Macromolecules **1998,** *31,* 9127−9133 **9127**

Living Anionic Copolymerization of 1-(Alkoxy)ethyl Methacrylates with Polar and/or Nonpolar Monomers and the Preparation of Amphiphilic Block Copolymers Containing Poly(methacrylic acid) Hydrophilic Segments at Higher Temperatures Than Usually Employed

Eli Ruckenstein* and Hongmin Zhang

Chemical Engineering Department, State University of New York at Buffalo,
Amherst, New York 14260

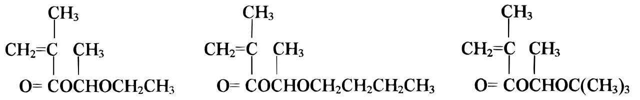
Received August 7, 1998; Revised Manuscript Received October 10, 1998

ABSTRACT: The anionic copolymerization of each of the following three novel methacrylate monomers—1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (tBEMA)—with methyl methacrylate (MMA) and/or styrene (St) was carried out. (1) The random copolymerization with MMA proceeded smoothly in tetrahydrofuran (THF), using 1,1-diphenylhexyllithium (DPHL) as the initiator, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 1$), at −40 °C. The copolymer thus obtained possessed controlled molecular weight and composition, and its molecular weight distribution (MWD) was narrow ($M_w/M_n = 1.08-1.10$). (2) The block copolymer of each of the new monomers with MMA was prepared by the sequential anionic polymerization of the two monomers; the polymerization sequence MMA−new monomer controlled better the molecular weight and led to a narrower MWD than the inverse one. (3) A well-controlled block copolymerization of St with EEMA or with tBEMA was achieved at higher temperatures (≥−35 °C) than usually employed (−78 °C), and it should be emphasized that, even at 0 °C, a well-defined diblock copolymer consisting of poly(St) and poly(tBEMA) could be obtained. (4) A block copolymer consisting of poly(St) and a random copolymer of MMA and EEMA, poly[St-*b*-(MMA-*co*-EEMA)], was prepared by the sequential monomer addition St−mixture of MMA and EEMA, for various weight ratios of MMA and EEMA. (5) In the preparation of the triblock copolymer with the sequence St, MMA, and EEMA, the molecular weight of the polymer increased step by step and the MWD remained narrow ($M_w/M_n = 1.09$). By changing the polymerization sequence, the hydrophilic segment could be located either in the middle or at the end of the copolymer chain. The protecting group, 1-(alkoxy)ethyl of each of the new monomers, could be easily eliminated after copolymerization, using a mild acidic environment. Thus a copolymer, containing poly(MAA) as hydrophilic segment, with different solubility than its precursor copolymer could be obtained.

Introduction

The amphiphilic block copolymers containing poly(methacrylic acid) (poly(MAA)) as hydrophilic segment have been widely investigated because of their interesting surface properties.[1] These copolymers exhibit microphase separation in solid state and form spherical micelles in selective solvents. The polar solvents allow the formation of micelles having hydrophobic cores. In addition, the copolymers containing poly(MAA) segments are useful in the preparation of ionomers and microgel particles.[2]

The block copolymers of MAA and polar monomers, such as alkyl methacrylates, could be prepared using the group transfer polymerization (GTP) method,[3] by protecting the carboxyl group of MAA with *tert*-butyl, benzyl, or trimethylsilyl. However, the block copolymer of MAA and a nonpolar monomer, such as styrene (St), cannot be obtained by this method, because GTP cannot be applied to nonpolar monomers. To prepare well-defined block copolymers of MAA and St, the anionic block copolymerization of *tert*-butyl methacrylate and St was carried out in tetrahydrofuran (THF) at −78 °C.[4] This was followed by the elimination of the *tert*-butyl side chains of the obtained copolymer. The latter step was usually accomplished by hydrolysis, using either an aqueous hydrochloric acid in 1,4-dioxane at 85 °C for about 5 h or *p*-toluenesulfonic acid in wet toluene at 80 °C for 4 h.


$CH_2{=}C(CH_3)-C(=O)-O-CH(CH_3)OCH_2CH_3$ $CH_2{=}C(CH_3)-C(=O)-O-CH(CH_3)OCH_2CH_2CH_2CH_3$ $CH_2{=}C(CH_3)-C(=O)-O-CH(CH_3)OC(CH_3)_3$

(1) EEMA (2) BEMA (3) tBEMA

Figure 1. Molecular structures of 1-(alkoxy)ethyl methacrylates: (1) 1-(ethoxy)ethyl methacrylate (EEMA), (2) 1-(butoxy)ethyl methacrylate (BEMA), and (3) 1-(*tert*-butoxy)ethyl methacrylate (tBEMA).

In a previous paper, we developed a new preparation method for a well-defined homopoly(MAA).[5] Three novel monomers, 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (tBEMA) (Figure 1), were first prepared. These monomers could undergo anionic polymerization at higher temperatures (−40 to 0 °C) than the common alkyl methacrylates, and the polymers thus obtained possessed controlled molecular weights and narrow molecular weight distributions (MWD, $M_w/M_n = 1.06-1.09$). In addition, these polymers were easily hydrolyzed under mild acidic conditions to generate well-defined poly(MAA). This method provides the possibility to prepare, at relatively high temperatures, amphiphilic block copolymers containing poly(MAA) as the hydrophilic segment. The present paper will focus on the syntheses of the following copolymers by the anionic copolymerizations of the new monomers with

---

* To whom correspondence should be addressed.

10.1021/ma9812534 CCC: $15.00

Table 1. Anionic Random Copolymerization of 1-(Alkoxy)ethyl Methacrylate (M_1) and MMA[a]

no.	$[M_1]_0$ (M)	$[MMA]_0$ (M)	$[DPHL]_0$ (mM)	[LiCl] (mM)	temp (°C)	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]
ME-1[d]	0.38	0.59	11.8	11.8	−80	10.3	12.7	1.11
ME-2[d]	0.38	0.59	11.8	11.8	−40	10.3	10.3	1.08
MB-1[e]	0.33	0.63	33.3	100	−60	3.98	3.31	1.22
MB-2[e]	0.12	0.71	16.6	33.3	−60	5.86	4.86	1.23
MB-3[e]	0.31	0.59	12.8	12.8	−40	9.35	10.2	1.09
MT-1[f]	0.31	0.90	31.9	100	−60	4.87	6.17	1.12
MT-2[f]	0.08	0.78	16.7	50.0	−60	5.81	7.06	1.18
MT-3[f]	0.30	0.59	11.8	11.8	−40	9.97	9.44	1.10

[a] The initiator, DPHL, was first prepared by the reaction of *n*-BuLi and DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), at the corresponding polymerization temperature, for 15 min. The copolymerization was carried out in THF, by adding a prechilled mixture of MMA and EEMA or BEMA or tBEMA to the THF solution of DPHL, and the reaction was allowed to last 45 min. The yields of the copolymers were quantitative in all cases. [b] Calculated number-average molecular weight. [c] Determined by GPC. [d,e,f] Random copolymers of MMA with EEMA, MMA with BEMA, and MMA with tBEMA, respectively.

methyl methacrylate (MMA) and /or St: (1) random and diblock copolymers of EEMA, BEMA, or tBEMA with MMA; (2) diblock copolymers of St with EEMA or tBEMA; (3) diblock copolymer containing a poly(St) block and a random copolymer block of MMA and EEMA; (4) ABC and ACB triblock copolymers of St, MMA, and EEMA. The copolymers prepared under appropriate conditions possessed controlled molecular weights and compositions, and their MWDs were narrow. The ester groups of poly(EEMA), poly(BEMA), or poly(tBEMA) segment in the copolymer could be easily eliminated by hydrolysis in a mild acidic environment to generate a copolymer containing poly(MAA) as hydrophilic segment. Compared to the method based on *tert*-butyl methacrylate, the polymerization temperature is much higher (−35 to 0 °C instead of −78 °C) and the elimination of the protecting group much easier (mild acidic conditions instead of strong ones and a very short reaction time instead of a very long one).

Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH_2 under reflux for more than 24 h, distilled, and distilled again from a solution of 1,1-diphenylhexyllithium (DPHL) just before use. Toluene was washed with concentrated sulfuric acid and then with water, dried over $MgSO_4$, distilled over CaH_2, and again distilled from a DPHL solution before use. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. Methyl methacrylate (MMA, Aldrich, 99%) and styrene (St, Aldrich, 99%) were washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with $MgSO_4$, and distilled over CaH_2. Prior to polymerization, these two monomers were finally distilled in the presence of triisobutylaluminum[6] and benzylmagnesium chloride, respectively. As described in the previous paper,[5] 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (tBEMA) were prepared through the reaction of methacrylic acid (MAA) and the corresponding alkyl vinyl ether, namely, ethyl, butyl, and *tert*-butyl vinyl ether, respectively. Prior to polymerization, these monomers were purified by two successive distillations over CaH_2 under reduced pressure. 1,1-Diphenylethylene (DPE, Aldrich, 97%) was distilled over CaH_2 and then distilled again in the presence of DPHL under reduced pressure. Lithium chloride (Aldrich, 99.99%) was dried at 120 °C for 24 h and dissolved in THF.[7] *n*-BuLi (Aldrich, 1.6 M solution in hexane) and *sec*-BuLi (Aldrich, 1.3 M solution in cyclohexane) were diluted with purified hexane.

Random and Block Copolymerizations of 1-(Alkoxy)ethyl Methacrylate and MMA. All copolymerizations were carried out with magnetic stirring in a round-bottom glass flask under an overpressure of argon. The random and block copolymerizations of EEMA, BEMA, or tBEMA with MMA were carried out in THF, at a selected temperature, in the presence of LiCl. After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to a selected temperature and *n*-BuLi (in hexane) was added. The deep red color of DPHL appeared at once, and the reaction between *n*-BuLi and DPE was allowed to continue for 15 min. For the random copolymerization, a prechilled mixture of MMA and EEMA or BEMA or tBEMA was added to the above system to induce the copolymerization. In the case of block copolymerization, the two monomers were sequentially added either from MMA to one of the new monomers or vice versa. After a certain time, the system was quenched by adding a small amount of methanol, evaporated to dryness, and then vacuum-dried overnight to obtain the copolymer.

Preparation of the Block Copolymers Containing Poly(St) Segments. Poly(St-*b*-EEMA), Poly(St-*b*-tBEMA), Poly[St-*b*-(MMA-*co*-EEMA)], Poly(St-*b*-MMA-*b*-EEMA), and Poly(St-*b*-EEMA-*b*-MMA). In the preparation of the block copolymers containing poly(St) segments, St was first polymerized via anionic polymerization. This was carried out using *sec*-BuLi as the initiator, in toluene, at 20 °C. After toluene and *sec*-BuLi were transferred to the flask placed in a 20 °C water bath, St was added to start the polymerization, and the reaction was allowed to last 50 min. Meanwhile, to a THF solution of LiCl ($\text{mol}_{\text{LiCl}}/\text{mol}_{sec\text{-BuLi}} = 1$) and of DPE ($\text{mol}_{\text{DPE}}/\text{mol}_{sec\text{-BuLi}} = 1.2$), *sec*-BuLi was first dropwise added until the red color of DPHL appeared, to remove the impurities. Then, this solution was immediately transferred to the above toluene solution of living poly(St). After the reaction between the living site of poly(St) and DPE was allowed to last 15 min, the system was cooled to a selected temperature and the second monomer was added. For the preparation of the diblock copolymer, poly(St-*b*-EEMA) or poly(St-*b*-tBEMA), the second step polymerization of EEMA (or tBEMA) was carried out at −35 °C and also between −20 and +20 °C for 50 min. For the preparation of poly[St-*b*-(MMA-*co*-EEMA)], the random copolymerization of MMA and EEMA with the living poly(St) was started by adding a mixture of the two monomers, and the reaction was allowed to last 30 min at −40 °C. In the case of the triblock copolymer, poly(St-*b*-MMA-*b*-EEMA), MMA was first polymerized with the living poly(St), at −65 °C, for 15 min, and this was followed by the third step, polymerization of EEMA, at −35 °C, for 50 min. For poly(St-*b*-EEMA-*b*-MMA), the monomer addition sequence St, EEMA, and MMA was used. After the polymerization of the last monomer, the system was quenched by adding a small amount of methanol, evaporated to dryness, and then vacuum-dried overnight to obtain the copolymer.

Elimination of the Protecting Groups. The protecting groups 1-(ethoxy)ethyl, 1-(butoxy)ethyl, and 1-(*tert*-butoxy)ethyl of 1-(alkoxy)ethyl methacrylate segments in the copolymers were eliminated by hydrolysis in a mild acidic environment. For instance, 3.0 g of vacuum-dried block copolymer of MMA and EEMA (MbE-1 in Table 2 and Table 6) was redissolved in 30 mL of THF, to which 3.0 mL of HCl aqueous solution (5.0 M) was added with magnetic stirring at room temperature. After 2 min, this mixture was poured into water to precipitate the polymer. The polymer thus obtained was washed with water and vacuum-dried at 40 °C for more than

Table 2. Anionic Block Copolymerization of 1-(Alkoxy)Ethyl Methacrylate and MMA[a]

no.	polymerization sequence $M_1 \rightarrow M_2$	$[M_1]_0$ (M)	$[M_2]_0$ (M)	$[DPHL]_0$ (mM)	first step			second step		
					$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]
EbM-1	EEMA→MMA	0.42	0.70	17.7	3.99	4.00	1.11	7.94	7.84	1.18
EbM-2	EEMA→MMA	0.42	0.67	11.4	6.06	5.69	1.07	12.2	12.9	1.17
MbE-1	MMA→EEMA	0.67	0.42	11.4	6.12	6.44	1.06	11.9	12.2	1.09
BbM-1	BEMA→MMA	0.33	0.63	20.5	3.23	3.10	1.15	6.30	6.80	1.38
MbB-1	MMA→BEMA	0.63	0.33	20.5	3.31	3.09	1.18	6.30	6.15	1.12
TbM-1	tBEMA→MMA	0.32	0.63	16.7	3.80	4.10	1.17	7.58	8.88	1.18
TbM-2	tBEMA→MMA	0.34	0.66	10.7	6.15	5.96	1.11	12.3	11.7	1.17
MbT-1	MMA→tBEMA	0.63	0.32	16.7	4.01	4.31	1.11	7.58	7.96	1.09
MbT-2	MMA→tBEMA	0.66	0.34	8.3	8.19	8.51	1.06	15.8	16.0	1.11

[a] The initiator, DPHL, was in situ prepared before the first monomer addition, by the reaction of *n*-BuLi and DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), in the presence of LiCl ($[LiCl]/[n\text{-BuLi}]_0 = 1$), at the corresponding polymerization temperature, for 15 min. The polymerization was induced by adding the first monomer (M_1) to the above system. After a selected time, the second monomer was continuously added. The temperatures for 1-(alkoxy)ethyl methacrylate and MMA were −40 and −65 °C, and the polymerization times were 45 and 15 min, respectively. The polymer yield was quantitative for every case. [b,c] See Table 1.

24 h. The block copolymers containing a poly(St) segment were hydrolyzed in a similar way. A mixture of water and methanol ($V_{water}/V_{methanol} = 4/1$) was used to precipitate the copolymers.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$, THF-d_8, or CD_3OD on a VXR-400 spectrometer. M_n and M_w/M_n of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. The GPC measurements were carried out using THF as solvent, at 30 °C, with a 1.0 mL/min flow rate and a 1.0 cm/min chart speed. Three polystyrene gel columns (Waters, 7.8 × 300 mm; one HR 5E, part no. 44228, one Linear, part no. 10681, and one HR 4E, part no. 44240) which were connected to a Waters 515 precision pump were used. After polymerization, a trace of THF solution (ca. 0.1 mL) was taken out, diluted with THF, and injected immediately. The FT-IR spectra were recorded on a Perkin-Elmer 1760-X spectrometer using KBr tablets.

Results and Discussion

Random Copolymerization of 1-(Alkoxy)ethyl Methacrylate with MMA. LiCl has been often employed in the anionic polymerization of either the common[7] or the functional[8] (meth)acrylates, because it controls the molecular weight and narrows the MWD of the polymer. Therefore, the random copolymerization of MMA and 1-(alkoxy)ethyl methacrylate was carried out in the presence of LiCl, using THF as the solvent. A bulky initiator, DPHL, was first prepared in situ before the monomer addition, via the reaction of *n*-BuLi with DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), at the selected polymerization temperature, for about 15 min. The copolymerization was induced by adding a prechilled mixture of MMA and EEMA or BEMA or tBEMA, and the reaction was allowed to last 45 min.

In the anionic homopolymerization of EEMA, BEMA, and tBEMA,[5] the optimum results were obtained for a molar ratio $[LiCl]/[DPHL]_0$ of unity, at a temperature around −40 °C. A higher molar ratio of $[LiCl]/[DPHL]_0 = 3$ and/or a lower temperature (−80 °C), which constitute the optimum conditions for the anionic polymerization of the common alkyl methacrylates, such as MMA, were not suitable for the new monomers. Under the latter conditions, the monomer conversion hardly reached 100%, the molecular weight was out of control, and the MWD was broad.

Because both MMA and one of the new monomers participate in the reaction simultaneously, the random copolymerization was examined not only under the optimum conditions for the new monomer but also under those for MMA. As shown in Table 1, under the suitable polymerization conditions for MMA (−80 to −60 °C, $[LiCl]/[DPHL]_0 = 3$, see ME-1, MB-1, MB-2, MT-1, and MT-2 in Table 1), copolymers with relatively narrow MWDs ($M_w/M_n = 1.11-1.23$) were obtained quantitatively, but the molecular weights were only fairly controlled. On the other hand, when the copolymerization was carried out under the optimum conditions for the new monomers (−40 °C, $[LiCl]/[DPHL]_0 = 1$, see ME-2, MB-3 and MT-3, in Table 1), the monomer conversion was 100% in every case, the molecular weight of the obtained copolymer was in good agreement with the calculated value, and the MWD was very narrow ($M_w/M_n = 1.08-1.10$). In addition, as proved by ^{1} H NMR, the composition of the copolymer coincided with the feed amounts of the two monomers. For instance, the weight ratio of the two kinds of units in the copolymer MB-3 determined from the peak intensities was $W_{MMA}/W_{BEMA} = 48/52$, which is close to the feed amount ratio (50/50). Hence, the composition of the copolymer was also well controlled. The above results indicate that the optimum conditions for the homopolymerization of 1-(alkoxy)ethyl methacrylate are also suitable for their copolymerizations with MMA.

Block Copolymerization of 1-(Alkoxy)ethyl Methacrylate with MMA. The block copolymerization was carried out in THF, using DPHL as the initiator, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 1$). The polymerization temperatures for 1-(alkoxy)ethyl methacrylate and MMA were −40 and −65 °C, and the polymerization times were 45 and 15 min, respectively. Both 1-(alkoxy)ethyl methacrylate and MMA are polar monomers and possess similar molecular structures. Therefore, their block copolymerization is expected to proceed similarly either in the sequence starting with MMA or vice versa. Indeed, as shown in Table 2, the block copolymers were obtained quantitatively in both cases, although the MWDs were somewhat different. For the polymerization sequence MMA−new monomer (MbE-1, MbB-1, MbT-1, and MbT-2 in Table 2), the molecular weight increased after the second step polymerization and was consistent with the designed value, and the MWD remained narrow ($M_w/M_n = 1.09-1.12$). For the opposite sequence, the MWDs of the obtained block copolymers were somewhat broader ($M_w/M_n = 1.17-1.38$; EbM-1, EbM-2, BbM-1, TbM-1, and TbM-2 in Table 2). This is caused by the slow transformation rate of the living site from poly[1-(alkoxy)ethyl methacrylate] to poly(MMA) compared to the propagation rate of MMA, which is very fast.[9]

Block Copolymerization of St and EEMA. The block copolymerization of St and EEMA was carried out using the sequence St−EEMA. For the anionic polym-

Table 3. Preparation of Diblock Copolymer of St and EEMA (SE) or St and tBEMA (ST)[a]

	living poly(St)				block copolymer				
no.	[*sec*-BuLi]$_0$/mM	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	temp/°C	[PSt$^-$Li$^+$]$_0$[d]/mM	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]
SE-1	31.2	2.62	2.63	1.12	−35	16.6	5.30	5.02	1.14
SE-2	15.6	5.19	5.13	1.07	−35	8.3	10.5	10.2	1.08
SE-3	8.0	10.0	10.7	1.07	−35	4.3	20.3	20.4	1.08
ST-1	16.0	5.06	5.28	1.09	0	9.5	10.2	11.1	1.12
ST-2	16.0	5.06	5.39	1.10	20	9.5	10.2	8.82	1.27[e]
ST-3	8.0	10.1	10.1	1.07	0	4.8	20.2	20.7	1.19
ST-4	8.0	10.1	10.3	1.09	−20	4.8	20.2	19.8	1.17

[a] The anionic polymerization of St was first carried out in toluene, at 20 °C, for 50 min ([St]$_0$ = 0.77 M). Then, a THF solution of LiCl (mol$_{LiCl}$/mol$_{sec-BuLi}$ = 1) and of DPE (mol$_{DPE}$/mol$_{sec-BuLi}$ = 1.2) was added. After 10 min, the second step polymerization was induced by introducing EEMA or tBEMA into the system ([EEMA]$_0$ = 0.28 M, [tBEMA]$_0$ = 0.26 M), and the reaction was allowed to last an additional 50 min. The polymer yield was quantitative for every case. [b] Calculated average number molecular weight. [c] Determined by GPC on the basis of a poly(St) calibration curve. [d] Concentration of the living sites of poly(St)s after the addition of the THF solution of LiCl and DPE. [e] Double peaks (see Figure 3B-b).

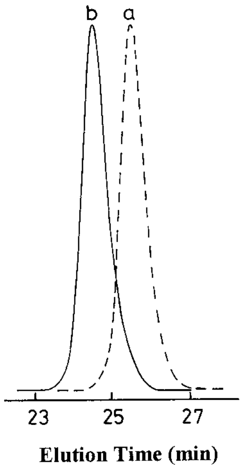


Figure 2. GPC traces of the diblock copolymer of St and EEMA (b, SE-3 in Table 3, M_n = 20 400, M_w/M_n = 1.08) prepared by the anionic block copolymerization of EEMA from its living poly(St) precursor (a, see SE-3 in Table 3, M_n = 10 700, M_w/M_n = 1.07).

erization of St, toluene and *sec*-BuLi were used as the solvent and the initiator, respectively, because St can undergo smoothly anionic polymerization in a nonpolar solvent at room temperature.[10] However, the second step living polymerization of EEMA is preferably carried out in a polar solvent (THF), in the presence of LiCl.[5,9] Further, the living site of poly(St) is too reactive and may attack the ester group of EEMA, causing unwanted side reactions. Considering the above factors, a THF solution of LiCl (mol$_{LiCl}$/mol$_{sec-BuLi}$ = 1) and of DPE (mol$_{DPE}$/mol$_{sec-BuLi}$ = 1.2) was added after the anionic polymerization of St. The reaction between the living site of poly(St) and DPE took place at once, and the color of the system changed from yellow to deep red, implying the formation of a bulkier and less reactive carbanion with a structure similar to DPHL.[11] After 15 min, the system was cooled to −35 °C, and the second step copolymerization was started by adding prechilled EEMA to the above system. Upon the addition of the monomer, the color changed from deep red to transparent immediately, indicating the fast transformation of the living site from the DPE capped poly(St) to poly(EEMA). The reaction was allowed to last 50 min at −35 °C.

As shown in Figure 2 and Table 3 (SE-3), a new sharp and symmetrical peak (b) corresponding to the block copolymer appears after the polymerization of EEMA, in the higher molecular weight side, and the peak (a) of its living poly(St) precursor (M_n = 10 700, M_w/M_n = 1.07) disappears. The molecular weight of the block copolymer (M_n = 20 400, M_w/M_n = 1.08) is about twice as large as that of poly(St), hence almost equal to the designed value, and the MWD is almost as narrow as that of its precursor. These results indicate that the living site of poly(St) initiated the second step, polymerization of EEMA, and that a pure diblock copolymer, poly(St-*b*-EEMA), free of homopolymer, was obtained. In addition, the weight ratio of the two blocks, determined by ^{1}H NMR (for SE-3, W_{St}/W_{EEMA} = 51/49), is very close to the feed amount ratio of St and EEMA (50/50).

Preparation of Diblock Copolymer of St and tBEMA (Poly(St-*b*-tBEMA)) at 0 °C. In a previous paper,[5] we found that tBEMA can undergo anionic polymerization smoothly at a higher temperature than EEMA and BEMA, because the bulky *tert*-butyl ester group stabilizes the propagating site. Even at +20 °C, this monomer could polymerize and a narrow MWD (M_w/M_n = 1.18) obtained. These results encouraged us to attempt its copolymerization with St at higher temperatures (≥0 °C). The experiments were carried out by using the procedure employed in the preparation of poly(St-*b*-EEMA), at a different temperature. As shown in Table 3, for a temperature in the second step of either −20 or 0 °C, the polymer yield was quantitative, and the obtained block copolymer possessed a well-controlled molecular weight and a narrow MWD (M_w/M_n = 1.12−1.19; ST-1, ST-3, and ST-4 in Table 3). As illustrated in Figure 3A, the chromatogram of the block copolymer obtained at 0 °C exhibits a single peak (A-b); the corresponding molecular weight (M_n = 11 100, M_w/M_n = 1.12; ST-1 in Table 3) is about twice that of its living poly(St) precursor (M_n = 5280, M_w/M_n = 1.09), and the MWD remains narrow. Therefore, the diblock copolymer, poly(St-*b*-tBEMA), can be smoothly prepared at 0 °C without side reactions. These results could be relevant from a practical point of view.

Furthermore, the block copolymerization of St and tBEAM was also attempted at room temperature. As shown in Figure 3B, the main peak of the produced diblock copolymer (peak B-b) is accompanied by a shoulder in the low molecular weight region. This means that a part of poly(St) remained unreacted in the second step. This was not caused by side reactions, because the main peak of the diblock copolymer is not broad and the polymer yield is quantitative. The possible reason is that the polymerization rate of tBEMA at this high temperature is much faster than the rate of transformation of the living site from poly(St) to poly(tBEMA).

Preparation of Poly[St-*b*-(MMA-*co*-EEMA)]. The hydrolysis of the poly(St-*b*-EEMA) or poly(St-*b*-tBEMA)

Table 4. Preparation of Poly[St-*b*-(MMA-*co*-EEMA)][a]

	living poly(St)				block copolymer					
no.	[*sec*-BuLi]$_0$/mM	$10^{-3}M_k{}^b$	$10^{-3}M_n{}^c$	$M_w/M_n{}^c$	[PSt$^-$Li$^+$]$_0{}^d$/mM	[MMA]$_0$	[EEMA]$_0$	$10^{-3}M_k{}^b$	$10^{-3}M_n{}^c$	$M_w/M_n{}^c$
SR-1	25.0	3.26	3.00	1.12	12.5	0.38	0.24	9.33	9.63	1.09
SR-2	15.0	5.34	5.45	1.09	7.5	0.56	0.12	15.3	15.0	1.12
SR-3	15.0	5.34	5.19	1.10	7.5	0.19	0.24	12.9	12.4	1.10

[a] The anionic polymerization of St was first carried out in toluene, at 20 °C, for 50 min ([St]$_0$ = 0.77 M). After a THF solution of LiCl (mol$_{\mathrm{LiCl}}$/mol$_{sec\text{-}\mathrm{BuLi}}$ = 1) and of DPE (mol$_{\mathrm{DPE}}$/mol$_{sec\text{-}\mathrm{BuLi}}$ = 1.2) was added, the second step polymerization was started by adding a mixture of MMA and EEMA to the above system, and the reaction was allowed to last 30 min at −40 °C. The polymer yield was quantitative for every case. [b,c,d] See Table 3.

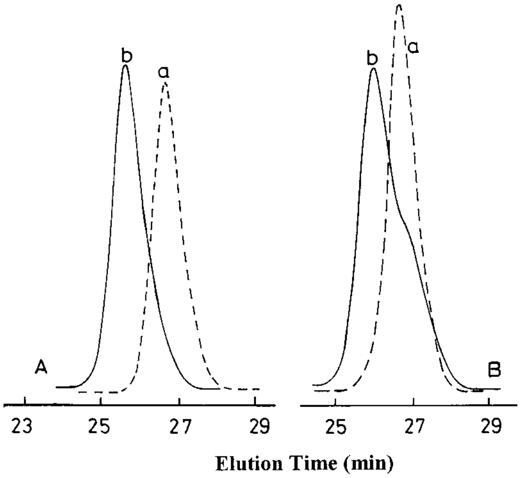


Figure 3. GPC traces of diblock copolymers of St with tBEMA and their precursors: A-a, living poly(St) (see ST-1 in Table 3, M_n = 5280, M_w/M_n = 1.09); A-b, poly(St-*b*-tBEMA) (ST-1 in Table 3, M_n = 11 100, M_w/M_n = 1.12) prepared by the anionic block copolymerization of tBEMA at 0 °C from A-a; B-a, living poly(St) (see ST-2 in Table 3, M_n = 5390, M_w/M_n = 1.10); B-b, poly(St-*b*-tBEMA) (ST-2 in Table 3, M_n = 8820, M_w/M_n = 1.27) prepared by the anionic block copolymerization of tBEMA at 20 °C from B-a.

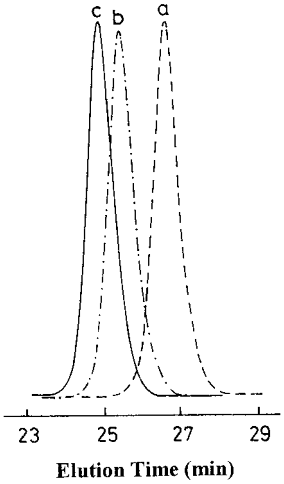


Figure 4. GPC traces of the triblock copolymer of St, MMA, and EEMA and its precursors: a, living poly(St) (see SME-2 in Table 5, M_n = 5130, M_w/M_n = 1.07); b, living diblock copolymer of St and MMA (see SME-2 in Table 5, M_n = 10 600, M_w/M_n = 1.09) prepared by the anionic copolymerization of MMA from a; c, triblock copolymer (SME-2 in Table 5, M_n = 15 500, M_w/M_n = 1.09) prepared by the continuous block copolymerization of EEMA from b.

prepared above generates an amphiphilic block copolymer, poly(St-*b*-MAA), in which the hydrophilic segment consists of 100% MAA. It is, however, useful to be able to control the carboxyl content. This can be achieved by the block copolymerization of St with a mixture of EEMA and MMA. The preparation conditions of this copolymer were as those for poly(St-*b*-EEMA), except that the second step, a random copolymerization, was carried out at −40 °C for 30 min. As shown in Table 4, upon the completion of the random copolymerization of EEMA and MMA, the molecular weight became larger than that of the precursor poly(St) and close to the calculated value; the MWD of the block copolymer was as narrow as that of poly(St). The copolymer composition can also be controlled. For SR-1 in Table 4, the weight ratios of the three components determined by ^{1}H NMR ($W_{\mathrm{St}}/W_{\mathrm{MMA}}/W_{\mathrm{EEMA}}$ = 35.8/30.8/33.4) coincide with the theoretical values (34.6/32.5/32.9). The compositions of the block copolymers SR-2 ($W_{\mathrm{St}}/W_{\mathrm{MMA}}/W_{\mathrm{EEMA}}$ = 34.8/48.6/16.6) and SR-3 ($W_{\mathrm{St}}/W_{\mathrm{MMA}}/W_{\mathrm{EEMA}}$ = 41.3/19.4/39.3) are different from that of SR-1, and each of them is almost equal to the monomer weight ratios. Hence, the content of EEMA in the copolymer can be controlled accurately.

Preparation of Triblock Copolymers of St, MMA, and EEMA. As indicated above, well-defined copolymers of St with EEMA, and of MMA with EEMA, have been obtained. This suggests that it is possible to prepare triblock copolymers by the sequential anionic copolymerization of St, MMA, and EEMA. Because the poly(EEMA) block can be changed to the poly(MAA) segment, one can obtain a triblock copolymer with the hydrophilic segment located at its end by using the polymerization sequence St−MMA−EEMA. On the other hand, by performing the copolymerization in the sequence St−EEMA−MMA, one can obtain a triblock copolymer with the hydrophilic segment located in the middle of the copolymer chain.

The preparation of the living poly(St) and its reaction with DPE were carried out as described above. The polymerizations of MMA and EEMA that followed were performed at −65 and −35 °C, respectively. As shown in Table 5, for the polymerization sequence St, MMA, and EEMA (SME-1 and SME-2), the three polymerization steps proceeded smoothly. The molecular weight increased step by step and was very close to the calculated value at every stage. As illustrated by the GPC measurements (Figure 4), the polymer obtained at each stage exhibited a very sharp and symmetrical peak, indicating that no deactivation of the living site occurred and that the final triblock copolymer was free of its precursors. The weight ratios of the three blocks in SME-2 determined by ^{1}H NMR are $W_{\mathrm{St}}/W_{\mathrm{MMA}}/W_{\mathrm{EEMA}}$ = 33.5/32.7/33.8, extremely close to the theoretical values (33.3/33.3/33.3).

When the polymerization sequence St−EEMA−MMA was employed, the copolymers were also obtained quantitatively. The second step copolymerization of EEMA from DPE capped living poly(St) proceeded smoothly, just like the preparation of the diblock copolymer, poly(St-*b*-EEMA). However, after the continuous polymerization of MMA, the GPC chromato-

Table 5. Preparation of Triblock Copolymer of St (S), MMA (M), and EEMA (E)[a]

	living poly(St)				living diblock copolymer				triblock copolymer		
no.	[s-BuLi]$_0$/mM	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	[PSt$^-$Li$^+$]$_0$[d]/mM	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]
SME−1[e]	26.0	2.62	2.65	1.11	14.2	5.19	5.19	1.11	7.75	7.92	1.10
SME−2[e]	13.0	5.18	5.13	1.07	7.1	10.3	10.6	1.09	15.4	15.5	1.09
SEM-1[f]	26.0	2.62	2.71	1.10	14.2	5.19	5.44	1.12	7.75	6.77	1.27[g]
SEM-2[f]	13.0	5.18	5.30	1.08	7.1	10.3	10.5	1.11	15.4	13.5	1.35[g]

[a] The anionic polymerization of St was first carried out in toluene, at 20 °C, for 50 min ([St]$_0$ = 0.64 M). Before the second step polymerization, a THF solution of LiCl (mol$_{\mathrm{LiCl}}$/mol$_{sec\text{-BuLi}}$ = 1) and of DPE (mol$_{\mathrm{DPE}}$/mol$_{sec\text{-BuLi}}$ = 1.2) was added. For second and third step polymerizations of MMA or EEMA, their initial concentrations were 0.36 and 0.23 M, the polymerization times were 15 and 50 min, and the temperatures were −65 and −35 °C, respectively. The polymer yield was quantitative for every case. [b,c,d] See Table 3. [e,f] Polymerization sequences were St→MMA→EEMA and St→EEMA→MMA, respectively. [g] Double peaks.

Table 6. Solubility Comparison of the Copolymers before and after Hydrolysis[a]

	hexane	benzene	$CHCl_3$	DMF[b]	dioxane	THF	acetone	CH_3OH	C_2H_5OH	H_2O	NaOH[c]
MB-3	I	S	S	S	S	S	S	D	D	I	I
h-MB-3[d]	I	I	I	S	I	D	D	S	S	I	D
MbE-1	I	S	S	S	S	S	S	D	D	I	I
h-MbE-1[d]	I	I	I	S	I	S	D	S	S	I	C
SE-3	I	S	S	S	S	S	S	I	I	I	I
h-SE-3[d]	I	I	I	S	D	S	I	C	C	I	I
SR-1	I	S	S	S	S	S	S	I	I	I	I
h-SR-1[d]	I	I	C	S	D	S	S	D	D	I	I
SME-2	I	S	S	S	S	S	S	I	I	I	I
h-SME-2[d]	I	I	C	S	D	S	S	C	C	I	I
SEM-1	I	S	S	S	S	S	S	I	I	I	I
h-SEM-1[d]	I	I	D	S	D	S	S	D	D	I	I

[a] The experiment was carried out at room temperature. The amounts of copolymer and the solvent were 0.06 g and 2.0 mL, respectively. S, soluble; D, dissolved slowly; C, cloudy; I, insoluble. [b] *N,N*-Dimethylformamide. [c] 5.0 M aqueous solution. [d] Hydrolyzed products from the corresponding copolymers.

gram of the obtained polymer exhibited a double-peak distribution. In the low molecular weight range of the main peak corresponding to the triblock copolymer, a shoulder appeared, which can be attributed to the diblock copolymer, poly(St-*b*-EEMA). Because of the presence of this unreacted diblock copolymer, the MWD of the final product was broader (M_w/M_n = 1.27−1.35, SEM-1 and SEM-2 in Table 5). The too fast polymerization rate of MMA might be the cause for the presence of the unreacted diblock copolymer, poly(St-*b*-EEMA). This does not occur in the polymerization sequence St−MMA−EEMA, because the polymerization rate of EEMA is much slower.

Elimination of the Protecting Groups. The 1-(alkoxy)ethyl groups of poly[1-(alkoxy)ethyl methacrylate)] segments in the copolymers were eliminated through hydrolysis reactions. As soon as a small amount of HCl aqueous solution was added to the THF solution of each copolymer, the reaction completed almost instantaneously. As an example, Figure 5 depicts the ^{1}H NMR spectra of poly[St-*b*-(MMA-*co*-EEMA)] (A; SR-1 in Tables 4 and 6) and its hydrolyzed product (B, in THF-d_8, and C, in CD_3OD). After hydrolysis, the peaks c, d, e, and f due to the protecting group, 1-(ethoxy)ethyl, disappeared completely, and peak j corresponding to the ester group (OCH_3) of MMA units remained unchanged. This means that the ester groups of the EEMA units can be selectively eliminated. The elimination reactions of the protecting groups were also carried out for the other copolymers. Figure 6 presents the FT-IR spectra of the following hydrolyzed copolymers: the random copolymer of MMA and BEMA (A; see MB-3 in Table 1); the diblock copolymer of St and EEMA (B; see SE-3 in Table 3); and the triblock copolymer of St, MMA, and EEMA (C; see SME-2 in Table 5). Each of them exhibits a broad absorption corresponding to the carboxyl group (peaks A-a, B-a and C-a; 2500−3800 cm^{-1}). All the above results indicate that the protecting group, 1-(alkoxy)ethyl, is sufficiently stable in a basic environment to allow the smooth anionic copolymerization of the corresponding monomers. In contrast, the protecting group is unstable even under mildly acidic conditions. This allows its much easier elimination than that of the *tert*-butyl group from poly(St-*b*-*tert*-butyl methacrylate). Therefore, it is more advantageous to prepare the

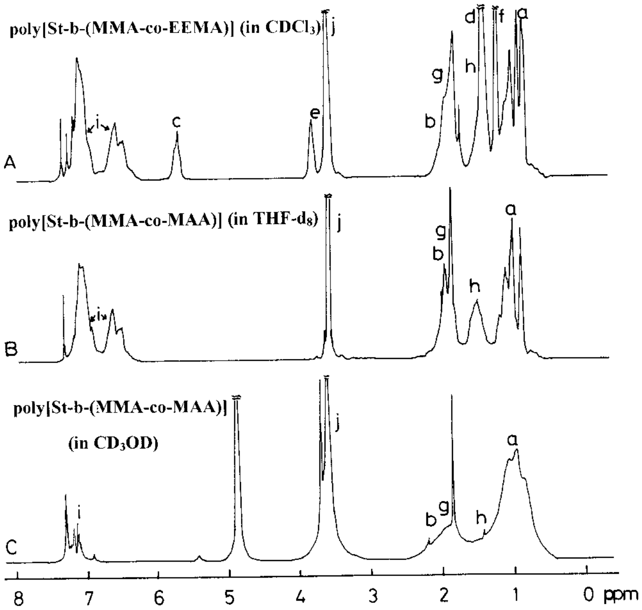


Figure 5. ^{1}H NMR spectra of poly[St-*b*-(MMA-*co*-EEMA)] (A, SR-1 in Table 4, in $CDCl_3$) and its hydrolyzed copolymer, poly[St-*b*-(MMA-*co*-MAA)] (B, in THF-d_8; C, in CD_3OD): peak a, α-CH_3 of MMA and EEMA (or MAA) units; peak b, $-CH_2-$ in the main chain of MMA and EEMA (or MAA) units; peaks c, d, e, and f, $OC\mathit{H}(CH_3)O$, $OCH(C\mathit{H}_3)O$, $C\mathit{H}_2CH_3$ and $CH_2C\mathit{H}_3$ in EEMA units, respectively; peaks g, h, and i, CH, CH_2, and C_6H_5 in poly(St) segment, respectively; peak j, OCH_3 in MMA units.

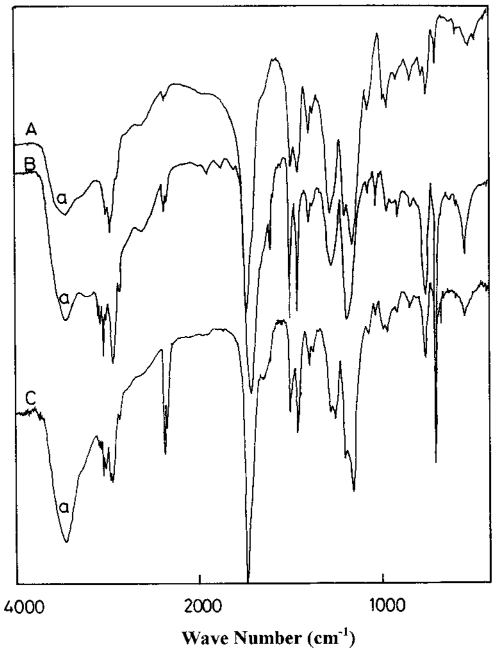


Figure 6. FT-IR spectra (KBr tablets) of the copolymers containing poly(MAA) segments. h-MB-3 (A), h-SE-3 (B), and h-SME-2 (C) were obtained by hydrolysis of MB-3 (Table 1), SE-3 (Table 3), and SME-2 (Table 5), respectively.

hydrophilic MAA segment using the present procedure than the traditional one based on *tert*-butyl methacrylate.

Each hydrolyzed copolymer has a quite different solubility than its precursor (see Table 6). Before hydrolysis, all the copolymers were soluble in benzene, $CHCl_3$, *N*,*N*-dimethylformamide, 1,4-dioxane, THF, and acetone but insoluble in hexane and water. In addition, the block copolymers containing poly(St) segments could be dissolved neither in methanol nor in ethanol. However, after hydrolysis, every copolymer became soluble in alcohol, due to the presence of poly(MAA) hydrophilic segment. For instance, poly[St-*b*-(MMA-*co*-EEMA)] (SR-1 in Tables 4 and 6) was insoluble in methanol and ethanol, because these are poor solvents for its poly(St) segment. However, its hydrolyzed copolymer (h-SR-1 in Table 6) could be slowly dissolved in the two solvents, generating transparent solutions. Because the latter copolymer is soluble in both THF and methanol, its ^{1}H NMR measurements were carried out separately in THF-d_8 and CD_3OD. Interestingly, quite different results were obtained. Figure 5B presents the ^{1}H NMR spectrum determined in THF-d_8. The peaks corresponding to the three components are very clear, and the weight ratios ($W_{St}/W_{MMA}/W_{EEMA} = 42/41/17$), calculated on the basis of the peak intensities, are close to the theoretical values (42/40/18). However, in CD_3OD (Figure 5C), the absorptions corresponding to the poly(St) segment are very weak and even hardly detectable (peaks g, h, and i). The ratios ($W_{St}/W_{MMA}/W_{EEMA} = 7.9/56.8/35.3$) calculated from the peak intensities are far from the theoretical values. This can be explained as follows. It is well-known that methanol is a good solvent for poly(MAA) but a poor one for poly(St). In methanol, this copolymer is expected to form micelles, in which the poly(St) segments are located inside, forming a hydrophobic core, and the copolymer segments of MMA and MAA are located outside, thus wrapping the poly(St) segments. For this reason, the poly(St) component could hardly be detected by the ^{1}H NMR measurement in CD_3OD.

References and Notes

(1) (a) Desjardins, A.; Vandeven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412. (b) Bosse, F.; Eisenberg, A.; Xu, R.; Schreiber, H. P. *J. Appl. Polym. Sci.* **1994**, *51*, 521. (c) Gandhi, J. V.; Maher, J. V.; Shaffer, K. A.; Chapman, T. M. *Langmuir* **1997**, *13*, 1592. (d) May-Colaianni, S. E.; Gandhi, J. V.; Maloy, K. J.; Maher, J. V.; Kuhar, K. A.; Chapman, T. M. *Macromolecules* **1993**, *26*, 6595.

(2) (a) Kutsumizu, S.; Hara, H.; Schlick, S. *Macromolecules* **1997**, *30*, 2320. (b) Kutsumizu, S.; Schlick, S. *Macromolecules* **1997**, *30*, 2329. (c) Saunders, B. R.; Crowther, H. M.; Vincent, B. *Macromolecules* **1997**, *30*, 482.

(3) Rannard, S. P.; Billingham, N. C.; Armes, S. P.; Mykytiuk, J. *Eur. Polym. J.* **1993**, *29*, 407.

(4) (a) Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541. (b) Desjardins, A.; Vandeven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412. (c) Zhang, H. M.; Ishikawa, H.; Ohata, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Polymer* **1992**, *33*, 828. (d) Selb, J.; Gollot, Y. Y. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Publishers: London, 1988; Vol. 2. (e) Long, T. E.; Allen, R. D.; McGrath, J. E. In *ACS Symposium Series No. 364;* Benham, J. L., Kinstle, J. F., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 19. (f) Pitsikalis, M.; Woodward, J.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 5384.

(5) Zhang, H. M.; Ruckenstein, E. *Macromolecules* **1998**, *31*, 7575.

(6) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127.

(7) (a) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1990**, *23*, 2618. (b) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (c) Kunkel, D.; Muller, A. H. E.; Janata, M.; Lochman, L. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.

(8) (a) Mori, H.; Wakisawa, O.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1994**, *195*, 3213. (b) Ruckenstein, E.; Zhang, H. M. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 1865. (c) Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* **1993**, *34*, 2875.

(9) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *10*, 189.

(10) (a) Norhay, A.; McGrath, J. E. *Block Copolymerization*; Academic Press: New York, 1977. (b) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87. (c) Rempp, P.; Franta, E.; Herz, J. E. *Adv. Polym. Sci.* **1988,** *86*, 145. (d) Norton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983. (e) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996. (f) Pitsikalis, M.; Pispas, S.; Ways, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.

(11) Schulz, G.; Hocher, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 219.

MA9812534