NOTES

Preparation of a Novel 1:1 Copolymer of 4-Hydroxystyrene and Sulfur Dioxide

Tsutomu SHINODA,* Mitsuhide YOSHIKAWA, and Tohru NISHIWAKI

Organic Division, Tokyo Metropolitan Industrial Technology Center,
Nishigaoka, Kita-ku, Tokyo 115, Japan

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Recently, silylated hydroxystyrene monomers are being utilized to synthesize resist materials for micro-lithography.¹ The authors in this study conducted the copolymerization of 4-trimethylsilyloxystyrene (**1**) and sulfur dioxide to prepare a silicon-containing positive-type photoresist. But the 1:1 copolymer of **1** and SO₂ was readily hydrolyzed to give a novel sulfone polymer with phenolic hydroxyl groups. Polymer backbone SO₂ groups may enhance the acidity of phenolic hydroxyl protons and facilitate hydrolysis of the trimethylsilyl groups.

We followed the copolymerization conditions of 4-trimethylsilylstyrene and sulfur dioxide reported by Matsuda *et al.*² Twice the molar quantity of distilled SO₂ was transferred under vacuum into a reaction tube containing degassed monomer **1**. After the monomer was dissolved, *tert*-butyl hydroperoxide (**2**) was added as the initiator and the solution was permitted to stand at –80°C for 68 h. The initiator to monomer mole ratio was 1:10³. The reaction was terminated by cooling at –196°C (liquid N₂) and excessive SO₂ was removed under vacuum. The solid residue, when exposed to air, changed color from white to bright purple but became colorless when dissolved in DMSO. The white polymer was isolated by precipitation in dichloromethane. The polymer was purified by reprecipitation and dried at 40°C in a vacuum oven until constant weight was reached.

The ¹H NMR spectrum of the polymer obtained is shown in Figure 1.³ No trimethylsilyl groups existed and the peak at 9.7 ppm decreased in intensity by the addition of D₂O. Figure 2 shows the ¹³C NMR spectrum of the polymer.³ In the aliphatic region of the spectrum,

only two broad peaks were observed at 45.4–48.2 ppm and 60.5–62.4 ppm and assigned to methylene and methine carbons, respectively.⁴ The IR spectrum of the polymer exhibited absorptions at 1124 and 1311 cm^{–1} due to SO₂ stretching (film from DMSO on KBr). The polymer structure was thus a 1:1 copolymer of 4-hydroxystyrene and SO₂, poly(4-hydroxystyrene sulfone) (**3**).⁵ The yield was 77%. Molecular weight and molecular weight dispersity of polymer **3** were determined as *M*_w = 76800 and *M*_w/*M*_n = 2.84 by gel permeation chromatographic (GPC) analysis.⁶ Results of thermogravimetric analysis (TGA) for polymer **3** are shown in Figure 3. Although rapid weight loss started at 130°C under O₂ and N₂ (5% weight loss at 150°C in both

Figure 2. ¹³C NMR spectrum of poly(4-hydroxystyrene sulfone). Figure 1. ¹H NMR spectrum of poly(4-hydroxystyrene sulfone). Figure 3. TGA curves for poly(4-hydroxystyrene sulfone) in oxygen and nitrogen atmosphere (heating rate = 10°C min^{–1}).

Figure 4. Relation between the chemical shifts of carbons substituted by hydroxyl groups and those of phenolic hydroxyl protons.

cases), the weight fraction of nonvolatile residue was much higher in nitrogen (30% at 600°C).

The phenolic hydroxyl protons of polymer **3** are deshielded by 0.7 ppm compared with those of poly(4-hydroxystyrene) (**4**). The benzene ring protons are also deshielded and give two splitting peaks at 6.7 and 7.1 ppm, while those of **4** resonate between 6.1 and 7.1 ppm in DMSO- d_6 . Methine and methylene proton resonances are observed at 4.4–5.0 and 3.1–4.1 ppm, respectively, and shift to much lower field than those of polymer **4** which resonate at 0.8–2.6 ppm. In addition, the C-4 carbon resonance shifts to 3.3 ppm lower field than that of **4**. All these changes can be attributed to the electron-withdrawing effect of the polymer backbone SO₂ groups. Figure 4 shows a plot of the chemical shifts of phenolic hydroxyl protons against those of carbons substituted by phenolic hydroxyl groups for polymer **3**, **4**, and 4-hydroxystyrene.⁷ Good correlation is observed and implies that the acidity of **3** is enhanced. This enhancement probably causes hydrolytic cleavage of the trimethylsilyl ethers.⁸

Uhrich *et al.*⁹ synthesized a 3:1 copolymer of **1** and SO₂ in a 4% yield and concluded that the propensity of the sulfone polymer to undergo hydrolysis may arise from difficulty to remove free SO₂ completely from the material upon isolation. We carried out copolymerization reactions in the absence of initiator **2**, and starting monomer **1** was recovered unchanged. When a drop of water was added to the starting mixture, the hydrolysis of monomer **1** occurred and poly(4-hydroxystyrene) was obtained as the main product in a 42% yield. These results indicate that hydrolysis of the trimethylsilyl groups does not occur only by mere contact with SO₂, and that a copolymer of **1** and SO₂ is produced as shown in scheme 1.

We also carried out the copolymerization of 4-*tert*-

Scheme 1.

butyldimethylsilyloxystyrene, a more hydrolytically stable monomer than **1**, with SO₂ at –60°C for 70 h. No sulfone polymer was produced and poly(4-*tert*-butyldimethylsilyloxystyrene) was obtained in a 78% yield with $M_w = 37600$ and $M_w/M_n = 2.24$.¹⁰

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REFERENCES AND NOTES

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2. H. Ito, T. Sakakibara, M. Matsuda, S. Ito, and H. Ono, *Polym. Prepr., Jpn.*, **37**, 3438 (1988).
3. ¹H and ¹³C NMR spectra were recorded on a JEOL EX-400 spectrometer at a resonance frequency of 400 MHz for proton and 100 MHz for carbon-13. The spectra were observed at room temperature for a 0.40 mol dm⁻³ solution in DMSO- d_6 . The chemical shifts were referred to tetramethylsilane (TMS) added as an internal standard for proton and to DMSO- d_6 (39.5 ppm) and converted to the TMS scale for carbon-13.
4. The assignments were made by comparison with those published previously for poly(styrene sulfone) and both methine and methylene carbon resonances corresponded to the SMS monomer triad sequence (S = sulfur dioxide; M = styrene); R. E. Cais, J. H. O'Donnell, and F. A. Bovey, *Macromolecules*, **10**, 254 (1977).
5. By hydrolyzing poly[4-((*tert*-butoxycarbonyl)oxy)styrene sulfone]s, poly(4-hydroxystyrene sulfone)s have been synthesized with the mole ratio of 4-hydroxystyrene to sulfur dioxide not less than 2; R. S. Kanga, J. M. Kometani, E. Reichmanis, J. E. Hanson, O. Nalamasu, L. F. Thompson, S. A. Heffner, W. W. Tai, and P. Trevor, *Chem. Mater.*, **3**, 660 (1991).
6. GPC analysis of polymer **3** was performed with a Tosoh Model 8020 chromatograph equipped with two TSKgel GMH_{HR}-H columns and a refractive index detector. Reproducible chromatograms were obtained when 50 mmol dm⁻³ DMSO solution of lithium bromide was used as the eluting solvent. The molecular weight reported here is equivalent to that of pullulan.
7. The NMR spectra were measured at room temperature for a 0.20 mol dm⁻³ solution in DMSO- d_6 . Resonance peak tops of phenolic hydroxyl protons of each compound were observed with an error of less than ±0.01 ppm, when measurements were made at 21–24°C, within ±10% variation of concentration, using a freshly opened ampule of Aldrich 99.9 atom% DMSO- d_6 .
8. Trimethylsilyl ethers of 4-hydroxystyrene and poly(4-hydroxystyrene) were stable enough to moisture to be handled in the air.
9. K. E. Uhrich, E. Reichmanis, S. A. Heffner, J. M. Kometani, and O. Nalamasu, *Chem. Mater.*, **6**, 287 (1994).
10. The eluting solvent was tetrahydrofuran. The molecular weight was polystyrene-equivalent.