/thaw method, and then distilled into the reactor. The reactor flask was sealed off and placed into a 65 °C bath. After 4–8 h, the flask was cooled to room temperature and acetone added. The polymer was simultaneously isolated and deprotected by precipitation of the reaction mixture into acidic methanol (0.5 mL of HCl in 3500 mL of methanol). For polymers containing sulfone (5–8), the polymer was isolated by precipitation into methanol only. The polymer was purified by redissolution into acetone followed by precipitation into petroleum ether (2×). The purified polymer was placed in a vacuum oven overnight at room temperature.

Polymer Characterization. The structures of the silyloxy-containing polymers were verified by ^1H NMR spectroscopy and had the following spectral characteristics: δ 1.55 (CCH_3), 2.0–3.5 (CH and CH_2), and 6.0–7.3 (ArH). The IR spectra displayed the following characteristics: 3460 (OH), 1759 (C=O), 1277 (CO of phenolic groups), and 1223 cm^{-1} (CO of BOC groups). The molecular weights reported are those of the (silyloxy)styrene polymers.

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 (NOE) and a pulse delay of 15 s. The samples were prepared in chloroform-*d* ($CDCl_3$) as 10–20 wt % solutions. Methanol was added to samples that contained more than 50% poly(4-hydroxystyrene) to aid in solubility. The spectra were referenced relative to $CDCl_3$ (77.0 ppm at 50 °C).

Polymer 1: Anal. Calcd: C, 80.0; H, 6.67. Found: C, 77.3; H, 7.23. GPC: M_w = 55200; M_n = 45200; D = 1.2; IV = 0.19 dL/g. OD: 0.20 AU/μm. Yield: 21% as a white solid.

Polymer 2: Anal. Calcd: C, 76.6; H, 6.90. Found: C, 76.2; H, 71.8. GPC: M_w = 68300; M_n = 53500; D = 1.3; IV = 0.23 dL/g. OD: 0.17 AU/μm. Yield: 29% as a white solid.

Polymer 3: Anal. Calcd: C, 74.1; H, 7.06. Found: C, 75.2; H, 7.46. GPC: M_w = 64500; M_n = 49000; D = 1.3; IV = 0.21 dL/g. OD: 0.14 AU/μm. Yield: 56% as a white solid.

Polymer 4: Anal. Calcd: C, 72.3; H, 7.20. Found: C, 71.8; H, 7.37. GPC: M_w = 75500; M_n = 46000; D = 1.6; IV = 0.21 dL/g. OD: 0.10 AU/μm. Yield: 54% as a white solid.

Polymer 5: Anal. Calcd: C, 67.9; H, 5.66; S, 7.55. Found: C, 65.6; H, 6.38; S, 6.92. GPC: M_w = 40500; M_n = 26000; D = 1.6; IV = 0.11 dL/g. OD: 0.59 AU/μm. Yield: 34% as a purple solid.

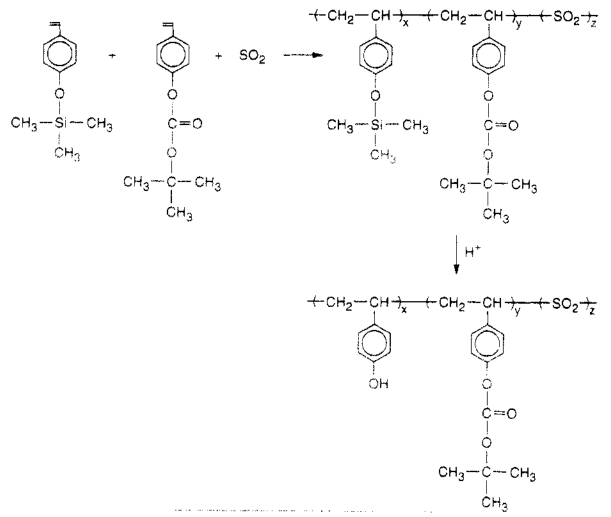
Polymer 6: Anal. Calcd: C, 63.2; H, 5.74; S, 8.36. Found: C, 62.1; H, 6.21; S, 7.84. GPC: M_w = 36700; M_n = 21900; D = 1.7; IV = 0.06 dL/g. OD: 0.51 AU/μm. Yield: 25% as a light yellow solid.

Polymer 7: Anal. Calcd: C, 64.7; H, 6.17; S, 6.32. Found: C, 63.7; H, 6.09; S, 5.68. GPC: M_w = 58100; M_n = 17700; D = 3.4; IV = 0.18 dL/g. OD: 0.37 AU/μm. Yield: 45% as a white solid.

Polymer 8: Anal. Calcd: C, 64.7; H, 6.42; S, 5.24. Found: C, 63.2; H, 6.50; S, 5.72. GPC: M_w = 38600; M_n = 19500; D = 2.0; IV = 0.12 dL/g. OD: 0.12 AU/μm. Yield: 43% as a white solid.

Results and Discussion

We have designed and developed a method by which polymers containing hydroxystyrene may be readily synthesized. Protection of the phenolic groups of 4-hydroxystyrene with the trimethylsilyl group allows facile incorporation of the monomer into a variety of polymers. Subsequent cleavage of the silyl ether appendage then affords the desired hydroxystyrene products. The monomer 4-((trimethylsilyl)oxy)styrene (TMSS) is prepared by treating 4-hydroxystyrene (HS) with hexamethyldisilazane (HMDS) at room temperature. The various silicon-containing polymers were synthesized by radical polymerization of 4-((trimethylsilyl)oxy)styrene monomer with or without ((*tert*-butoxycarbonyl)oxy)styrene (TBS) and sulfur dioxide (Figure 1). In previous work, almost all of the silicon-containing polymers could be readily synthesized by this method.[22] The copolymer of TMSS and sulfone could not be isolated without hydrolytic cleavage of the Si–O bond. Incomplete removal of sulfur dioxide from the reaction solution followed by precipitation into methanol apparently cleaved the Si–O bond of the polymers to generate the free phenol. It is presumed that excess sulfur dioxide in the reaction mixture reacted with



POLYMER	x	y	z
1	1	0	0
2	3	1	0
3	1	1	0
4	1	3	0
5	3	0	1
6	2.25	0.75	1
7	1.5	1.5	1
8	0.75	2.25	1

Figure 1. Chemical compositions of polymers 1–8.

water upon exposure to air to generate weak acids which subsequently cleaved the silyl ether group.

Two approaches were taken for the isolation of the hydroxystyrene-containing materials. In one method, the (silyloxy)styrene polymers were isolated and characterized. This was done to more readily determine molecular parameters such as molecular weight and dispersity of the polymers. After full characterization of the (silyloxy)-styrene polymers, the hydroxystyrene polymers could be generated by precipitation into acidic methanol.

The hydroxystyrene materials could also be obtained directly without prior isolation of the silylated analogs. For the sulfone-containing polymers (5–8), the trimethylsilyl (TMS) groups could be cleaved in the initial isolation process by precipitation into methanol, while for the sulfone-free materials (1–4), the silyl ether appendage was cleaved during the isolation process by precipitation of the reaction mixture into acidic methanol. It should be noted that cleavage of the silyl group would not occur when any of the (silyloxy)styrene polymers were precipitated into acidic, dry 2-propanol or petroleum ether. The presence of water in the precipitating solution was required for silyl ether hydrolytic cleavage to occur. Thus it is possible to isolate either a polymer containing trimethylsilyl ether or phenolic groups depending upon the solvent mixture used for precipitation. Poly(4-hydroxystyrene) generated from the isolated poly(4-((trimethylsilyl)oxy)-styrene) has the same characteristics as poly(4-hydroxystyrene) generated directly from the initial reaction mixture.

Full characterization of the (trimethylsilyl)oxy-substituted polymers is reported elsewhere.[24] The weight-average molecular weights for these materials range from 37000 to 76000 and the number-average molecular weights range from 18000 to 54000. Yields are reported for the hydroxystyrene materials generated directly upon initial precipitation of the reaction mixtures and ranged from 21 to 56%. This range is similar to that reported for the (silyloxy)styrene-containing precursors.[24] Elemental analysis indicated that no silicon was present in any of the polymers after purification.

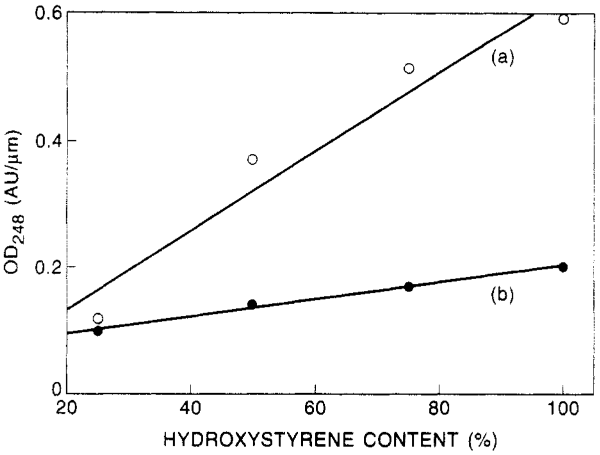


Figure 2. Plot of the optical densities of polymer films at 248 nm versus hydroxystyrene content in the polymers. The upper curve (a) is a fit to the data for polymers 5–8 and the lower curve (b) is a fit to the data for polymers 1–4.

Table 1. Polymer Molecular Characteristics

polymer	$T_{\mathrm{BOC\ deprotection}}$ (°C)	$T_{\mathrm{decomposition}}$ (°C)	T_g (°C)	M_w
1		170	179	55 200
2	120	362	182	68 300
3	136	361	186	64 500
4	159	365	190	75 500
5		200		40 500
6	117	216		36 700
7	131	224		58 100
8	138	207		38 600

The optical densities for polymers 1–8 at 248 nm are plotted against the percent incorporation of hydroxystyrene in Figure 2. The upper curve represents the data obtained for the sulfone-containing polymers (5–8), while the lower curve shows the effect of hydroxystyrene incorporation on the polymers in the absence of sulfone (1–4). Overall, the optical densities increase as the percentage of hydroxystyrene in the polymer increases. Of particular interest is the fact that hydroxystyrene composition has a more profound effect on the sulfone-containing materials (5–8). For polymers 1–4, the optical density increases slowly with an increase in hydroxystyrene composition, while the optical density for polymers containing sulfone (5–8) rises dramatically. Mixon et al. have observed similar trends.[20] Quinone formation was not observed by infrared spectroscopy. Therefore, oxidation of the phenolic groups is presumed not to be occurring.

A partial summary of the thermodynamic properties of polymers 1–8 is shown in Table 1. Increasing the content of hydroxystyrene tends to decrease the onset temperature of BOC group deprotection. The acidic phenolic hydrogen most likely catalyzes the cleavage of the BOC groups.[25] Polymers that incorporated sulfone have similar onset temperatures of BOC group deprotection to polymers 1–4. However, the presence of the sulfone moiety in the polymer serves to reduce the decomposition temperature of the material to ≈200 °C. In general, the onset of thermal decomposition did not appear to be affected by the level of hydroxystyrene incorporation in the polymer.

The glass transition temperatures (T_g) for polymers 2–8 could not be detected as the T_g's were higher than the temperature of BOC deprotection. Therefore, the glass transition temperatures shown in Table 1 are for the polymers in which the BOC group has been thermally removed. Under these conditions, we expected that the T_g's for polymers 2–4 would be identical to that of polymer 1. Yet, a slight increase in this parameter was observed as the amount of hydroxystyrene in the original polymer

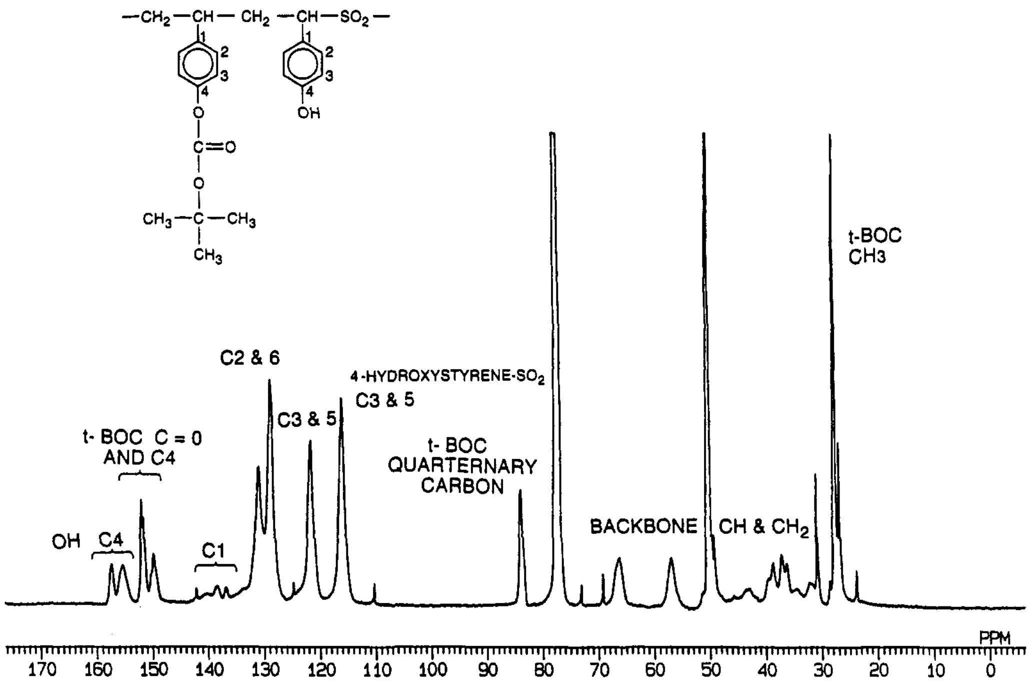


Figure 3. ^{13}C NMR spectrum of poly(hydroxystyrene-*co*-((*tert*-butoxycarbonyl)oxy)styrene-*co*-sulfone) having a hydroxystyrene to TBS ratio of 1:1 and a styrene to SO$_2$ ratio of 3:1.

Table 2. Compositional Analysis by NMR of Selected TMSS–TBS Materials after TMS Deprotection

		styrene monomer (%)		
polymer	parent polymer comp[a]	HS	TBS	TMSS
3	TMSS$_1$:TBS$_1$	46	54	0
7	TMSS$_{1.5}$:TBS$_{1.5}$:SO$_2$	58	42	0
8	TMSS$_{0.75}$:TBS$_{2.25}$:SO$_2$	22	78	0

[a] The TMSS:TBS ratios given here represent the monomer feed ratios during synthesis. [b] The values were determined from ^{13}C NMR data.

decreased. Similarly, it was predicted that the T_g's for the thermally deprotected polymers **6**–**8** should match that of polymer **5**. However, even for the fully deprotected sulfone-containing materials, the T_g's were above the onset temperature of decomposition. These results correspond with other work which has shown that inclusion of sulfone into a polymer raises the glass transition temperature by 30–40 °C.[16,22]

Several hydroxystyrene-containing polymers obtained via hydrolysis of the corresponding TMSS materials were analyzed by ^{13}C NMR (Table 2). The silyloxy-containing protected polymers were analyzed previously.[24] The ^{13}C NMR spectrum of **7**, a terpolymer of HS, TBS, and SO$_2$ having a HS to TBS ratio of 1:1 and a styrene to SO$_2$ ratio of ~3:1, is shown in Figure 3. The methyl of the BOC group (27.75 ppm), the C3 and C5 of the 4-hydroxystyrene component (114–118 ppm), and the methyls of the TMS group (0.275–1.86 ppm)[24] are the resonances used for quantification of each monomer group. After deprotection, the silyl ether methyls are completely removed in all of the polymers; note that no resonances are observed between 0.275 and 1.86 ppm. These NMR data support the elemental analysis results indicating that no silicon is present after purification. From the chemical formulas of materials **3** and **8**, all of the hydroxystyrene originated from the TMSS units of the parent, fully protected polymers. While the chemical formula of **7** suggests that there should be equal amounts of TBS and hydroxystyrene, analysis by NMR before deprotection indicated that 13% hydroxystyrene was present in the polymer as isolated, resulting in a polymer containing 58% hydroxystyrene after TMS deprotection. Clearly then, some degree of deprotection occurs during the synthesis and workup of these polymers.

As the reactivity ratios of both the TBS and TMSS monomers are equal to 1 within experimental error, the monomer units are expected to be randomly placed along the polymer backbone.[24] Deprotection of the Si-containing groups therefore affords a polymer with random incorporation of TBS and hydroxystyrene units. The precise placement of the BOC and TMS groups cannot be distinguished by NMR.

Polymers with structures similar to those described here have been synthesized by alternate routes. For instance, poly(((*tert*-butoxycarbonyl)oxy)styrene-*co*-hydroxystyrene) can be prepared by acid hydrolysis of poly(((*tert*-butoxycarbonyl)oxy)styrene)[21] and the same method can be applied to the preparation of the sulfone polymer analogs.[26] However, the characteristics of these films were found to differ in some respects. Notably, curves of the optical densities of the sulfone polymers prepared via controlled BOC acidolysis were nonlinear relative to the hydroxystyrene composition. Additionally, the polymers prepared via acid hydrolysis of the BOC groups were found to deprotect and discolor on standing even during storage as highly purified solids. Thus, it is imperative that such materials be carefully and thoroughly purified as traces of acid will continue to cleave the BOC groups on storage, deleteriously affecting polymer shelf life. In contrast, the materials prepared from the trimethylsilyl ether precursor exhibit enhanced stability. No change in materials characteristics was observed even for polymers stored for >6 months.

Conclusion

A simple method to achieve random incorporation of hydroxystyrene into various polymers is described. Polymerization of the protected phenolic monomer allows for easy incorporation of hydroxystyrene into various polymers. We have demonstrated that this (silyloxy)styrene monomer can be polymerized with sulfone and TBS. Other styrene monomers should also be readily polymerized with

TMSS to afford hydroxystyrene precursor copolymer materials.

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