Novel Monodisperse Functional (Co)polymers Based on the Selective Living Anionic Polymerization of a New Bifunctional Monomer, *trans*,*trans*-1-Methacryloyloxy-2,4-hexadiene

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ABSTRACT: A new bifunctional monomer, *trans*,*trans*-1-methacryloyloxy-2,4-hexadiene (MAHE), was prepared through the reaction between the sodium salt of 2,4-hexadien-1-ol and methacryloyl chloride. Using 1,1-diphenylhexyllithium (DPHL) as initiator, in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −70 °C, the anionic polymerization of MAHE proceeded quantitatively, generating monodisperse polymers ($M_w/M_n = 1.04-1.05$) with well-controlled molecular weights. Under similar conditions, well-defined block copolymers with controlled molecular weights and compositions as well as very narrow molecular weight distributions ($M_w/M_n = 1.04-1.06$) were prepared by the anionic block copolymerization of MAHE and MMA, regardless of the polymerization sequence (MAHE followed by MMA or vice versa). Similarly, the copolymers resulting from the random copolymerization of these two monomers possessed monodispersity ($M_w/M_n = 1.04-1.05$), regardless of the feed amount ratio. Further, block copolymers of St and MAHE with various compositions were obtained by the anionic block copolymerization of MAHE to a 1,1-diphenylethylene-capped anionic living poly(St). In both the homopolymerization of MAHE and its copolymerization with MMA or St, its 2,4-hexadienyl side group remained unreacted. This side group was further reacted with bromine or osmium tetroxide. Using an excess amount of bromine, at room temperature, the bromination efficiency reached 95%, generating a new functional polymer, poly(2,3,4,5-tetrabromohexyl methacrylate). The osmylation was carried out by reacting the (co)polymer with an excess of *N*-methylmorpholine *N*-oxide, in the presence of a small amount of osmium tetroxide as catalyst, at room temperature. This osmylation reaction changed poly(MAHE) to a new functional polymer, poly(2,3,4,5-tetrahydroxyhexyl methacrylate), with an extremely high water solubility. Well-defined amphiphilic block copolymers were also obtained via the osmylation after block copolymerizations.

Introduction

The properties and performances of a functional polymer depend mainly on the kind and number of functional groups. For instance, the presence of halogen atoms can greatly increase the flame retardancy of the polymer,[1] and the introduction of hydroxyl groups can improve its hydrophilicity. It is well-known that the polymers of alkyl methacrylates are insoluble in alcohol and water, because of their poor hydrophilicity. However, poly(2-hydroxyethyl methacrylate) [poly(HEMA)], which possesses one hydroxyl group in each repeating unit, is soluble in alcohol but insoluble in water.[2] When an additional hydroxyl group was introduced into the side chain, the poly(2,3-dihydroxypropyl methacrylate) [poly(DHPMA)] thus obtained became water-soluble.[3] It is expected that an increasing hydrophilicity of methacrylate polymers can be achieved by a further increase of the hydroxyl groups in the side chains.

The molecular weight distribution (MWD) is also a very important factor which can affect the properties and the performances of functional polymers. For a polymer to possess uniform properties, its MWD should be narrowly controlled, and even an effort should be made to obtain monodisperse functional polymers ($M_w/M_n \leq 1.05$). The present paper presents an approach to several novel monodisperse functional homo- and copolymers via the selective living anionic polymerization of a new bifunctional monomer followed by additional reactions.

It is well-known that the methacrylate monomers are much more reactive than the conjugated dienes in an anionic polymerization, and for this reason, the diblock copolymer of these two monomers can only be obtained via a polymerization sequence of diene followed by methacrylate.[4] The new bifunctional monomer, *trans*,*trans*-1-methacryloyloxy-2,4-hexadiene (MAHE, **1** in Scheme 1), possesses both a methacryloyl type and a conjugated diene type polymerizable group. The reactivity of the former group is greater than that of the latter. In addition, the steric hindrance due to the presence of a methyl and an ester group at the two ends of the diene further reduces its reactivity. Therefore, it is expected that the methacryloyl type C═C bond can be selectively polymerized under suitable conditions to generate a functional polymer with a reactive dienyl group in each of its repeating units (**2** in Scheme 1). Furthermore, because the diene side groups can undergo many kinds of reactions, such as bromination, osmylation, Diels−Alder reaction, etc., a number of novel functional polymers can be obtained by reactions after the polymerization. As shown in Scheme 1, the bromination of poly(MAHE) can introduce four bromine atoms into each of its repeating units (**3** in Scheme 1). On the other hand, its reaction with *N*-methylmorpholine *N*-oxide (NMO) in the presence of osmium tetroxide as catalyst generates a functional polymer (**4** in Scheme 1) that possesses very high water solubility because of the presence of four hydroxyl groups in each of its repeating units. In addition, a number of novel functional copolymers, such as amphiphilic copolymers, can also be

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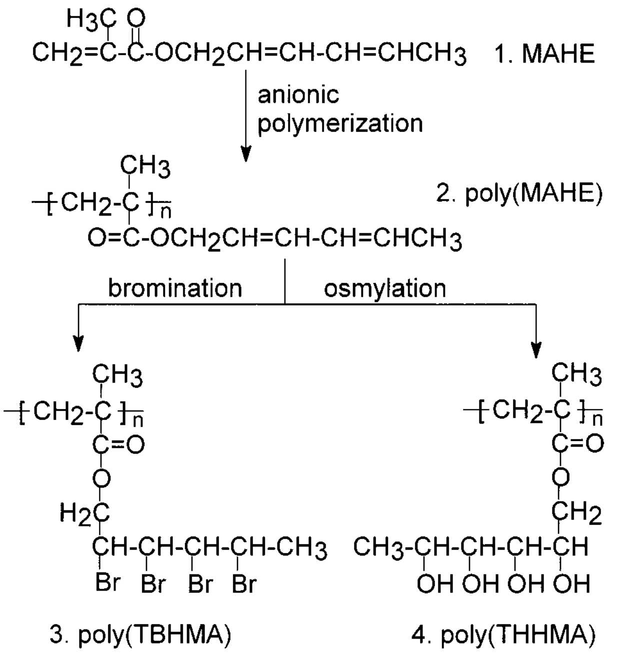
Scheme 1



obtained by the copolymerization of MAHE with other monomers, such as styrene (St), methyl methacrylate (MMA), etc., followed by additional reactions.

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 distilled again 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%) was dried over CaH_2 with magnetic stirring under reduced pressure and vacuum-distilled twice over CaH_2. Styrene (St, 99%, Aldrich) was washed with a 10% aqueous NaOH solution and then with water, dried overnight with $MgSO_4$, distilled over CaH_2, and finally distilled in the presence of phenylmagnesium chloride just before use. 1,1-Diphenylethylene (DPE, Aldrich, 97%) was distilled over CaH_2 and then distilled 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.[5] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane. Methacryloyl chloride (Acros, 97%), *trans,trans*-2,4-hexadien-1-ol (Aldrich, 97%), bromine (Aldrich, 99.5%), osmium tetroxide (Aldrich, 4.0 wt % aqueous solution), and *N*-methylmorpholine *N*-oxide (NMO, Aldrich, 97%) were used as received.

Synthesis of *trans,trans*-1-Methacryloyloxy-2,4-hexadiene (MAHE). MAHE was prepared through the reaction between the sodium salt of *trans,trans*-2,4-hexadien-1-ol (HDO) and methacryloyl chloride. A 1000 mL round-bottom flask equipped with a condenser, a paddle stirrer, and a dropping funnel with a pressure-equalization arm was degassed and heated under reduced pressure. To this flask, 400 mL of CaH_2-purified toluene was added, followed by the addition of sodium hydride (Aldrich; 60% dispersion in mineral oil; 10.4 g, 0.26 mol). Under the protection of nitrogen, 100 mL of toluene solution of HDO (25 g, 0.25 mol) was dropwise added in 1.5 h. The reaction mixture was stirred for 1 h at room temperature to generate the sodium salt of HDO. The reaction system was cooled to 0 °C, and methacryloyl chloride (24 g, 0.22 mol) was dropwise added in 1.0 h. After about 1.5 h, the reaction was terminated by carefully adding an aqueous solution of sodium hydroxide (1.0 M, 100 mL). The reaction mixture was washed three times with water, evaporated to remove toluene, and distilled under reduced pressure (bp: 42 °C/0.5 Torr; yield: 74% based on the amount of methacryloyl chloride employed). The monomer thus obtained was distilled twice over CaH_2 and finally distilled in the presence of $Al(C_2H_5)_3$[6] prior to polymerization. As shown later in Figure 3A, the chemical shifts and their intensities in the ^1H NMR spectrum of the prepared MAHE are consistent with its molecular structure.

Anionic (Co)polymerizations. All polymerizations, namely, the anionic homopolymerization of MAHE, its random and block copolymerizations with MMA, and its block copolymerization with St, were carried out in a round-bottom flask under argon with magnetic stirring.

Homopolymerization. The anionic homopolymerization of MAHE was performed in THF, at −70 °C, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$).[5] Before the monomer addition, the initiator DPHL was first prepared in situ. After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to −40 °C and *n*-BuLi (in hexane) was added. The reaction between *n*-BuLi and DPE was allowed to last 15 min. Then, the system was cooled to −70 °C, and the polymerization reaction was induced by the addition of prechilled MAHE to the above system. About 1 h later, the polymerization was quenched with a small amount of methanol (ca. 1 mL). Usually, the polymerization solution was divided into three parts. Two parts were further used for the bromination and osmylation, and the third part was treated with a trace amount of inhibitor BHT, evaporated to dryness, and vacuum-dried for 24 h at room temperature.

Copolymerization with MMA. The anionic block copolymerization of MAHE and MMA was carried out by using the monomer addition sequence of MAHE followed by MMA or vice versa, in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$), at −70 °C. The polymerization times for MMA and MAHE were 30 and 50 min, respectively. The random copolymerization of the two monomers was carried out under the same conditions, except that the two monomers were added at the same time. The initiator preparation and the polymer purification were carried out in ways similar to those employed for the homopolymer of MAHE.

Block Copolymerization with St. The block copolymer of MAHE and St was prepared using the polymerization sequence of St, followed by MAHE. The living poly(St) was first prepared by the anionic polymerization of St, which was carried out in a mixture of toluene and THF (3:1 by volume), at −55 °C, using *n*-BuLi as the initiator. After toluene, THF, and a hexane solution of *n*-BuLi were introduced into a flask kept at −55 °C, the polymerization was started by adding prechilled St. While the polymerization was proceeding, THF, DPE ($mol_{DPE}/mol_{n-BuLi} = 1.4$), and a THF solution of LiCl ($mol_{LiCl}/mol_{n-BuLi} = 3$) were introduced into another flask, to which a hexane solution of *n*-BuLi was dropwise added until the red color of DPHL appeared, to remove the impurities. Then, this mixture was immediately introduced into the living poly(St) solution. The color of the system changed instantaneously from yellow to deep red, implying that the living end of poly(St) was rapidly capped by DPE. This reaction was allowed to last 20 min to ensure a complete transformation of the living site. Subsequently, prechilled MAHE was added and its polymerization allowed to last 40 min. After the termination with methanol (ca. 1 mL), the bromination, osmylation, and the polymer purification were carried out in ways similar to those for the homopoly(MAHE).

Bromination. The reaction between the diene side chains of the resulting (co)polymers and bromine was carried out by directly employing the polymerization solution in the next bromination step. The (co)polymer was allowed to react with an excess amount of bromine at room temperature, in a dark box, under nitrogen, with magnetic stirring. After a selected time, the polymer was precipitated by pouring the reaction mixture into methanol, washed three times with methanol, immersed in methanol overnight, and finally vacuum-dried at 45 °C for 24 h.

Osmylation. The osmylation reactions of the homopolymer of MAHE and of its block copolymer with MMA or St were carried out with magnetic stirring, under nitrogen, at room

Table 1. Selective Anionic Homopolymerization of MAHE[a]

	$[\mathrm{DPHL}]_0$, mM	$[\mathrm{MAHE}]_0$, M	$10^{-4}M_n$		M_w/M_n[b]
			calcd	obsd[b]	
PMAHE-1	10.0	0.48	0.82	0.81	1.05
PMAHE-2	6.7	0.60	1.51	1.51	1.04
PMAHE-3	4.0	0.48	2.02	1.94	1.04
PMAHE-4	2.0	0.48	4.01	4.04	1.04
PMAHE-5	1.0	0.48	8.00	8.55	1.05

[a] The initiator DPHL was prepared in situ before the monomer addition via the reaction between *n*-BuLi and an excess amount of DPE ($[\mathrm{DPE}]/[n\text{-BuLi}]_0 = 1.4$) at −40 °C for about 15 min. The polymerization was carried out in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −70 °C, for 45−60 min. The monomer conversion was 100% in each case. [b] Determined by GPC.

temperature. Upon the (co)polymerization, a solution containing a certain amount of (co)polymer was transferred into a nitrogen-protected flask, to which THF, acetone, methanol, and NMO were sequentially added. Then, the system was degassed and reprotected with nitrogen, and the reaction was started by adding osmium tetroxide (4.0 wt % aqueous solution) with a syringe. After a certain time, the resulting polymer was precipitated by pouring the reaction solution into a mixture of hexane and ethanol (1:1 by volume). Then, the polymer was redissolved in hot methanol (for homopolymer) or pyridine (for block copolymer), and the precipitation into the above mixture was twice repeated. The (co)polymer thus obtained was kept in the above mixture overnight, washed with ethanol, vacuum-dried at 40 °C for 24 h, and finally freeze-dried from a 1,4-dioxane solution containing a small amount of water.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$, D_2O, or pyridine-d_5 on an Inova-400 spectrometer. M_n and M_w/M_n of the (co)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) were used, which were connected to a Waters 515 precision pump. FT-IR spectra were recorded using KBr pellets on a Perkin-Elmer 1760-X spectrometer. The elemental analysis was carried out by Atlantic Microlab, Inc.

Results and Discussion

Anionic Polymerization of MAHE. The monomer purification played an important role in the anionic polymerization of MAHE. Calcium hydride-purified MAHE was not pure enough for the anionic polymerization. Even though a high initiator concentration was employed ($[\mathrm{DPHL}]_0 = 50$ mM, $[\mathrm{MAHE}]_0 = 0.6$ M), no polymer could be obtained because of the presence of a trace amount of unreacted alcohol (HDO) during the monomer preparation procedure (see Experimental Section). To remove this impurity, CaH_2-purified MAHE was further distilled in the presence of triethylaluminum,[6] and the monomer thus obtained was employed in the polymerization immediately. Using DPHL as the initiator, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), in THF, at −70 °C, the anionic polymerization of MAHE proceeded smoothly, generating poly(MAHE) quantitatively. As shown in Table 1, monodisperse polymers ($M_w/M_n = 1.04-1.05$) with well-controlled molecular weights were obtained in every case. Even when the initiator concentration was very low ($[\mathrm{DPHL}]_0 = 1.0$ mM, PMAHE-5 in Table 1), the resulting large molecular weight poly(MAHE) still possessed monodispersity ($M_n = 8.55 \times 10^4$, $M_w/M_n = 1.05$). As shown in Figure 1A, its GPC chromatogram exhibits a sharp, symmetrical peak, which is even narrower than that of the poly(St) standard (Figure 1C, $M_n = 17\,500$, $M_w/M_n < 1.06$). Very few polar functional polymers were reported to possess such a narrow MWD.

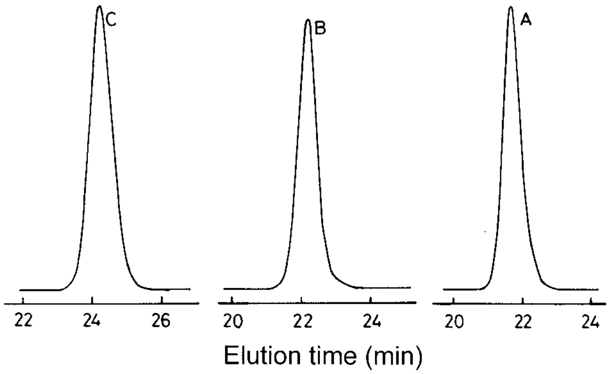


Figure 1. GPC traces of poly(MAHE) (A; PMAHE-5 in Table 1, $M_n = 85\,500$, $M_w/M_n = 1.05$), poly(MAHE-*co*-MMA) (B; random-4 in Table 3, $M_n = 66\,900$, $M_w/M_n = 1.04$), and polystyrene standard (C; from Pressure Chemical, lot no. 41220, $M_n = 17\,500$, $M_w/M_n < 1.06$).

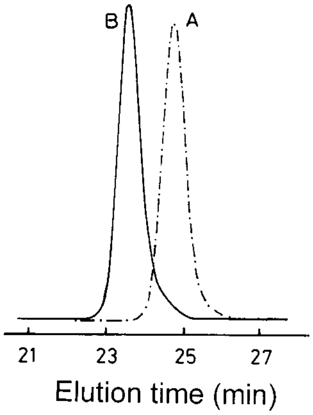


Figure 2. GPC traces of poly(MAHE)s obtained by a two-time the same amount of monomer addition experiments. (A) First-time monomer addition, $M_n = 12\,000$, $M_w/M_n = 1.04$ ($[\mathrm{DPHL}]_0 = 5.19$ mM, $[\mathrm{MAHE}]_0 = 0.344$ M, $[\mathrm{LiCl}] = 15.6$ mM, at −70 °C). (B) Second-time monomer addition, $M_n = 24\,000$, $M_w/M_n = 1.05$.

To verify the living nature of the anionic polymerization of MAHE, two successive monomer addition experiments were carried out. The polymerization conditions and the GPC results are presented in Figure 2. In the first stage, poly(MAHE) with a very narrow MWD (peak A, $M_n = 12\,000$, $M_w/M_n = 1.04$) was obtained. After the same amount of MAHE was added to the system, the GPC peak shifted toward the high molecular weight, but the MWD remained narrow (peak B, $M_n = 24\,000$, $M_w/M_n = 1.05$), and no precursor polymer remained. The above results clearly indicate that the anionic polymerization of MAHE proceeded in a living manner.

Parts A and B of Figure 3 present the ^{1}H NMR spectra of MAHE and its polymer, respectively. After polymerization, peaks a, b, and b′ in Figure 3A due to α-CH_3 and $H_2C{=}$ (b and b′) of the methacryloyl group disappeared completely, and two new absorptions corresponding to $-CH_3$ (peak a in Figure 3B) and $-CH_2-$ of poly(MAHE) main chain emerged at 0.75−1.10 and 1.88 ppm, respectively. On the other hand, peaks c−h due to the 2,4-hexadienyl ester group remained unchanged after polymerization. Furthermore, as shown later in Table 8, the resulting poly(MAHE) is soluble in

Table 2. Anionic Block Copolymerization of MAHE and MMA[a]

	polymerization sequence	$[DPHL]_0$, mM	$[M_1]_0$, M	$[M_2]_0$, M	first step		second step		W_{MAHE}/W_{MMA}[c]
					$10^{-4}M_n$[b]	M_w/M_n[b]	$10^{-4}M_n$[b]	M_w/M_n[b]	
block-1	MAHE→MMA	8.4	0.30	1.50	0.64 (0.62)	1.06	2.56 (2.41)	1.05	27/73 (25/75)
block-2	MAHE→MMA	4.2	0.30	0.50	1.32 (1.21)	1.04	2.60 (2.40)	1.06	51/49 (50/50)
block-3	MAHE→MMA	3.3	0.30	0.75	1.68 (1.54)	1.05	3.95 (3.81)	1.04	39/61 (40/60)
block-4	MMA→MAHE	6.3	0.50	0.30	1.08 (0.82)	1.05	1.96 (1.61)	1.05	48/52 (50/50)
block-5	MMA→MAHE	3.3	0.33	0.60	1.12 (1.03)	1.05	4.56 (4.05)	1.04	26/74 (25/75)

[a] The copolymerization was carried out by a sequential monomer addition of MAHE followed by MMA or vice versa, in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$), at −70 °C. The polymerization times for MAHE and MMA were 50 and 30 min, respectively. The polymer yield was quantitative in each case. [b] Determined by GPC. The data in parentheses are the calculated M_n. [c] The weight ratio of MAHE and MMA segments in the resulting copolymer, which was determined by ^{1}H NMR. The data in parentheses are the calculated weight amount ratios of the two monomers.

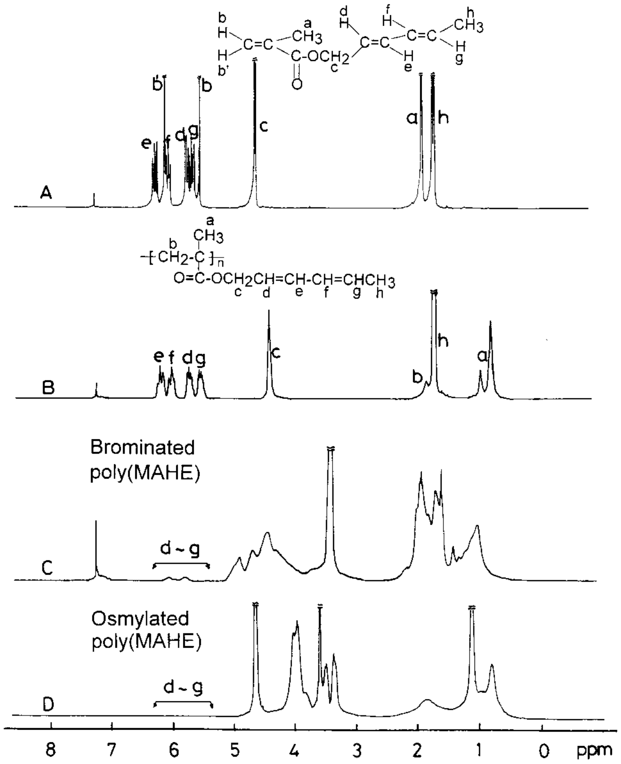


Figure 3. ^{1}H NMR spectra of MAHE (A; in $CDCl_3$), poly(MAHE) (B; in $CDCl_3$; PMAHE-2 in Table 1), brominated poly(MAHE) (C; in $CDCl_3$; Br-PMAHE-2′, see Tables 1 and 5) and osmylated poly(MAHE) (D; in D_2O; o-PMAHE-2, see Tables 1 and 6).

a number of solvents, such as benzene, chloroform, THF, 1,4-dioxane, acetone, etc. Therefore, one can conclude that the methacryloyl type C═C bond of MAHE was selectively polymerized, that no cross-linking and any other side reaction occurred during polymerization, and that the polymer thus obtained is a functional polymer possessing a conjugated diene group in each of its repeating units.

Anionic Copolymerization of MAHE and MMA. Both the anionic block and random copolymerizations of MAHE and MMA were carried out under conditions similar to those for its homopolymerization. For the block copolymerization, a two-step sequential monomer addition, namely, MAHE followed by MMA or vice versa, was employed. As shown in Table 2, regardless of the polymerization sequence, well-defined block copolymers were obtained in both cases. The molecular weight could be controlled at each step, the MWD of either the precursor or the final copolymer possessed monodispersity ($M_w/M_n = 1.04-1.06$), and the composition determined by ^{1}H NMR was in good agreement with that designed. As an example, Figure 4A presents the GPC chromatograms of poly(MAHE-*b*-MMA) (peak A-b; block-3 in Table 2) and of its living poly(MAHE) precursor (peak A-a; $M_n = 16\,800$, $M_w/M_n = 1.05$). After the second step polymerization of MMA from the living end of poly(MAHE), the M_n of the resulting copolymer increased ($M_n = 39\,500$, $M_w/M_n = 1.04$), while the monodispersity remained unchanged. This result further confirmed the living nature of the anionic polymerization of MAHE.

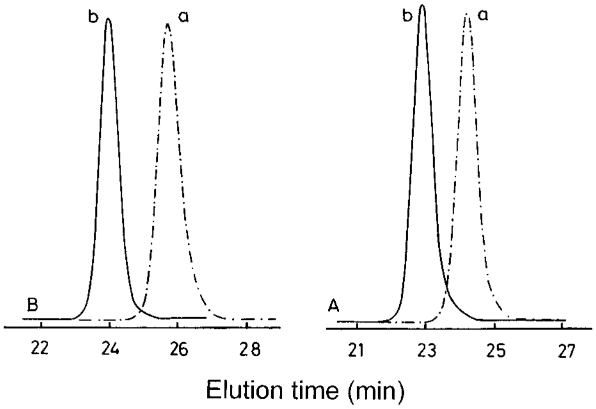


Figure 4. GPC traces of block copolymers and their precursors. A-a: living poly(MAHE) (see block-3 in Table 2, $M_n = 16\,800$, $M_w/M_n = 1.05$). A-b: block copolymer, poly(MAHE-*b*-MMA) (block-3 in Table 2, $M_n = 39\,500$, $M_w/M_n = 1.04$) obtained via the successive anionic polymerization of MMA from A-a. B-a: living poly(St) (see StMA-1 in Table 4, $M_n = 4900$, $M_w/M_n = 1.05$). B-b: block copolymer, poly(St-*b*-MAHE) (StMA-1 in Table 4, $M_n = 19\,500$, $M_w/M_n = 1.04$) obtained via the anionic polymerization of MAHE from B-a.

Similar to the block copolymerization, the random copolymerization of MAHE and MMA also proceeded smoothly to generate their copolymers. As shown in Table 3, no matter how the feed amount ratio of the two monomers changed (W_{MAHE}/W_{MMA} = 30/70, 40/60, 50/50, and 67/33), the monomer conversion was 100%, and any of the copolymers possessed monodispersity ($M_w/M_n = 1.04-1.05$) as well as well-controlled composition. As illustrated in Figure 1B, the GPC chromatogram of a copolymer (random-4 in Table 3, $M_n = 66\,900$, $M_w/M_n = 1.04$) exhibits a single, sharp peak, which is as narrow as that of homopoly(MAHE) (peak A).

Anionic Block Copolymerization of St and MAHE. In contrast to the block copolymerization of MAHE with MMA, the diblock copolymer of St and MAHE can only be obtained by using an one-way polymerization sequence of St followed by MAHE, due to the large difference between the reactivities of the two monomers.[4d] The anionic polymerization of St was carried out using *n*-BuLi as the initiator, in a mixture of toluene and THF

Table 3. Anionic Copolymerization of MAHE with MMA[a]

	$[\mathrm{DPHL}]_0$, mM	$[\mathrm{MAHE}]_0$, M	$[\mathrm{MMA}]_0$, M	$10^{-4}M_n$ (calcd)	$10^{-4}M_n$ (obsd)[b]	M_w/M_n[b]	$W_{\mathrm{MAHE}}/W_{\mathrm{MMA}}$[c]
random-1	6.8	0.24	0.60	1.49	1.59	1.05	40/60 (40/60)
random-2	4.0	0.30	0.50	2.52	2.81	1.05	52/48 (50/50)
random-3	4.0	0.18	0.70	2.52	2.95	1.04	33/67 (30/70)
random-4	1.3	0.30	0.25	5.80	6.69	1.04	65/35 (67/33)

[a] The anionic copolymerization was carried out in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −78 °C, for 50 min. The polymer yield was quantitative in each case. [b] Determined by GPC. [c] Weight ratio of MAHE and MMA units in the copolymer, determined by ^{1}H NMR. The data in parentheses are the feed amount ratios of the two monomers.

Table 4. Anionic Block Copolymerization of St with MAHE

	living poly(St)[a]				block copolymer[b]				
	$[n\text{-BuLi}]_0$, mM	$[\mathrm{St}]_0$, M	$10^{-4}M_n$[c]	M_w/M_n[c]	[living PSt]$_0$, mM	$[\mathrm{MAHE}]_0$, M	$10^{-4}M_n$[c]	M_w/M_n[c]	$W_{\mathrm{St}}/W_{\mathrm{MAHE}}$[d]
StMA-1	13	0.60	0.49 (0.49)	1.05	5.0	0.45	1.95 (2.01)	1.04	26/74 (25/75)
StMA-2	10	0.96	1.10 (1.00)	1.04	4.4	0.27	2.01 (2.02)	1.05	48/52 (50/50)
StMA-3	6.7	0.96	1.68 (1.50)	1.06	3.3	0.10	2.24 (2.01)	1.07	76/24 (75/25)

[a] The anionic block copolymerization was carried out using a polymerization sequence of St followed by MAHE. The anionic polymerization of St was performed using *n*-BuLi as initiator, in a mixture of toluene and THF (3/1 by volume), at −55 °C, for about 50 min. [b] After the polymerization of St, a THF solution of DPE ($[\mathrm{DPE}]/[\text{living PSt}]_0 = 1.4$) and LiCl ($[\mathrm{LiCl}]/[\text{living PSt}]_0 = 3$) was added. In this manner, the living poly(St) solution was diluted, and its living end was capped with DPE. Then, MAHE was added and polymerized at −70 °C for 40 min. The copolymer yield was 100% in each case. [c] Determined by GPC. The data in parentheses are the calculated M_n. [d] The weight ratio of St and MAHE segments in the copolymer, determined by ^{1}H NMR. The data in parentheses are the feed amount ratios of the two monomers.

Table 5. Bromination of the (Co)polymers[a]

	precursor/g[b]	C=C/ mmol[c]	$\mathrm{Br_2}$/ mmol	time/ h	function-ality/%[d]
Br-PMAHE-2	PMAHE-2/1.0	12	36	20	87
Br-PMAHE-2′	PMAHE-2/0.5	6	36	75	95
Br-random-3	random-3/1.0	3.6	20	75	92
Br-block-2	block-2/1.0	6	29	75	90
Br-StMA-2	StMA-2/1.0	6	39	54	93

[a] A polymerization solution was directly employed and was diluted to 5% (w/v) with THF. The reaction was carried out by adding bromine with a dry syringe under nitrogen with magnetic stirring. [b] See Tables 1−4. [c] The molar amount of single double bonds, which is twice that of the conjugated diene side chains. [d] Determined by ^{1}H NMR.

(3:1 by volume), at −55 °C, for 50 min. Then, a THF solution of LiCl ($\mathrm{mol_{LiCl}/mol_{\mathit{n}-BuLi}} = 3$) and of DPE ($\mathrm{mol_{DPE}/mol_{\mathit{n}-BuLi}} = 1.4$) was added to change the living end to a bulkier and less reactive diphenyl carbanion.[7] Subsequently, the anionic polymerization of MAHE proceeded from this DPE-capped living site by adding MAHE to the above system. As shown in Figure 4B and Table 4, a new single peak (B-b) due to the block copolymer (StMA-1 in Table 4) appeared in the higher molecular weight side after the polymerization of MAHE, and the peak (B-a) of its living poly(St) precursor ($M_n = 4900$, $M_w/M_n = 1.05$) disappeared. The molecular weight of the resulting copolymer ($M_n = 19\,500$, $M_w/M_n = 1.04$) increased and was close to the designed value [M_n(calcd) = 20 100], whereas the MWD remained very narrow. Consequently, a pure diblock copolymer, poly(St-*b*-MAHE), free of its precursor polymers, was obtained. In addition, the weight ratios of St and MAHE segments in the block copolymers determined by ^{1}H NMR were very close to the feed amount ratios of the two monomers (Table 4).

Polymer Reactions. The diene compounds possess multiple and useful reactivities. Just as St, the dienes, especially 1,3-butadiene and isoprene, constitute some of the most important nonpolar monomers, and their polymerizations have been extensively investigated.[8] Besides their polymerization capability, they can also undergo many other reactions. The addition reaction of a diene with a halogen or a halogen hydride produces halogenated compounds.[9] The osmylation of a diene with osmium tetroxide generates hydroxylated products. Another most widely known reaction is the Diels−Alder reaction between conjugated diene and unlimited number of dienophiles, such as maleic anhydride, acrolein, alkyl propenoate, cyanoethene, etc.[10]

Because of its very reactive properties, dienyl groups have been recently introduced at the ends of the common polymers, such as poly(MMA), to prepare end-functional polymers or macromers.[11] The present paper intends to develop an approach for new functional polymers with diene side groups and further to other new functional polymers. Obviously, numerous monodisperse functional polymers can be obtained through the reactions between the anionically prepared (co)polymers of MAHE with other reagents. As examples, two kinds of reactions are reported in what follows.

Bromination. The addition between a conjugated diene and the same molar amount of bromine usually generates both 1,2- and 1,4-addition products.[9] If an excess amount of bromine is employed, the remaining single C=C bond can further react with $\mathrm{Br_2}$ to generate tetrabrominated products. As shown in Table 5, the bromination of the (co)polymers of MAHE was carried out by reacting the (co)polymer with a large excess amount of bromine ($\mathrm{mol_{Br_2}/mol_{C=C}} = 3{-}6.5$) with the goal to obtain poly(2,3,4,5-tetrabromohexyl methacrylate) [poly(TBHMA), **3** in Scheme 1] or its copolymer. The polymerization solution was directly used for the reaction with $\mathrm{Br_2}$ at room temperature. Because the atomic weight of bromine is large (80) and the number of atoms added to a single repeating unit can be up to 4, the polymer weight was greatly increased after reaction. For instance, after 1.0 g of PMAHE-2 (Table 5) was reacted with 2.9 g of bromine for 20 h, 2.6 g of adduct was recovered. The functionality calculated for this polymer yield was 89%, which was close to that (87%) determined by ^{1}H NMR. Regardless if the homopolymer of MAHE or its copolymer with St or MMA was used for bromination, it was found that the functionality easily reached about 90% but hardly reached 100%. Figure 3C presents the ^{1}H NMR spectrum of a brominated poly(MAHE) (Br-PMAHE−2′ in Table 5), which was obtained by reacting 0.5 g of PMAHE-2 ($\mathrm{mol_{C=C}} = 6$ mmol) with 2.9 g of $\mathrm{Br_2}$ (36 mmol) for 75 h.

Table 6. Osmylation of the (Co)polymers[a]

	precursor[b] (g)	C═C (mmol)[c]	NMO (mmol)[d]	OsO_4[e] (mL)	solvents (by vol, mL)[f] THF/toluene/acetone/CH_3OH	time (h)	functionality[g] (%)
o-PMAHE-2	PMAHE-2/0.5	6	10	0.7	10/0/3/7	24	100[h]
o-PMAHE-3	PMAHE-3/1.0	12	18	1.5	16/0/3/10	48	100[h]
o-block-5	block-5/0.53	4.8	8	0.5	10/0/4/4	36	100
o-StMA-1	StMA-1/0.5	4.6	7	0.5	8/2/3/4	28	100
o-StMA-2	StMA-2/0.53	3.2	6	0.5	10/2/2/4	26	100

[a] The reaction was carried out with magnetic stirring, under nitrogen, at room temperature. The polymer yield was 100% in each case. [b] A polymerization solution containing a certain amount of (co)polymer was directly employed. [c] Molar amount of single C═C bonds, which is twice that of the conjugated diene side chains of poly(MAHE) units. [d] Molar amount of *N*-methylmorpholine *N*-oxide (NMO). [e] A 4.0 wt % of aqueous solution, which contained 1.3−1.8 mol % of OsO_4 compared to the molar amount of C═C bonds in MAHE segments, was employed. [f] To a polymerization solution, THF, acetone, and methanol were sequentially added. [g] Determined by ^1H NMR. [h] The quantitative functionality was also confirmed by elemental analysis.

Table 7. Elemental Analyses of Poly(MAHE) and Its Osmylated Product

		C (%)		H (%)		N (%)	
		theory	found	theory	found	theory	found
PMAHE-3[a]	$C_{10}H_{14}O_2$	72.24	72.70	8.51	8.57		
o-PMAHE-3[b]	$C_{10}H_{18}O_6 \cdot 0.2H_2O$[c]	50.49	50.51	7.81	7.87	0.00	0.00

[a] See Table 2. [b] See Table 7. [c] Each repeating unit contains 0.2 water molecule.

Table 8. Solubilities of the (Co)polymers[a]

	hexane	Bz	$CHCl_3$	DMF	pyridine	1,4-dioxane	THF	acetone	C_2H_5OH	CH_3OH	H_2O
PMAHE-3	P	S	S	S	S	S	S	S	I	I	I
o-PMAHE-3	I	I	I	S	D	I	I	I	I	D,P[b]	SS[c]
PDHPMA[d]	I	I	I	S	S	I	I	I	I	S	S
PHEMA[e]	I	I	I	S	S	I	I	I	S	S	I
Br-PMAHE-2′	I	S	S	S	S	C	S	P	I	I	I
block-4	I	S	S	S	S	S	S	S	I	I	I
o-block-4	I	I	I	S	D	I	I	I	I	D	SW
StMA-2	I	S	S	S	S	S	S	S	I	I	I
o-StMA-2	I	I	I	S	S	I	I	I	I	I	SW

[a] The experiment was carried out at room temperature (23 °C). The amounts of polymer and the solvent were 0.03 g and 1.0 mL, respectively. S = soluble; D = dissolved slowly; P = partially soluble; C = cloudy; SW = swollen; I = insoluble. [b] Only partially dissolved after 24 h. [c] Dissolved completely in a few seconds. [d] Poly(2,3-dihydroxypropyl methacrylate) prepared in a previous paper [ref 3b]. [e] Poly(2-hydroxyethyl methacrylate); see ref 2.

Comparing Figure 3C with the spectrum of its poly(MAHE) precursor (Figure 3B), one can observe that the conjugated diene (peaks d−g) are no longer present after bromination. However, a small fraction (5%) of single C═C bonds (5.75−6.14 ppm, Figure 3C) remained in the reaction product. The functionality calculated according to the intensity ratio was 95%.

Parts A, B, and C of Figure 5 depict the FT-IR spectra of MAHE, poly(MAHE), and brominated poly(MAHE), respectively. In the spectrum of the monomer (A), the absorption of the olefinic bond conjugated with the carbonyl group appeared at 1637 cm^{-1} (A-b). The olefinic bond stretching vibration of the conjugated diene produces two C═C stretching bands because of the absence of a center of symmetry. One absorption is located at 1662 cm^{-1} (A-a), and the other one (A-a′, 1630 cm^{-1}) is overlapped with that (A-b) of the methacryloyl type C═C bond. After selective polymerization, the absorption (b) of the methacryloyl type C═C bonds disappeared, while those (a and a′, Figure 5B) corresponding to the diene groups remained unchanged. After this sample was subjected to bromination (Figure 5C), the two peaks of the diene group disappeared almost completely (functionality 95%).

Osmylation. We have demonstrated that the osmylation of the C═C bond-containing polymer constitutes a perfect approach to functional polymers with excellent hydrophilicities.[3b] During this process, the C═C bond reacted with NMO in the presence of a trace amount of osmium tetroxide as catalyst. The dihydroxylation of C═C bond proceeded smoothly without cross-linking or any other side reaction, and the functionality reached 100% under suitable conditions. However, the polymers previously subjected to osmylation contained only a single C═C bond in each repeating unit, which was changed to two hydroxyl groups. In the present paper, the osmylation of poly(MAHE), which contains a diene group in each of its repeating units (two single C═C bonds), was carried out to prepare the new functional polymer, poly(2,3,4,5-tetrahydroxyhexyl methacrylate) [poly(THHMA), **4** in Scheme 1].

The osmylation was carried out with magnetic stirring, under nitrogen, at room temperature. The polymerization solution was directly subjected to reaction without polymer separation. Compared to the molar amount of C═C bonds, an excess of NMO ($mol_{NMO}/mol_{C=C}$ = 1.5−1.8) and a small amount of OsO_4 ($mol_{OsO_4}/mol_{C=C}$ = 1.3−1.8/100) were employed (Table 6). Figure 3D presents the ^1H NMR spectrum of an osmylated poly(MAHE) (o-PMAHE-2 in Table 6). Compared to its poly(MAHE) precursor (Figure 3B), peaks d−g corresponding to the diene side groups of poly(MAHE) disappeared completely after osmylation. The FT-IR also confirmed the quantitative hydroxylation. Figure 5D presents the FT-IR spectrum of o-PMAHE-2. After osmylation, peaks a and a′ (Figure 5B) due to the conjugated diene C═C double bond of poly(MAHE) disappeared, and a strong, broad band, D-c, corresponding to the hydroxyl groups emerged. For the osmylated block copolymers, similar NMR and FT-IR results were obtained.

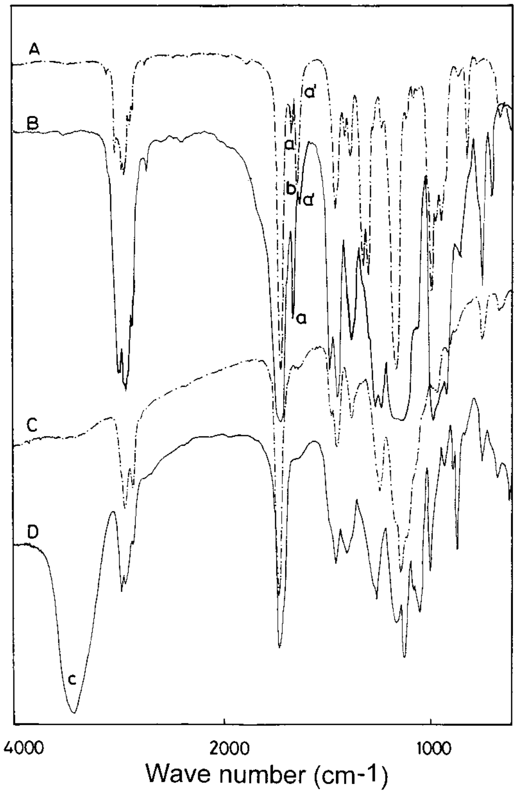


Figure 5. FT-IR spectra of MAHE (A), PMAHE-2 (B; Table 1), and its brominated (C; Table 5) and osmylated (D; Table 6) products.

As shown in Table 7, the elemental analysis results of homopoly(MAHE) and its osmylated product are consistent with the calculated values. The calculations indicated that each repeating unit of poly(THHMA) contained 0.2 water molecule. On the other hand, even though a nitrogen-containing compound, NMO, was employed in the osmylation process, the elemental analysis did not indicate the presence of nitrogen in the resulting polymer. Consequently, the reagents were completely removed during the purification process, and a very pure poly(THHMA) was obtained. The combination of ^{1}H NMR, FT-IR, and the elemental analysis clearly indicates that this osmylation procedure is not only suitable for single C═C bond-containing polymer but also suitable for the polymers with conjugated diene side groups.

Solubility. Poly(MAHE) and its osmylated product poly(THHMA) exhibit different solubilities. For instance, as shown in Table 8, PMAHE-3 is soluble in benzene, chloroform, DMF, pyridine, 1,4-dioxane, THF, and acetone but insoluble in ethanol, methanol, and water. For poly(THHMA) (o-PMAHE-3 in Table 8), water became the best solvent, and the dissolution was completed in only a few seconds. Ethanol and methanol are poor solvents because their polarity is less than that of water. Poly(THHMA) is insoluble in ethanol and can only partially dissolve in methanol at room temperature, although heating can accelerate its dissolution rate. For comparison, solubility experiments for poly(HEMA) and poly(DHPMA) were also carried out. Compared to the four hydroxyl groups in each repeating unit of poly(THHMA), poly(HEMA) and poly(DHPMA) possess only one and two hydroxyl groups in each of their repeating units, respectively. As shown in Table 8, poly(HEMA) is soluble in ethanol and methanol but insoluble in water. While poly(DHPMA) is insoluble in ethanol, methanol is its best solvent and it can dissolve slowly in water. It is clear that the hydrophilicity of the polymers increases as the hydroxyl number in the side chain increases, and poly(THHMA) possesses the highest water solubility. In addition, as shown in Table 8, the osmylated block copolymers possess quite different solubilities compared to those of their precursors. They are soluble only in DMF and pyridine and become swollen in water.

Conclusion

The new bifunctional monomer, *trans*,*trans*-1-methacryloyloxy-2,4-hexadiene (MAHE), underwent selective living anionic polymerization without cross-linking and any other side reaction, generating a monodisperse polymer ($M_w/M_n = 1.04-1.05$) with a well-controlled molecular weight. The 2,4-hexadienyl side groups of the resulting polymer could further react with bromine. This bromination introduced four bromine atoms into each of the repeating units of poly(MAHE). The diene side groups of poly(MAHE) could also react with *N*-methylmorpholine *N*-oxide in the presence of a trace amount of osmium tetroxide as catalyst. This osmylation changed poly(MAHE) to a new functional polymer, poly(2,3,4,5-tetrahydroxyhexyl methacrylate), which possessed extremely high water solubility because of the presence of four hydroxyl groups in each of its repeating units. Under suitable conditions, well-defined block and random copolymers of MAHE with MMA and the block copolymer of MAHE with St were also prepared. These copolymers possessed controlled molecular weights and compositions as well as monodispersity. The osmylation after the block copolymerization generated well-defined novel amphiphilic block copolymers.

References and Notes

(1) (a) Green, J. *J. Fire Sci.* **1996**, *14*, 426. (b) Camps, M.; Jebri, A.; Dronet, J. C. *J. Fire Sci.* **1996**, *14*, 251.

(2) (a) Hirao, A.; Kata, H.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1986**, *19*, 1294. (b) Ruckenstein, E.; Zhang, H. M. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 1865.

(3) (a) Mori, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 35. (b) Zhang, H. M.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 4738.

(4) (a) Noshay, 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) Morton, M. *Anionic Polymerization: Principle and Practice*; Academic Press: New York, 1983. (d) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996.

(5) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442.

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

(7) (a) Schulz, G.; Hocher, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 219. (b) Ruckenstein, E.; Zhang, H. M. *Macromolecules* **1998**, *31*, 9127.

(8) For examples: (a) Kobatake, S.; Harword, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1999**, *32*, 10. (b) Pispas, S.; Allorio, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 2903.

(9) Vollhardt, K. P. C.; Schore, N. E. *Organic Chemistry*; Freeman, W. H. and Company: New York, 1994; p 515.

(10) (a) Diels, O.; Alder, K. *Ann.* **1928**, *460*, 98. (b) Diels, O.; Alder, K. *Ber.* **1929**, *62*, 2081. (c) Solomons, T. W. G. *Organic Chemistry*; John Wiley & Sons: New York, 1992; p 501.

(11) (a) Mizawa, T.; Takenaka, K.; Shiomi, T. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 3464. (b) Mizawa, T.; Takenaka, K.; Shiomi, T. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 237.

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