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Functionalization of Polymeric Organolithium Compounds. Amination of Poly(styryl)lithium

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ABSTRACT: The amination of poly(styryl)lithium ($\bar{M}_n$ = 2000–4000) has been examined by using the reagent generated from methoxyamine and methyllithium at −78 °C. A 92% yield of poly(styryl)amine was obtained by using a twofold excess of this aminating species. Pure poly(styryl)amine can be isolated by column chromatography. Poly(styryl)amine was characterized by vapor pressure osmometry, elemental analysis, and end-group titration.

One of the goals of synthetic polymer chemistry is to prepare polymers with control of the major variables affecting polymer properties. In this regard, alkyllithium-initiated anionic polymerization is one of the most important synthetic methods, since polymers can be prepared with predictable molecular weights and narrow molecular weight distributions.[2-5] Since these polymerizations often proceed without the incursion of spontaneous termination or chain-transfer reactions, they generate stable carbanionic chain ends which, in principle, can be converted into a diverse array of functional end groups.[3] Chain-end-functionalized polymers are useful for a variety of further reactions including (a) chain extension, branching, and cross-linking reactions with polyfunctional reagents, (b) coupling and linking reactions with reactive groups on other oligomer or polymer chains, and (c) block polymerization of other monomers using the functional groups as initiation sites.[3] In order to exploit the full potential of these chain-end-functionalized polymers, well-defined, general procedures for quantitative chain-end functionalization must be available. Unfortunately, many of the reported examples of anionic chain-end functionalizations have not been well characterized.[3]

We have previously reported the results of careful investigations of the solution carbonation[6] and oxidation[7] of polymeric organolithium compounds. Although several new methods for preparing amine-terminated polymers have been described recently,[8-12] the synthesis of polymers with primary alkylamine functionality has been a challenge.[13,14] Herein are reported our results of studies of the use of the aminating reagent generated from methoxyamine and methyllithium[15] to prepare polymers with primary amine end-group functionality.

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Experimental Section

Materials. Styrene and benzene were purified as described in detail previously.[6] Tetrahydrofuran (THF) (MCB, distilled in glass, no preservatives) was stirred over lithium aluminum hydride, degassed, and distilled onto sodium dispersion. After the THF was stirred over the dispersion, it was distilled onto a sodium mirror with benzophenone. Fresh THF was obtained from this dark-purple solution by distillation onto a fresh sodium mirror, degassing, and then distillation into the reaction flask. *sec*-Butyllithium (Lithium Corp. of America, 12.0 wt % in cyclohexane) was used as the initiator for styrene polymerizations. Methyllithium (Alfa, 1.45 M in diethyl ether) was used to metalate methoxyamine. Methoxyamine was generated on the vacuum line by adding 10 g (0.12 mol) of methoxyamine hydrochloride (Fisher) to 100 mL of degassed poly(ethylene glycol) (Fisher, laboratory-grade Carbowax PEG 400) followed by addition of 10 g (0.18 mol) of ground KOH and then slowly stirring the resulting suspension overnight. After degassing, methoxyamine was distilled into a flask containing freshly ground KOH. The suspension was stirred for several hours and then distilled again onto freshly ground KOH. This procedure was repeated three times; methoxyamine was stored over 4-Å molecular sieves in a sealed flask at −20 °C and then freshly distilled into ampules with hexane for the amination reactions.

Polymerization and Amination Procedures. Polymerizations of styrene were carried out in benzene at room temperature in all-glass, sealed reactors by using break seals and standard high-vacuum techniques.[16] After polymerization was complete, 75% of the benzene was distilled out of the reactor and replaced by an equivalent amount of THF. The THF solution of poly(styryl)lithium was stored at −78 °C for no longer than 1 day. For a typical amination, a 7.5-mL aliquot (40.5 mmol) of 0.54 M methyllithium in diethyl ether was reacted with methoxyamine (1.885 g, 40.1 mmol) in a hexane/THF (70/50) mixture at −78 °C for 15 min with stirring. After degassing, 200 mL (20 mmol) of poly(styryl)lithium in THF/C_6H_6 (75/25) at −78 °C was transferred to the reactor via a cannula by using a combination of vacuum and argon pressure. The solution was slowly warmed to −15 °C, stirred for 2 h, and then quenched with degassed methanol. The polymer was isolated by precipitation into

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Table I
Effects of Variation of Solvent, Stoichiometry, and Temperature on Amination Yields for Poly(styryl)lithium (PsLi)

reaction	PsLi solvent	CH_3Li solvent	CH_3ONH_2 solvent	stoichiometry ([PsLi]/[$CH_3LiCH_3ONH_2$])	temp, °C	% yield[d] $PsNH_2$
1[a]	toluene	Et_2O	toluene	1/2	−78 to −15	0
2[b]	toluene	Et_2O	toluene	1/2	−78 to −15	5
3[b]	60% C_6H_6/40% THF	Et_2O	neat	1/2	−78 to −15	50
4[b]	80% C_6H_6/20% THF	Et_2O	hexane	1/2	−78 to −15	60
5[b]	80% C_6H_6/20% THF	Et_2O	hexane	1/2.8	−78 to −15	50
6[b]	80% C_6H_6/20% THF	Et_2O	hexane	1/4	−78 to −15	40
7[b]	80% C_6H_6/20% THF	Et_2O	hexane	1/3	−30 to −15	20
8[c]	80% C_6H_6/20% THF	Et_2O/THF	hexane	1/2	−78 to −15	92

[a] $\bar{M}_n$(PsLi) = 4000. [b] $\bar{M}_n$(PsLi) = 2500. [c] $\bar{M}_n$(PsLi) = 2000. [d] Yields determined by potentiometric titration with $HClO_4$/HOAc and assuming that $\bar{M}_n$ corresponds to the stoichiometric molecular weight.

methanol. The yield of isolation polymer was 97%.

Characterization. Number-average molar masses were determined by using a vapor pressure osmometer (VPO) (Hitachi 117 molecular weight apparatus) at 54.8 ± 0.1 °C in toluene (Fisher Scientific, Certified ACS), which was distilled from freshly crushed CaH_2. The VPO apparatus was calibrated with pentaerythritol tetrastearate (Pressure Chemical). Size exclusion chromatographic (GPC) analyses were performed in THF by HPLC (Perkin-Elmer 601 HPLC) using six μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å) after calibration with standard polystyrene samples.

Thin-layer chromatographic (TLC) analyses were carried out on silica gel plates (Eastman 13181) with a fluorescent indicator with toluene as eluent. Column chromatographic separations were carried out on silica gel (60–200 mesh, Baker Analyzed Reagent) with toluene and then toluene/methanol (50/1 (v/v)) as eluting solvents. Infrared spectra of samples cast from solutions onto KBr plates were obtained with a Beckman Model IR-33 spectrometer.

Benzoyl and terephthaloyl derivatives of poly(styryl)amine were prepared in toluene/pyridine (2/1 (v/v)) mixtures with benzoyl chloride (Aldrich, 99%) and terephthaloyl chloride, respectively. Terephthaloyl chloride (97%, Aldrich) was recrystallized from petroleum ether [mp 82–83 °C (lit.[17] mp 83–84 °C)]. The polymeric amide derivatives were isolated by precipitation into methanol and then passage of a toluene solution of the yellow product through a silica gel chromatography column.

The concentrations of aminated chain ends were determined by titrating polymer samples dissolved in 100 mL of a 1/1 (v/v) mixture of chloroform and glacial acetic acid with standard $HClO_4$ in glacial acetic acid by using a Corning Model 10 pH meter with a calomel–glass electrode.[18] The concentrations of simple and polymeric organolithiums were analyzed by the double-titration procedure of Gilman and Cartledge[19] using 1,2-dibromoethane. Anal. Calcd for C_4H_9–$(CH_2CHC_6H_5)_{21}$–NH_2 ($\bar{M}_n^{VPO}$ = 2260): C, 91.41; H, 7.98; N, 0.62. Found: C, 91.74; H, 7.88; N, 0.58. Anal. Calcd for C_4H_9–$(CH_2CHC_6H_5)_{21}$–$NHCOC_6H_5$: C, 90.85; H, 7.88; N, 0.59. Found: C, 91.54; H, 7.94; N, 0.54. The elemental analyses were performed by Organic Microanalysis, Tuscon, AZ 85717.

Results and Discussion

One of the major challenges in the area of anionic functionalization reactions has been to synthesize polymers with primary amine end-group functionality, since primary amine hydrogens undergo proton transfer to anionic chain ends.[20] Beak and Kokko[15] have recently described an efficient amination procedure for simple organolithium compounds using the reagent generated at −78 °C from methoxyamine and methyllithium (eq 1). The application

$$C_6H_5CH_2Li \xrightarrow[\substack{(1)\ -78\ °C\\(2)\ -15\ °C}]{CH_3ONH_2/CH_3Li} \xrightarrow[(4)\ C_6H_5COCl]{(3)\ H_2O} C_6H_5CH_2NHC(=O)C_6H_5 \quad (1)$$
97%

of this amination procedure to polymeric organolithium compounds was not straightforward because of the obvious solubility problems encountered with polymers at low temperatures. The variation of solvent, stoichiometry, and temperature was examined in order to find suitable procedures for amination of poly(styryl)lithium (see Table I). Poly(styryl)lithium was prepared in hydrocarbon solution by using standard high-vacuum techniques.[16] Use of hydrocarbon solvents maximizes carbanionic chain-end stability[21] and should allow the adoption of similar procedures for the preparation of poly(dienyl)lithium compounds with high 1,4 microstructure.[3]

Several observations are important in evaluating the results presented in Table I. In reactions 1 and 2, the solutions of methyllithium in diethyl ether were cloudy at −78 °C, and during the addition of PsLi the first portions (ca. 10%) of the red solution became colorless before warming. This suggests that the initial metalation reaction between methyllithium and methoxyamine (eq 2) does not

$$CH_3ONH_2 + CH_3Li \rightarrow CH_3ONHLi + CH_4 \quad (2)$$

proceed efficiently when methyllithium is not in solution. If the metalation of methoxyamine is not complete prior to addition of poly(styryl)lithium, methoxyamine will react with poly(styryl)lithium to protonate the anionic chain end (eq 3). The yield of aminated poly(styryl)lithium was

$$PsLi + CH_3ONH_2 \rightarrow PsH + CH_3ONHLi \quad (3)$$

optimized (reaction 8) when a THF/Et_2O mixture was used to solubilize methyllithium at −78 °C and to facilitate the efficient metalation of methoxyamine (eq 2). It is noteworthy that the solubility of methyllithium is also improved by only cooling to −30 °C (reaction 7); however, at this temperature the aminating agent is apparently not stable (compare with reaction 5). Variation of the stoichiometry of the aminating agent to the poly(styryl)lithium indicates that more than a 2/1 ratio results in decreased yields also (compare reactions 6 and 4). The optimum procedure (reaction 8) maximized the solubility of all of the reagents at −78 °C by using primarily THF as solvent to maximize the efficiency of the initial metalation reaction (eq 2) and also utilized a 2/1 ratio of aminating agent to poly(styryl)lithium.

Two mechanisms can be written for these amination reactions:

$$CH_3ONHLi \rightarrow \underset{\text{nitrene}}{:\ddot{N}H} + CH_3OLi \quad (4)$$

$$PsLi + NH \rightarrow PsNHLi \quad (5)$$

or

$$PsLi + CH_3ONHLi \rightarrow PsNHLi + CH_3OLi \quad (6)$$

The first mechanism (eq 4 and 5) proceeds via a nitrene intermediate that then reacts with the organometallic chain end. In the second mechanism (eq 6), the aminating species is an electrophilic nitreneoid species, analogous to

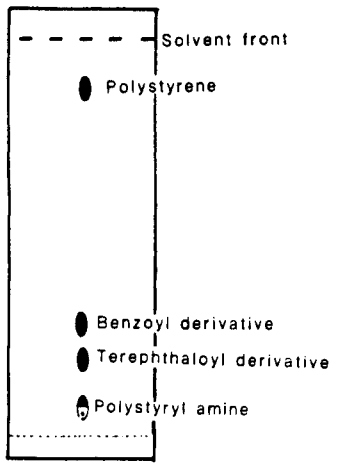

Figure 1. Thin-layer chromatographic separation of polystyrene, poly(styryl)amine, and amide derivatives of poly(styryl)amine.

the carbenoid species implicated in reactions of α-haloorganolithium compounds with olefins.[22] Since nitrenes are known to undergo insertion reactions with C–H bonds[23] and addition reactions with aromatic substrates,[24] it was important to examine the possibility that unselective amination reactions of nitrenes with the backbone chain vs. the organometallic chain ends were occurring in these amination reactions.

A control reaction was performed to determine if the amination reaction could take place on the polystyrene backbone in the absence of the carbanionic chain end. A polystyrene sample ($\bar{M}_n$ = 2000) was reacted with the reagent generated from methoxyamine and methyllithium by using conditions identical with those used to aminate poly(styryl)lithium. The final product was analyzed by TLC and by amine end-group titration. No aminated polystyrene was detected by either of these methods. Therefore, it can be concluded that this amination reaction requires the carbanionic chain end and does not involve unselective insertion reactions with the polymer backbone.

In spite of the fact that this amination procedure is not quantitative, it is possible to isolate and characterize pure primary amine-terminated polystyrenes by chromatography. Aminated polystyrene (R_f 0.10) can be readily observed and separated from unfunctionalized polystyrene (R_f 0.78) by SiO_2 thin-layer chromatography (TLC) with toluene as eluent, as shown in Figure 1; the benzoyl (R_f 0.28) and terephthaloyl derivatives (R_f 0.13) of poly(styryl)amine are also separable, as shown in Figure 1. These TLC results indicated that it should be possible to separate the functionalized and unfunctionalized polymers by column chromatography. In fact, the aminated polystyrene could be readily separated from unfunctionalized polystyrene by silica gel column chromatography using toluene as the eluent until all of the polystyrene had eluted, followed by toluene/methanol (50/1 (v/v)) to elute the poly(styryl)amine.

Attempts to analyze the amination reactions and characterize poly(styryl)amine by size exclusion chromatography were not successful. As shown in Figure 2, the size-exclusion chromatogram for poly(styryl)amine in THF was very broad and unsymmetrical. In contrast, the chromatograms for the base polymer [obtained by methanol quenching of an aliquot of poly(styryl)lithium prior to the amination reaction] and the terephthaloyl derivative were very narrow and symmetrical (see Figure 3). These results suggest that physical adsorption effects are complicating the size exclusion process for this amine-functionalized polymer.

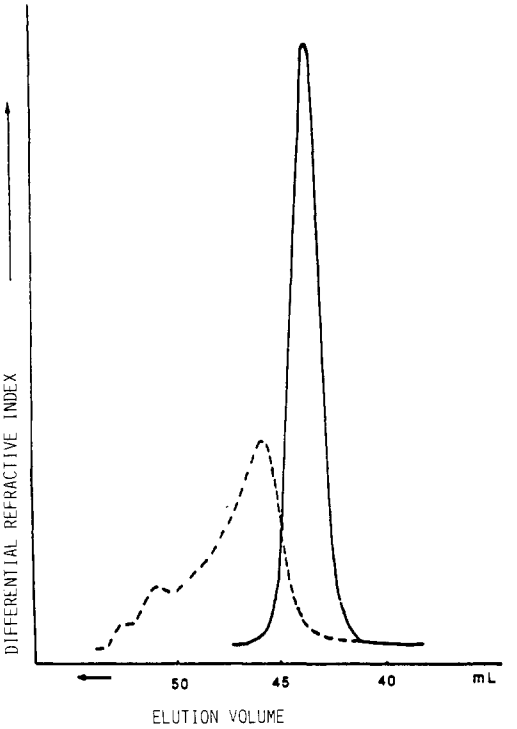

Figure 2. Size exclusion chromatography of polystyrene (—) and poly(styryl)amine (- - -).

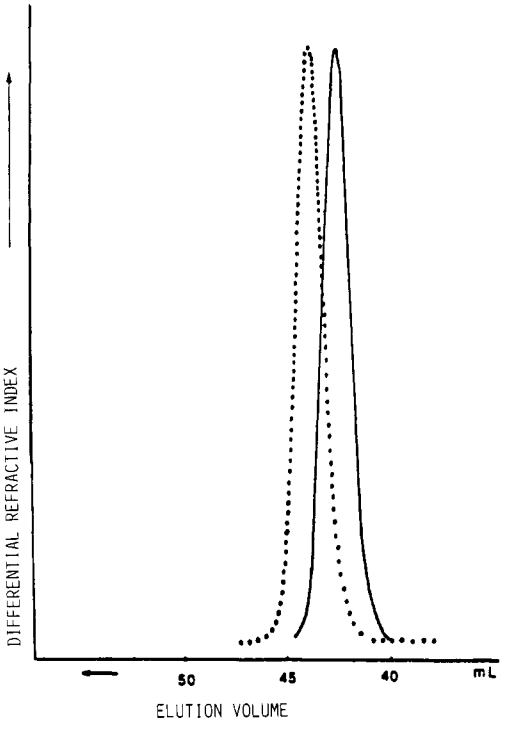

Figure 3. Size exclusion chromatography of polystyrene (···) and the terephthaloyl derivative of poly(styryl)amine (—).

The purified amine-functionalized polymer was characterized by size exclusion chromatography (amide derivatives; see Figure 3), viscosity, vapor phase osmometry, elemental analysis, and preparation of amide derivatives. The results of the various methods used to determine the molecular weight and degree of functionality of poly(styryl)amine are shown in Table II. It is noteworthy that the elemental analysis results (based on nitrogen analysis) are consistent with the presence of high amine functionality for the purified amine fraction isolated by column chromatography. The ability to prepare a corresponding

Table II
Characterization of Poly(styryl)amine

analytical method	$\bar{M}_n$	analytical method	$\bar{M}_n$
VPO[a]	2360	elem anal.[b]	2420
VPO[b]	2260	elem anal.[d]	2590
VPO[c]	4430	end-group titration[b]	2090

[a] Polystyrene sample from methanol quenching of poly(styryl)-lithium prior to amination; $\bar{M}_w/\bar{M}_n$(GPC) = 1.15. [b] Poly(styryl)-amine. [c] Terephthaloyl derivative of poly(styryl)amine; $\bar{M}_w/\bar{M}_n$-(GPC) = 1.15. [d] Benzoyl derivative of poly(styryl)amine; $\bar{M}_w/\bar{M}_n$-(GPC) = 1.15.

terephthaloyl derivative with twice the molecular weight ($\bar{M}_n$, VPO) is also consistent with high amine end-group functionality (eq 7). Finally, in support of the ability to

$$\underset{\bar{M}_n^{VPO} = 2260}{PsNH_2} + ClCOC_6H_4COCl \xrightarrow[\text{toluene}]{\text{pyridine}} \underset{\bar{M}_n^{VPO} = 4430}{PsNHCOC_6H_4CONHPs} \quad (7)$$

prepare poly(styryl)amine of high end-group functionality, it should be noted that a polymeric amine sample, exhibiting one TLC spot, could be isolated in 85% yield by column chromatography of the products from an amination reaction which proceeded in 92% yield by amine end-group titration. Thus, although the amine functionalization reaction described herein using the reagent generated from methoxyamine and methyllithium is not quantitative, pure amine end-group functionalized polymer can be isolated in high yield.[25] Therefore, this procedure should be extremely useful for the preparation of difunctional[26] and polyfunctional polymeric amines.

Registry No. Poly(styryl)lithium, 36345-04-7.

References and Notes

(1) A brief account of portions of this paper has been presented in the following preprint: Quirk, R. P.; Cheng, P.-L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(2), 461.
(2) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic: New York, 1983.
(3) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(4) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.
(5) Bywater, S. *Prog. Polym. Sci.* **1974**, *4*, 27.
(6) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(7) Quirk, R. P.; Chen, W.-C. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2993.
(8) Eisenbach, C. D.; Schnecko, H.; Kern, W. *Makromol. Chem. Suppl.* **1975**, *1*, 151.
(9) Angood, A. C.; Hurley, S. A.; Tait, P. J. T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *13*, 2437.
(10) Koenig, R.; Riess, G.; Banderet, A. *Eur. Polym. J.* **1967**, *3*, 723.
(11) Schulz, D. N.; Halasa, A. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2401.
(12) Cheng, T. C. In *Anionic Polymerization, Kinetics, Mechanisms, and Synthesis*; McGrath, J., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 166, p 513.
(13) Hirao, A.; Hattori, I.; Sasagawa, T.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 59.
(14) Hattori, I.; Hirao, A.; Yamaguchi, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem.* **1983**, *184*, 1355.
(15) Beak, P.; Kokko, B. J. *J. Org. Chem.* **1982**, *47*, 2822.
(16) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(17) *Dictionary of Organic Compounds*, 4th ed.; Oxford University: New York, 1965; p 2950.
(18) Fritz, J. S. *Acid-Base Titration in Nonaqueous Solvents*; Allyn and Bacon: Boston, 1973; Chapter 2.
(19) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(20) Higginson, W. C. E.; Wooding, N. S. *J. Chem. Soc.* **1952**, 760.
(21) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133.
(22) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Elmsford, NY, 1974; p 165.
(23) Dobson, R. C.; Hayes, D. M.; Hoffman, R. *J. Am. Chem. Soc.* **1971**, *93*, 6188.
(24) Abramovitch, R. A.; Uma, V. *J. Org. Chem.* **1974**, *39*, 1101.
(25) Samples of the purified amine-functionalized polymer were stable (GPC) when stored in a sealed, argon-filled sample bottle in a refrigerator.
(26) Quirk, R. P.; Chen, W.-C.; Cheng, P.-L. *Reactive Oligomers*; Harris, F., Spinelli, H., Eds.; American Chemical Society: Washington, DC, 1985; ACS Symp. Ser. No. 282, Chapter 12, p 139.

Polymerization of Monomers Containing Functional Groups Protected by Trialkylsilyl Groups. 5. Synthesis of Poly(2-hydroxyethyl methacrylate) with a Narrow Molecular Weight Distribution by means of Anionic Living Polymerization

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ABSTRACT: Anionic polymerization of 2-[(trimethylsilyl)oxy]ethyl methacrylate (1) was investigated with various initiators. They included 1,4-dilithio-, 1,4-disodio-, and 1,4-dipotassio-1,1,4,4-tetraphenylbutane, (1,1-diphenylhexyl)lithium, phenylmagnesium chloride, benzylmagnesium chloride, and lithium aluminum hydride. Polymers of predictable molecular weights with relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.17–1.33) were obtained when either 1,4-dilithio-1,1,4,4-tetraphenylbutane or (1,1-diphenylhexyl)lithium was used in tetrahydrofuran (THF) at −78 °C. After complete removal of the trimethylsilyl protective group by hydrolysis, linear polymers of 2-hydroxyethyl methacrylate (HEMA) were produced. Addition of 1 to poly(α-methylstyryl)lithium capped with 1,1-diphenylethylene resulted after hydrolysis in the formation of triblock copolymers of the type poly(HEMA-*b*-α-methylstyrene-*b*-HEMA). The molecular weights of these polymers ranged between 38 000 and 71 000. $\bar{M}_w/\bar{M}_n$ lay in the range 1.14–1.37. The incorporation of HEMA in these copolymers was in the range 16–86 mol %. Microphase separation of the copolymers could be observed.

Introduction

Anionic living polymerizations of vinyl monomers have attracted both potential and practical interest because these systems permit the synthesis of polymers of predictable molecular weight and of narrow molecular weight distribution and the preparation of block copolymers of uniform composition and molecular weight.[1] However, a disadvantage of this method is that monomers with

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