Preparation and Halogenation of Silylated Polystyrene

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Over the past several years, the preparation of functionalized polymers has been investigated intensively.[1] Cross-linked polystyrene resins have proven particularly interesting, due to both the properties of the resins and the reactivity of the aromatic rings.

While functionalization is generally accomplished via Friedel–Crafts type reactions,[2] polystyrene resins can be lithiated and the highly reactive organometallic polymer subjected to further reaction.[3] Alkali-metalated polymers offer great advantages in reactivity, although some disadvantages are evident. Specifically, little is known about the structure of such intermediates and general methods of analysis are not available. While a method for analysis of poly(styryllithium) has been reported,[4] quenching is required, thus rendering the polymer unreactive. Also, adsorbed organolithium species often can interfere with efficient functionalization of the polymer. We report herein the synthesis of a silylated polystyrene, a stable, isolable species which retains favorable reactivity characteristics.

Results and Discussion

Treatment of polystyrene–2% divinylbenzene copolymer beads with *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in cyclohexane at 60 °C for 24 h afforded the lithiated species.[5] Addition of an excess of chlorotrimethylsilane to the cooled (0 °C) slurry afforded the silylated species (eq 1).

$$\mathrm{PSH} \xrightarrow[\text{TMEDA}]{n\text{-BuLi}} \mathrm{PSLi} \xrightarrow{\mathrm{ClSiMe_3}} \mathrm{PS\text{-}SiMe_3} \tag{1}$$

The silylated polymer is an air- and moisture-stable species, with IR stretching frequencies (1250, 840 cm^{-1}) characteristic of organosilanes. Functionalizations obtained in representative experiments are listed in Table I. As has been previously noted,[4] the degree of lithiation does not necessarily correspond directly to the amount of butyllithium added.

Table I
Silicon Incorporation onto Lithiated Polystyrene with Chlorotrimethylsilane

equiv of *n*-BuLi (per arene)	% Si	mmol of Si/g of polymer	% functionalization
1.2	7.83	2.78	36.3
1.11	3.64	1.30	14.9
0.50	2.53	0.90	10.03

The silyl species shows reasonable stability toward protodesilation. Treatment of the polymer with acetic acid for 24 h at room temperature results in no reaction, while similar treatment with trifluoroacetic acid in acetonitrile produces complete protodesilation.

The trimethylsilyl substituent has been shown[6] to activate that position to electrophilic attack. In order to assess the relative reactivities of silylated to nonsilylated sites, halogenation of the silylated polymer was carried out (eq 2).

$$\mathrm{PS\text{-}SiMe_3} \xrightarrow{\mathrm{XY}} \mathrm{PS\text{-}X} + \mathrm{Y\text{-}SiMe_3} \tag{2}$$

$$\mathrm{X = Y = Br}$$

$$\mathrm{X = I;\ Y = Cl}$$

Addition of the halogenating agent (Br_2 or ICl) to a suspension of the silylated styrene copolymer in dichloromethane was carried out at room temperature without the addition of Lewis acids. Filtration and washing (acetone, methanol) afforded the partially halogenated polymer.

Table II summarizes analyses of the halogenation studies. As can be seen from inspection of the data, bromodesilation takes place cleanly, within experimental error.[7] A full equivalent of bromine can be used, regardless of the degree of functionalization.

In the case of iodine monochloride, however, the reaction appears less selective. As the limiting reagent, ICl reacts to afford iododesilation cleanly. As a stoichiometric reagent, some iododeprotonation competes. When large loads of silicon are employed, this competing reaction occurs to a large extent.

In view of this marked selectivity, the lithiation–silylation sequence (eq 1) provides a method to afford a species which is activated to electrophilic attack at certain sites, yet can be analyzed, stored, and manipulated without special precautions.

Experimental Section

General Methods. All reactions of air- and water-sensitive materials were carried out under an argon atmosphere. Hydrocarbon and ethereal solvents were distilled from CaH_2 prior to use, as was TMEDA. Halogenated solvents were distilled from $CaCl_2$. Polystyrene–2% divinylbenzene copolymer beads (200–400 mesh) were purchased from Eastman Kodak Co. and were treated as described below. Elemental analyses were carried out by Galbraith Laboratories, Inc., or Atlantic Microlab, Inc. IR spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer.

The usual workup procedure for each polymer reaction consisted of filtration of the polymer on a Büchner funnel, washing with cyclohexane, acetone, and methanol, and drying in an Abderhalden apparatus at 0.4 torr and 65 °C.

Table II
Halogenodesilation of Silylated Polystyrene

starting material				product			
% arene silylated	(elem anal.)	equiv of XY (per SiAr)	XY	% arene silylated	(elem anal.)	% arene halogenated	(elem anal.)
36.3	(7.83)	0.06	Br_2	30.67	(6.73)	2.11	(1.32)
36.3	(7.83)	1.0	Br_2	1.99	(0.418)	35.22	(21.10)
14.9	(3.64)	1.0	Br_2	1.50	(0.35)	14.80	(10.16)
36.3	(7.83)	0.5	ICl	14.37	(2.93)	18.31	(16.87)
36.3	(7.83)	1.0	ICl	19.50	(3.26)	39.76	(29.98)
10.0	(2.53)	1.0	ICl	4.20	(1.00)	9.30	(9.95)

Pretreatment of Polystyrene Copolymer Beads.[5] A 1-L round-bottomed flask was charged with 400 mL of cyclohexane and 77 g (0.739 equiv) of polystyrene–2% divinylbenzene copolymer beads. The polymer was allowed to swell with stirring, for 24 h at 60 °C and then cooled to 0 °C. TMEDA (112 mL, 86.2 g, 0.742 equiv) was added, followed by *n*-butyllithium (0.731 equiv). After stirring for 1 h at room temperature, the slurry was heated to 60 °C for 8 h, at which point it was cooled to 0 °C and quenched with methanol. The usual workup afforded the material used in subsequent steps.[8]

General Procedure for the Preparation of Silylated Copolymer Beads. In a similar fashion, the pretreated beads (50.8 g, 0.48 equiv) were allowed to swell in cyclohexane (300 mL) at 60 °C for 24 h and then cooled to 0 °C. Following addition of the requisite amount of TMEDA and *n*-butyllithium (in a 1:1 molar ratio), the temperature was raised to 60 °C and the slurry stirred for 24 h. The lithiated polymer was cooled to 0 °C and excess chlorotrimethylsilane (twofold based on butyllithium) added. The usual workup afforded the silylated polymer (ν(KBr) 1250, 840 cm^{-1}). Analytical data are summarized in Table I.

General Procedure for Halogenation of PS-SiMe$_3$. A slurry of CH_2Cl_2 (75 mL) and silylated polystyrene (5 g) was allowed to swell at room temperature for 12 h. To the slurry was added a solution of the requisite amount of halogenating agent in CH_2Cl_2 (15 mL). After 8 h of stirring at room temperature, the usual workup afforded either partially brominated polymer or partially iodinated polymer, depending on halogenating agent. Analyses are summarized in Table II. IR analysis showed partial loss of the silyl stretching frequencies. C–X stretching frequencies could not be readily discerned within the aromatic region.

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References and Notes

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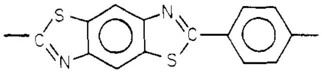
(7) At these levels, a change of 0.2% elemental composition leads to a change of approximately 1.0–1.5% in degree of functionalization calculated therefrom.
(8) Failure to pretreat the beads in this fashion resulted in consistent overhalogenation, probably due to extra vinyl groups in the polymer.[5]

Communications to the Editor

Mechanical Studies of High-Strength, High-Modulus Poly(*p*-phenylenebenzobisthiazole) Fibers

This work deals with the evolution of the mechanical properties of fibers produced from anisotropic solutions of poly(*p*-phenylenebenzobisthiazole) (PBT) by dry-jet wet spinning. PBT, with repeat unit



is characteristically a rigid-rod polymer (details of the synthesis, preparation, and chemical structure of PBT can be found in other articles in this issue). PBT was prepared as part of the Air Force Ordered Polymers Research Program,[1] which is aimed at the attainment of high strength, high temperature resistance, and environmental stability in a material of an organic base for use as a structural material. Of the polymers investigated in this program PBT has shown the most promise. The PBT fibers, as spun and heat treated, exhibit both a high specific modulus and a high strength, and their environmental stability in all but strong acid environments is excellent.

Experimental Details. The PBT fibers investigated in this work were produced by a dry-jet, wet-spinning process at Celanese Research Co. and at Carnegie-Mellon University. A schematic of the spinning apparatus is given in Figure 1. Fibers designated as PBT/PPA were spun from solutions of 5–6% polymer in poly(phosphoric acid) (PPA), while those designated as PBT/MSA were spun from solutions of roughly 10% polymer in a dissolvent of 97.5% methanesulfonic acid/2.5% chlorosulfonic acid. Coagulation baths of water or water/methanesulfonic acid were used. Heat treating of the fibers was accomplished by drawing them through a tubular oven under a nitrogen atmosphere.

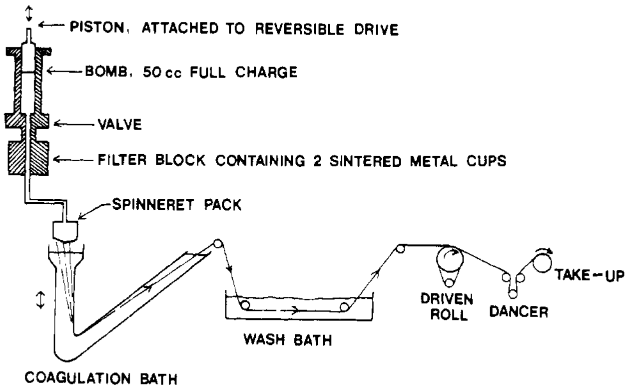


Figure 1. Schematic diagram of PBT spinning apparatus.

The tensile mechanical properties of the as-spun and heat-treated PBT fibers reported here were determined in compliance with ASTM D3379-75e. A Toyo Tensilon Model UTM-II and an Instron universal testing machine were used for the tensile tests to determine axial mechanical properties. A strain rate of 1%/min was commonly used. Fiber deniers were determined by the vibroscope technique (ASTM D1-577-73).

Fiber Properties. PBT fibers as spun and after heat treating have demonstrated both high modulus and high strength. Moduli of 800 g/denier are typical for as-spun fibers with strengths around 8 g/denier. Heat treatment yields fibers with moduli as high as 2100 g/denier and strengths of 20 g/denier. Table I summarizes typical strength and modulus values for both as-spun and heat-treated fibers produced from PBT/MSA and PBT/PPA

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