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Notes

Perdeuterated Polystyrene Synthesized with Identical Chain Ends

Daniel Bucca and Bernard Gordon, III*

Department of Material Science and Engineering, Polymer Science Program, The Pennsylvania State University, University Park, Pennsylvania 16802

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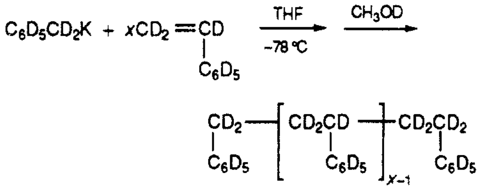
Introduction

Deuterated polystyrenes have been used in neutron reflectrometry experiments to investigate density profiles of polymer interfaces.[1–3] It has been observed that substituting deuterium for hydrogen on polystyrene represents enough of a perturbation to cause deuterated/protonated polystyrene blends to phase separate. Experiments have determined that the deuterated segment of a polymer blend will preferentially migrate to the air surface, of an air/polymer interface, when the polymers are of equal molecular weight.[1] However, recent neutron reflectometry experiments on polystyrene blends have shown that when the protonated/deuterated blends are composed of a lower molecular weight protonated polymer, the protonated component partitions preferentially to the air surface.[2] Other studies have demonstrated that small end groups on the polymer chains can be sufficient to cause differences in interfacial segregation behavior.[3] In order to better study the subtleties of chain ends and molecular weight effects of interfacial segregation behavior, deuterated polystyrenes of specific molecular weights and chain ends which resemble the bulk of the polymer are needed.

By anionically initiating styrene-d_8 with benzyl-d_7-potassium and terminating the polymerization with methanol-d_1, perdeuterated polystyrene with identical benzylic chain ends can be synthesized (eq 1). Our interest has been in the synthesis of carbanionic initiators by LICKOR (from Li–C and K–OR) mixed base systems. Part of our research has attempted to exploit these mixed base systems to prepare anionic and polyanionic reagents for the syntheses of novel polymer architectures.[4,5] A number of authors have reported the use of LICKOR mixed base systems as a facile route for generating organopotassium reagents.[6,7] These carbanions can be isolated in high yields and have been shown to behave as organopotassium reagents in the nucleophilic substitution/addition synthesis of low molecular weight compounds.[7] Herein, we describe the preparation of a deuterated benzylpotassium initiator for the polymerization of styrene-d_8 and analogously prepared protonated polystyrene.



$$C_6D_5CD_2K + x\,CD_2{=}\underset{\displaystyle C_6D_5}{\underset{|}{CD}} \xrightarrow[-78\,^\circ C]{THF} \xrightarrow{CH_3OD} \underset{\displaystyle C_6D_5}{\underset{|}{CD_2}}-\left[\underset{\displaystyle C_6D_5}{\underset{|}{CD_2CD}}-\right]_{x-1}-\underset{\displaystyle C_6D_5}{\underset{|}{CD_2CD_2}}$$

(1)

Experimental Section

Materials. Toluene-d_8 (MSD Isotopes), methanol-d_1 (Aldrich), *n*-butyllithium (1.6 M), *tert*-pentyl alcohol, heptane, dibutylmagnesium in heptane, and potassium metal were used as received from commercial sources. Styrene-d_8 (Cambridge Isotope Laboratories) and styrene (Aldrich) were titrated with dibutylmagnesium until a persistent yellow color developed. They were then vacuum distilled prior to use. Potassium *tert*-pentoxide was prepared by refluxing pentyl alcohol with potassium metal.[7a] The product was recrystallized from heptane, sublimed at 110 °C under vacuum, and stored under argon until needed. Tetrahydrofuran (THF) was freshly distilled on a high-vacuum line from a green sodium/anthracene dispersion. Hexane was washed with concentrated sulfuric acid, distilled water, saturated aqueous sodium bicarbonate, and finally distilled water. It was then dried over magnesium sulfate, filtered, and distilled from potassium onto molecular sieves where it was stored under argon until needed.

Preparation of Initiator. Potassium *tert*-pentoxide (0.699 g, 5.54 mmol) and toluene-d_8 (0.650 g, 6.50 mmol) were combined with 20 mL of hexane in a 50-mL round-bottomed flask equipped with a glass stirring bar under argon. *n*-Butyllithium (6.0 mL, 9.6 mmol)[8] was added to this suspension, causing the immediate observance of an orange precipitate. The suspension was stirred for 3-$^1/_2$ h and then filtered through a glass frit in an argon-filled glovebox. The precipitate was rinsed with three 10-mL portions of hexane and vacuum dried, yielding 0.681 g of the product (90% yield based on potassium *tert*-pentoxide). The nondeuterated benzylpotassium initiator was prepared analogously with typical yields of ≥90%.[9] NMR spectra were obtained with a broad-band Bruker AM-300 NMR instrument operating at 300 MHz for proton and 92 MHz for deuterium.

Preparation of Polystyrene. Polymerizations were carried out on a high-vacuum manifold which had been flamed dried and evacuated for >12 h. Additional glassware was baked dry in an oven at 150 °C for >12 h. All reagents were degassed by 2–4 freeze/pump/thaw cycles prior to use. A weighed amount of initiator (powder or in solution) was placed into a 100-mL round-bottomed flask fitted with a graduated addition funnel and vacuum adapters. The apparatus was assembled in an argon-filled drybox and then fitted onto the vacuum manifold, where it was completely evacuated. THF was vacuum-transferred into the round-bottomed flask and allowed to warm to dry ice/acetone temperature. Styrene was transferred into the addition funnel and upon thawing added dropwise into the round-bottomed flask containing the initiator. The reaction was carried out at dry ice/acetone temperatures for ca. 20 min, at which time 1 mL of methanol-d_1 was vacuum-transferred into the round-bottomed flask to terminate the reaction.

The polymers were precipitated into a 10-fold excess of methanol and isolated by vacuum filtration. They were dried in a vacuum oven set at 100 °C overnight. Yields of polymer were quantitative. Molecular weights of polymers were characterized by a Waters 150C ALC/GPC using three Ultrastyragel columns with pore sizes 100, 10^3, and 10^4 Å. Calibration was performed using a linear set of narrow molecular weight polystyrene standards ranging from 10^7 to 10^3 obtained from Pressure Chemical.

Results and Discussion

The initiator was measured as a dry powder or as a solution in anhydrous THF. It was necessary to prepare initiator solutions to accurately measure small amounts (on the order of 10^{-5} mol) of initiator in order to obtain polymer of molecular weight $>10^5$. The difficulty arose in synthesizing the deuterated polystyrene. Because of its expense, the least amount of deuterated monomer was used in the polymerization reaction. This in turn required

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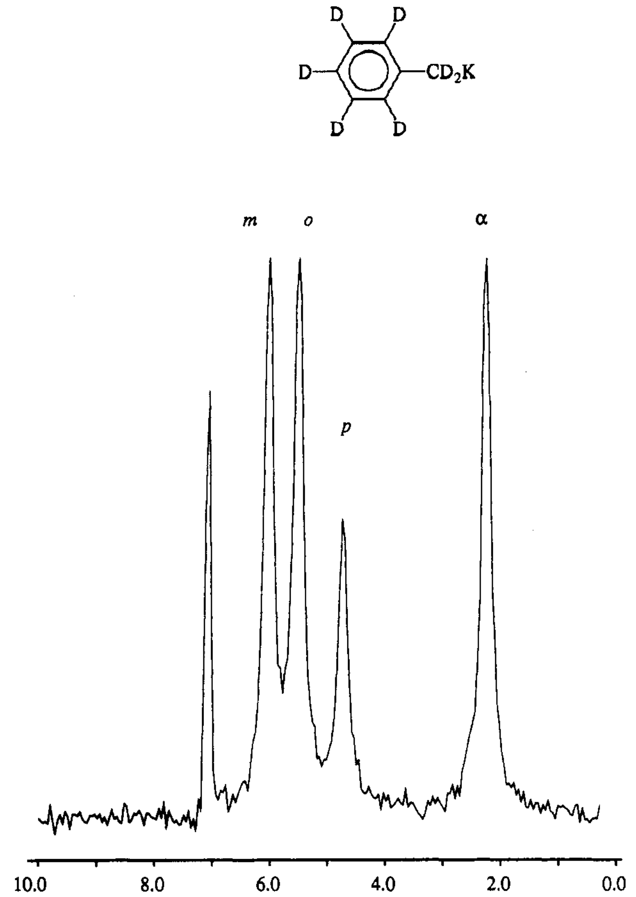

Figure 1. 92-MHz deuterium NMR of benzyl-d_7-potassium in THF. Peak assignments, relative to toluene at δ 7.10, are as follows: *meta*, δ 6.04; *ortho*, δ 5.44; *para*, δ 4.70, *alpha*, δ 2.17.

the measurement of small amounts of initiator (1–3 mg). Solutions were prepared by adding weighed amounts of initiator to weighed amounts of THF in the glovebox.[10] Typically, the initiator solutions were >80% of the expected concentrations.[11] The concentration of active initiator was checked prior to the polymerizations by titrating a solution of 2,5-dimethoxybenzyl alcohol in THF to a faint yellow with the initiator solution.[12]

Table 1. Molecular Weight Data of Deuterated Polystyrene (DPS) and Protonated Polystyrene (HPS)

		GPC[a]		
polymer	M_n[b]	M_w	M_n	M_w/M_n
DPS-1	81 000	75 600	67 900	1.11
DPS-2	187 000	578 000	558 000	1.04
HPS-3	17 700	32 100	29 500	1.09
HPS-4[c]	24 000	57 600	49 200	1.17
HPS-5	23 700	75 700	67 900	1.11
HPS-6	100 000	169 000	164 000	1.03

[a] Measured weights are relative to polystyrene standards. [b] Calculated molecular weights based on monomer to initiator ratios. [c] Includes a high molecular weight shoulder.

Figure 1 represents a deuterium NMR of benzyl-d_7-potassium in THF. The peak assignments are similar to those recorded previously for protonated benzylpotassium.[13] However, since deuterium has a smaller magnetic moment and a smaller angular momentum relative to hydrogen (due to its smaller charge to mass ratio), deuterium NMR is less sensitive than proton NMR.[14] This can be seen in the breadth of the peaks and the inability to resolve spin–spin coupling patterns in the ^{2}H spectrum. In Figure 1, the *meta*, *ortho*, *para*, and *alpha* signals have a 2:2:1:2 relative intensity but are devoid of any spin–spin coupling. Also seen in the spectrum is approximately 15% of deuterated toluene at δ 7.10, the appearance of which was the result of water impurities in THF reacting with the benzyl-d_7 carbanion. The methyl deuterium nuclei of toluene (δ 2.31) cannot be resolved from the *alpha* deuterium signal of the benzyl anion (δ 2.17). The two peaks overlap and the methyl deuterium nuclei are seen as a should on the low-field side of the *alpha* deuterium nuclei's signal. Proton NMR of the deuterated product revealed no alkoxide or other impurities that may have coprecipitated with the carbanion.

Table 1 summarizes the molecular weight averages of the deuterated polystyrenes (DPS) and protonated polystyrenes (HPS) synthesized in this study. Typically, the molecular weight of the actual polymer is greater than its calculated value. Calculated molecular weights are based on the monomer to initiator ratios, and greater than calculated values are caused by the loss of initiator activity due to impurities. Polymer DPS-2 has the greatest error in this regard, which can be expected, since it required the most accuracy for its preparation. Polymer HPS-4 showed

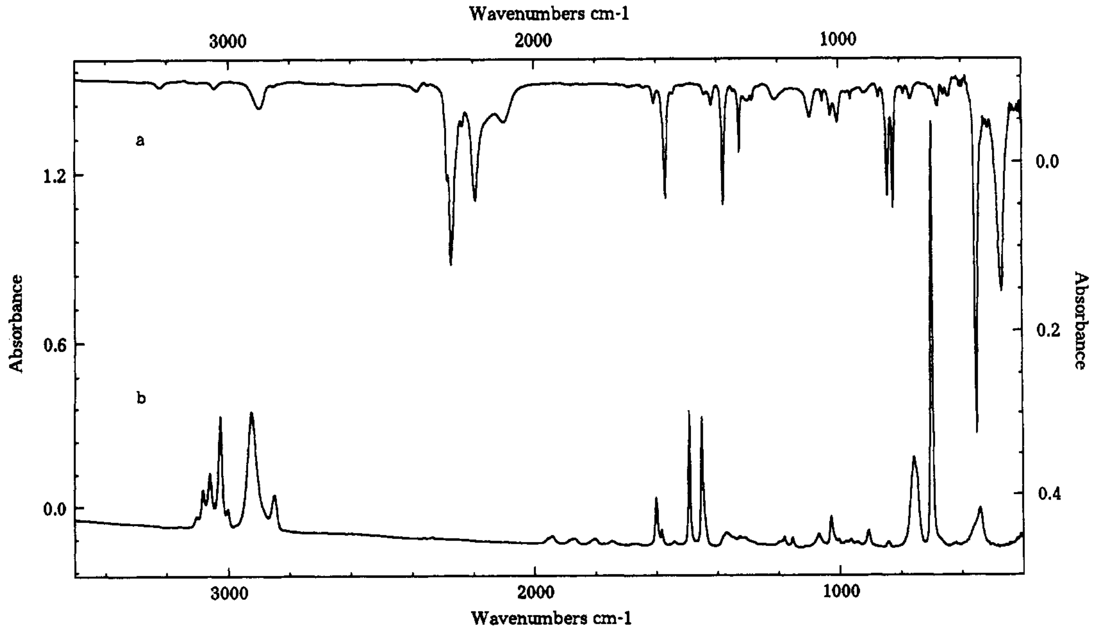

Figure 2. FTIR spectra of (a) deuterated polystyrene (top-right axis) and (b) protonated polystyrene (bottom-left axis).

a high molecular weight shoulder, which seemed monodisperse and double the molecular weight of the parent polymer. The most likely cause of the high molecular weight shoulder was oxidative coupling of the living ends.[15] All other polymers had symmetrical GPC distributions composed of a single peak and were relatively narrow in molecular weight. HPS-4 and 6 closely represent the extremes (1.17 and 1.03) that typically can be expected in these laboratories when the polymerizations are conducted without impurities and adequate mixing.

Figure 2 compares the FTIR spectra of deuterated polystyrene to its protonated analog. The most obvious feature difference between the spectra are the C–H symmetric and asymmetric stretching modes (3230–2020 cm^{-1}) shifted to lower wavenumbers (2270–2100 cm^{-1}). This shift is indicative of C–D stretching modes. Absorptions between 3230 and 2920 cm^{-1} for the deuterated polymer reflect residual protons (predominantly on the backbone at 2930 cm^{-1}) of the polymer. Quantitatively this can be determined by measuring the ratio of areas under the C–H to C–D stretching modes and adjusting for their optical constants. The ratio of areas was found to be 0.10, and the ratio of their optical constants is approximately 0.5,[16] which yields approximately 5% of residual protons. The source of these protons appears to come from residual protons on styrene-d_8.

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(8) Butyllithium was used in a larger excess to avoid the possible coprecipitation of alkoxide as has been observed in this laboratory and others: see ref 7a.
(9) These organopotassium salts are pyrophoric. They are more reactive as powders and will blacken and/or ignite immediately upon exposure to air.
(10) Generally, these solutions were used within 1 h of preparation. During this time period we did not notice any loss of the benzylpotassium through metalation of THF.
(11) Initiator concentrations were on the order of 10^{-4} M. Loss of benzylpotassium resulted in the inability to dry THF to those levels.
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