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A Novel Successive Route to Well-Defined Water-Soluble Poly(2,3-dihydroxypropyl methacrylate) and Amphiphilic Block Copolymers Based on an Osmylation Reaction

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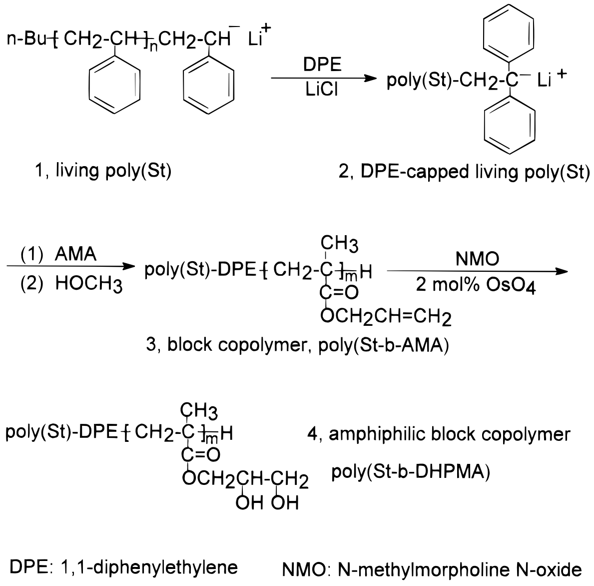
ABSTRACT: A novel two-step successive route to well-defined water-soluble poly(2,3-dihydroxypropyl methacrylate) [poly(DHPMA)] and the amphiphilic block copolymers of DHPMA with styrene (St) or methyl methacrylate (MMA) was developed by combining the living anionic polymerization method with an osmylation reaction. Homopolymers of allyl methacrylate (AMA) with various molecular weights (M_n = 5900−170 000) and narrow molecular weight distributions (MWD; M_w/M_n = 1.06−1.16) were first prepared by the anionic polymerization of AMA using 1,1-diphenylhexyllithium (DPHL) as the initiator, in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$), at −70 °C. Under similar conditions, the anionic block copolymerization of AMA with MMA generated well-defined di- and triblock copolymers with controlled molecular weights and compositions as well as narrow MWDs (M_w/M_n = 1.05−1.16). Further, block copolymers of St and AMA with various compositions were prepared by performing the anionic block copolymerization of AMA from a 1,1-diphenylethylene-capped anionic living poly(St). In both the homopolymerization of AMA and its block copolymerization with MMA or St, its allyl side group remained unreacted. Without the (co)polymer separation from the (co)polymerization solution, the allyl groups of the (co)polymer were directly reacted with an excess of *N*-methylmorpholine *N*-oxide (NMO), in the presence of a small amount of osmium tetroxide as catalyst, at room temperature. This osmylation procedure changed the poly(AMA) component to poly(DHPMA). During this process, no cross-linking or polymer chain damage occurred, and well-defined water-soluble poly(DHPMA) and amphiphilic block copolymers were obtained. The molecular weight, molecular architecture, and the copolymer composition affect the hydrophilicities of the osmylated (co)polymers, and all these factors can be accurately controlled during the (co)polymerization step.

Introduction

A number of amphiphilic block copolymers have been prepared via the living anionic polymerization technique.[1] In these copolymers, poly(methacrylic acid) and poly(2-hydroxyethyl methacrylate) [poly(HEMA)] were most usually used as hydrophilic segments,[2] although they are not water-soluble. Mori et al.[3] reported an anionic synthetic method of poly(2,3-dihydroxypropyl methacrylate) [poly(DHPMA)] using a three-step approach. First, a protected monomer, (2,2-dimethyl-1,3-dioxalan-4-yl)methyl methacrylate, was prepared through the reaction between isopropylidene glycerol and methacryloyl chloride. Then, the protected monomer was subjected to anionic polymerization. Finally, the acetal protecting group was eliminated by hydrolysis to obtain poly(DHPMA). Compared to poly(HEMA), poly(DHPMA) is more hydrophilic and even water-soluble, because of the presence of two hydroxyl groups in each of its repeating units. In addition, the block copolymer containing poly(DHPMA) as hydrophilic segment exhibits interesting surface properties.[3b]

Scheme 1



In the present paper, a more convenient and successive route to well-defined poly(DHPMA) and further to several kinds of amphiphilic block copolymers containing poly(DHPMA) hydrophilic segments was developed. As an example, the approach to the amphiphilic block copolymer consisting of polystyrene [poly(St)] and poly(DHPMA) is presented in Scheme 1. The anionic living poly(St) was reacted with 1,1-diphenylethylene (DPE) to obtain a DPE-capped living poly(St) (**2** in Scheme 1), from which the anionic block copolymerization of allyl methacrylate (AMA) was performed, generating a block copolymer, poly(St-*b*-AMA) (**3** in Scheme 1). During this process, the allyl side group of AMA remained unreacted. Without polymer separation from the polymerization solution, the allyl side groups were directly reacted with *N*-methylmorpholine *N*-oxide (NMO) in the presence of a trace amount of osmium tetroxide. This

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osmylation changed the poly(AMA) segment to poly(DHPMA), and an amphiphilic block copolymer, poly(St-*b*-DHPMA) (**4** in Scheme 1), was thus obtained. This osmylation process was also applied to homopoly(AMA), and in this case, a well-defined water-soluble poly(DHPMA) was prepared. Furthermore, the block copolymerization of AMA and MMA, followed by the successive osmylation, generated several di- and triblock amphiphilic copolymers, such as poly(DHPMA-*b*-MMA), poly(MMA-*b*-DHPMA-*b*-MMA), and poly(DHPMA-*b*-MMA-*b*-DHPMA). This (co)polymer synthetic route has the following advantages: (i) all the monomers employed are commercially available; (ii) only two synthetic steps are involved and can be performed successively; (iii) this is a general method which is expected to be suitable for a number of polymers containing C═C bonds in their side groups, such as 1,2-poly(butadiene),[4] poly[4-(vinylphenyl)-1-butene],[5] etc.

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%) and allyl methacrylate (AMA; Aldrich, 98%) were dried over CaH_2 with magnetic stirring under reduced pressure, vacuum distilled over CaH_2, and finally distilled in the presence of Al(*sec*-Bu)$_3$.[6] Styrene (St; 99%, Aldrich) was washed with 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.[7] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane. Osmium tetroxide (Aldrich, 2.5 wt % in 2-methyl-2-propanol), *N*-methylmorpholine *N*-oxide (NMO; Aldrich, 97%), and benzoic anhydride (Aldrich, 90%) were used as received.

Polymerization. All polymerizations, namely, the anionic homopolymerization of AMA and its block copolymerization with MMA or St, were carried out in a round-bottom flask under an overpressure of argon with magnetic stirring.

The anionic homopolymerization of AMA was performed in THF, at −70 °C, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$).[8] Before 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 20 min. Then, the system was cooled to −70 °C, and the polymerization reaction was induced by the addition of prechilled AMA to the above system. One hour later, the polymerization system was quenched with a small amount of methanol (ca. 1 mL). After a certain amount of the polymerization solution was taken out and was directly subjected to the osmylation reaction, the remaining part of the polymerization solution was poured into a mixture of water and methanol (4:1 by volume) to precipitate the polymer. The polymer was washed with methanol, vacuum-dried overnight at 40 °C, and finally freeze-dried from its benzene solution.

The anionic block copolymerization of AMA and MMA was carried out by using the monomer addition sequence of AMA followed by MMA, or vice versa, in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$), at −70 °C. For the preparation of triblock copolymers of AMA and MMA, a three-step sequential monomer addition, namely, AMA → MMA → AMA or MMA → AMA → MMA, was adopted. The polymerization times for MMA and AMA were 40 and 60 min, respectively. The initiator preparation and the polymer purification were performed in the ways similar to those employed for the homopolymer of AMA.

The block copolymer of AMA and St was prepared using a polymerization sequence of St, followed by AMA. The living poly(St) was first prepared by the anionic polymerization of St, which was carried out in a mixture of toluene and THF (1:1 by volume), at −60 °C, using *n*-BuLi as the initiator. After toluene, THF, and a hexane solution of *n*-BuLi were introduced into a flask kept at −60 °C, the polymerization was started by adding prechilled St to the above system. While the polymerization was proceeding, a certain amount of THF, DPE ($mol_{DPE}/mol_{n-BuLi} = 1.2$), 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, the prechilled AMA was added, and its polymerization lasted 1 h. After the termination with methanol (ca. 1 mL), a fraction of the polymerization solution was directly subjected to osmylation. For the remaining part, the precipitation and purification of the polymer were carried out in the ways similar to those for homopoly(AMA).

Osmylation. The osmylation reactions of the homopolymer of AMA and of its block copolymer with MMA or St were carried out with magnetic stirring, under the protection of nitrogen, at room temperature, for 24 h. Upon the (co)polymerization, a solution containing a certain amount of (co)polymer was transferred into a nitrogen-protected flask, to which acetone, methanol, water, and NMO (solid) were sequentially added. Then, the system was degassed and reprotected with nitrogen, and the reaction was started by adding osmium tetroxide (2.5 wt % solution in 2-methyl-2-propanol) with a syringe. As the reaction was proceeding, the system became turbid gradually. To keep the reaction proceeding homogeneously, a small amount of methanol was added. After 24 h, the resulting (co)polymer was precipitated by pouring the reaction solution into a mixture of hexane and ethanol (1:1 by volume). The (co)polymer was kept in this 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 methanol.

Reprotection of the Hydroxylated (Co)polymer. To verify by GPC whether the osmylation affected the main chain structures of the (co)polymers and/or whether the cross-linking occurred during the process, the osmylated products were reprotected by reacting the formed hydroxyl groups with benzoic anhydride. A small amount of osmylated PAMA-2 (Table 1; 0.35 g) was dissolved in 12 mL of pyridine, to which 4.2 g of benzoic anhydride was added, and the reaction was allowed to last 24 h at room temperature. Then, the polymer was precipitated into methanol, washed with methanol, and vacuum-dried overnight.

Measurements. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_3OD, or a mixture of CD_3OD with THF-d_8 on an Inova-500 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 tablets on a Perkin-Elmer 1760-X spectrometer. The elemental analysis was carried out by Atlantic Microlab, Inc.

Results and Discussion

Anionic Homopolymerization of AMA and Its Block Copolymerization with MMA. The anionic

Table 1. Anionic Homopolymerization of AMA[a]

	$[\mathrm{DPHL}]_0$ (mM)	$[\mathrm{AMA}]_0$ (M)	$10^{-4}M_n$ calcd	$10^{-4}M_n$ obsd[b]	M_w/M_n[b]
PAMA-1	15.7	0.660	0.55	0.59	1.12
PAMA-2	10.0	0.794	1.02	0.98	1.06
PAMA-3	2.8	0.743	3.34	3.78	1.08
PAMA-4	0.7	0.743	13.4	17.0	1.16

[a] The polymerization was carried out in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −70 °C, for 1 h. The monomer conversion was 100% in each case. [b] Determined by GPC.

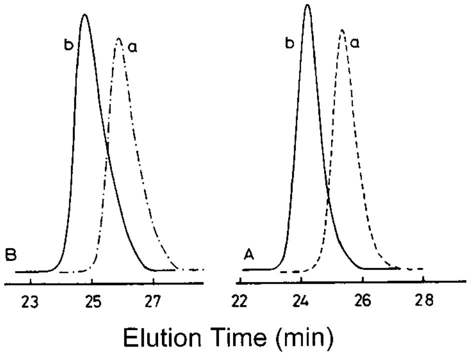


Figure 1. GPC traces of diblock copolymers and their precursors. A-a: living poly(AMA) (see AbM-1 in Table 2, $M_n = 11\,200$, $M_w/M_n = 1.06$). A-b: block copolymer, poly(AMA-*b*-MMA) (AbM-1 in Table 2, $M_n = 22\,300$, $M_w/M_n = 1.05$) obtained via the successive anionic polymerization of MMA from A-a. B-a: living poly(St) (see SbA-1 in Table 4, $M_n = 6800$, $M_w/M_n = 1.07$). B-b: block copolymer, poly(St-*b*-AMA) (see SbA-1 in Table 4, $M_n = 14\,100$, $M_w/M_n = 1.09$) obtained via the anionic polymerization of AMA from B-a.

homopolymerization of AMA has been systematically investigated in a previous paper.[8] Using the bulky DPHL as initiator, in the presence of LiCl, in THF, at a low temperature (−30 to −70 °C), AMA could undergo living anionic polymerization smoothly, generating a uniform size functional polymer with a reactive allyl group in each repeating unit. To investigate the effect of molecular weight on the hydrophilicity of the osmylated poly(AMA), in the present paper, several homopolymers of AMA with different molecular weights ($M_n = 6000-170\,000$) were prepared using DPHL as the initiator, in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −70 °C. As shown in Table 1, the monomer conversion was 100% in each case, the molecular weight was well-controlled, and the molecular weight distribution (MWD) was very narrow ($M_w/M_n = 1.06-1.16$).

The di- and triblock copolymers of AMA and MMA were prepared under conditions similar to those for homopoly(AMA). For diblock copolymers, a two-step sequential monomer addition, namely, MMA followed by AMA, 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 was very narrow ($M_w/M_n = 1.05-1.12$), and the composition determined by ^{1}H NMR was in good agreement with that designed. As an example, Figure 1A presents the GPC chromatograms of poly(AMA-*b*-MMA) (peak A-b; AbM-1 in Table 2) and of its precursor [peak A-a; poly(AMA), $M_n = 11\,200$, $M_w/M_n = 1.06$]. After the second step polymerization of MMA from the living end of poly(AMA), the M_n was almost doubly increased ($M_n = 22\,300$, $M_w/M_n = 1.05$), while the MWD remained very narrow. The above results confirmed the living nature of the anionic polymerization of AMA.

To investigate the effects of molecular architectures of the block copolymers on the hydrophilicities of their osmylated products, ABA and BAB type triblock copolymers of AMA and MMA were also prepared using a three-step sequential anionic polymerization technique. As shown in Table 3, the weight ratios of AMA and MMA for both MbAbM and AbMbA were designed to be $W_{\mathrm{AMA}}/W_{\mathrm{MMA}} = 50/50$. However, the former triblock copolymer possesses one poly(AMA) segment in the middle of the polymer chain. On the other hand, the latter triblock copolymer has two poly(AMA) segments at the two ends of the polymer chain. Therefore, after osmylation, the hydrophilic poly(DHPMA) segments will be located in different places, and this might have a contribution to their hydrophilicities. As shown in Table 3 and Figure 2, despite a three-step polymerization

Table 2. Preparation of Diblock Copolymers of AMA (A) and MMA (M) via Their Anionic Copolymerization[a]

					first step			second step				
	polymerization sequence	$[\mathrm{DPHL}]_0$ (mM)	$[\mathrm{M}_1]_0$ (M)	$[\mathrm{M}_2]_0$ (M)	$10^{-4}M_n$ calcd	$10^{-4}M_n$ obsd[b]	M_w/M_n[b]	$10^{-4}M_n$ calcd	$10^{-4}M_n$ obsd[b]	M_w/M_n[b]	$W_{\mathrm{AMA}}/W_{\mathrm{MMA}}$[c] calcd	$W_{\mathrm{AMA}}/W_{\mathrm{MMA}}$[c] obsd[d]
MbA-1	MMA → AMA	5.00	0.500	0.400	1.02	1.04	1.05	2.03	2.23	1.06	50/50	47/53
MbA-2	MMA → AMA	5.00	0.330	0.530	0.68	0.72	1.08	2.06	2.39	1.11	67/33	66/34
AbM-1	AMA → MMA	5.00	0.400	0.500	1.03	1.12	1.06	2.03	2.23	1.05	50/50	49/51
AbM-2	AMA → MMA	4.00	0.270	0.670	0.87	0.93	1.07	2.55	2.88	1.12	33/67	35/65

[a] The copolymerization was carried out by means of a sequential monomer addition of MMA followed by AMA, or vice versa, in THF, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −70 °C. The polymerization times for MMA and AMA were 40 and 60 min, respectively. The polymer yield was quantitative in each case. [b] Determined by GPC. [c] The weight ratio of AMA and MMA segments in the resulting copolymer. [d] Determined by ^{1}H NMR.

Table 3. Preparation of ABA and BAB Triblock Copolymers of AMA and MMA by A Three-Step Sequential Anionic Copolymerization of the Two Monomers[a]

	polymerization sequence (weight, g)[b]	DPHL (mmol)	$10^{-4}M_n$ calcd	$10^{-4}M_n$ obsd[c]	M_w/M_n[c]	$W_{\mathrm{AMA}}/W_{\mathrm{MMA}}$[d] calcd	$W_{\mathrm{AMA}}/W_{\mathrm{MMA}}$[d] obsd[e]
MbAbM	MMA(2.0) → AMA(4.0) → MMA(2.0)	0.35	2.31	2.54	1.16	50/50	50/50
AbMbA	AMA(2.0) → MMA(4.0) → AMA(2.0)	0.30	2.69	2.92	1.14	50/50	48/52

[a] The anionic copolymerization was carried out using a three-step sequential monomer addition, in THF, in the presence of LiCl ($\mathrm{mol}_{\mathrm{LiCl}}/\mathrm{mol}_{\mathrm{DPHL}} = 3$), at −70 °C. The total volume of the polymerization system was 60 mL. The polymerization times for MMA and AMA were 40 and 60 min, respectively. The copolymer yield was 100% in each case. [b] The data in the parentheses are the weights of monomers added to the polymerization system sequentially. [c] Determined by GPC. [d] The weight ratio of AMA and MMA segments in the resulting copolymer. [e] Determined by ^{1}H NMR.

Table 4. Preparation of Diblock Copolymers of St (S) and AMA (A) via Their Anionic Copolymerization

	living poly(St)[a]					block copolymer[b]					W_{St}/W_{AMA}[d]	
	$[n\text{-BuLi}]_0$ (mM)	$[St]_0$ (M)	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[c]	M_w/M_n[c]	$[\text{living PSt}]_0$ (mM)	$[AMA]_0$ (M)	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[c]	M_w/M_n[c]	calcd	obsd[e]
SbA-1	15.0	0.962	6.73	6.80	1.07	7.50	0.400	13.5	14.1	1.09	50/50	51/49
SbA-2	20.0	0.641	3.39	4.15	1.12	8.57	0.680	13.4	13.8	1.13	25/75	26/74
SbA-3	12.0	1.15	10.0	10.7	1.08	7.50	0.200	13.4	13.5	1.09	75/25	77/23
SbA-4	7.5	0.962	13.4	15.0	1.09	3.75	0.400	26.8	29.0	1.10	50/50	52/48

[a] The living poly(St) was first prepared by the anionic polymerization of St, which was carried out in a mixture of toluene and THF (1:1 by volume), at −60 °C, for 1 h. [b] After the polymerization of St, a THF solution of DPE ($[DPE]/[\text{living PSt}]_0 = 1.2$) and LiCl ($[LiCl]/[\text{living PSt}]_0 = 3$) was added. The living end of poly(St) was reacted with DPE for 20 min at −60 °C, and this was followed by the introduction of AMA. The polymerization of AMA lasted 1 h. The copolymer yield was 100% in each case. [c] Determined by GPC. [d] The weight ratio of St and AMA segments in the copolymer. [e] Determined by ^1H NMR.

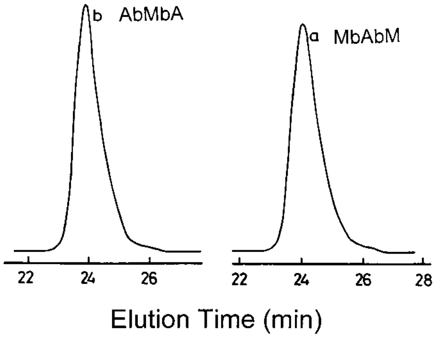
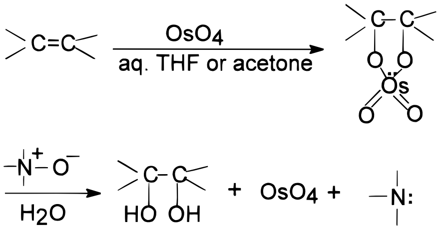


Figure 2. GPC traces of triblock copolymers: (a) poly(MMA-*b*-AMA-*b*-MMA) (MbAbM in Table 3, $M_n = 25\,400$, $M_w/M_n = 1.16$). (b) poly(AMA-*b*-MMA-*b*-AMA) (AbMbA in Table 3, $M_n = 29\,200$, $M_w/M_n = 1.14$).

procedure, the block copolymers thus obtained were almost free of their precursors, the molecular weights and compositions were well-controlled, and their MWDs were narrow ($M_w/M_n = 1.14-1.16$).

Anionic Block Copolymerization of St and AMA. A block copolymer of St and AMA was prepared using the polymerization sequence of St followed by AMA. The anionic polymerization of St was carried out in a mixture of toluene and THF (1:1 by volume), at −60 °C, for 1 h. However, the second step living polymerization of AMA proceeded better in a polar solvent (THF) and in the presence of LiCl.[8] In addition, the living site of poly(St) is too reactive and may attack the ester group of AMA, causing unwanted side reactions. Considering the above factors, a THF solution of LiCl ($\text{mol}_{LiCl}/\text{mol}_{n-BuLi} = 3$) and of DPE ($\text{mol}_{DPE}/\text{mol}_{n-BuLi} = 1.2$) was added after the anionic polymerization of St. A rapid addition reaction between the living site of poly(St) and DPE occurred, generating a DPE-capped living poly(St) containing a bulkier and less reactive end carbanion (**2** in Scheme 1), whose structure is similar to that of DPHL.[9] Subsequently, the anionic polymerization of AMA proceeded from the living site of the DPE-capped poly(St) by adding AMA to the above system. As shown in Figure 1B and Table 4 (SbA-1), a new single peak (B-b) corresponding to the block copolymer appeared in the higher molecular weight side after the polymerization of AMA, and the peak (B-a) of its living poly(St) precursor ($M_n = 6800$, $M_w/M_n = 1.07$) disappeared. The molecular weight of the block copolymer ($M_n = 14\,100$, $M_w/M_n = 1.09$) is about twice as large as that of poly(St) and almost equal to the designed value, and the MWD is almost as narrow as that of its precursor. Consequently, a pure diblock copolymer, poly(St-*b*-AMA), free of homopolymers, was obtained. In addition, the weight ratios of St and AMA segments in the block copolymers determined by ^1H NMR were very close to the feed amount ratios of the two monomers (Table 4).

Scheme 2



Osmylation of (Co)polymers. As well-known, the reaction of small olefin molecules with osmium tetroxide has been the most reliable method for cis-dihydroxylation of the C═C bond.[10] However, when OsO_4 is used stoichiometrically, its high cost greatly limits its application in organic synthesis. In addition, the tedious separation of the main product from the byproducts is also a shortcoming of this reaction. VanRheenen et al.[11] improved the osmylation process by combining osmium tetroxide with a tertiary amine *N*-oxide, such as *N*-methylmorpholine *N*-oxide (NMO) (Scheme 2). Using this method, the amount of OsO_4 can be reduced to 1 mol % compared to the molar amount of C═C bonds.

In the present paper, this osmylation process was applied to the dihydroxylation of homopoly(AMA) and the block copolymer of AMA with MMA or St, with the goal to prepare well-defined water-soluble poly(DHPMA) and hydrophilic−hydrophobic block copolymers.

The osmylation was carried out with magnetic stirring, under the protection of nitrogen, at room temperature, for 24 h. Because the homopolymerization and block copolymerization were carried out in THF, the polymerization solution was directly subjected to osmylation without polymer separation. As shown in Table 5, to a certain amount of polymerization solution, acetone, methanol, water, and NMO were sequentially added under the protection of nitrogen. The methanol was needed to dissolve the solid NMO. For the regeneration of OsO_4, a small amount of water was necessary (Scheme 2). In addition, the presence of acetone increased the compatibility between methanol, water, THF, and toluene. Compared to the molar amount of C═C bonds, an excess of NMO ($\text{mol}_{NMO}/\text{mol}_{C=C} = 1.2-1.5$) and a small amount of OsO_4 ($\text{mol}_{OsO_4}/\text{mol}_{C=C} = 2/100$) were employed. As soon as the alcohol solution of OsO_4 was introduced into the above system, a light-red color appeared at once, indicating a rapid formation of a complex between the C═C bond and OsO_4 (Scheme 2). As the reaction proceeded, the system became gradually turbid, indicating that the osmylated product has a different solubility than its precursor. To keep the reaction proceeding homogeneously, methanol was dropwise added during the osmylation process. About 24 h later, the resulting polymer was precipitated by pouring

Table 5. Osmylation of the Homopolymer of AMA and of Its Block Copolymer with MMA or St[a]

	(co)polymer[b] weight (g)	AMA (mmol)[c]	NMO (mmol)[d]	OsO_4[e] (mL)	solvents (by vol, mL)[f] THF/toluene/acetone/CH_3OH/H_2O	CH_3OH[g] (mL)	functionality[h] (%)
PAMA-1	0.50	4.0	5.6	0.8	5.5/0/2.0/2.0/0.5	0.5	100
PAMA-2	0.50	4.0	6.0	0.8	6.0/0/4.0/2.0/0.5	1.0	100
PAMA-4	0.50	4.0	6.0	0.8	8.0/0/5.0/1.0/0.5	4.0	100
MbA-1	1.0	4.0	4.8	0.8	8.5/0/3.0/1.5/0.5	1.5	100
MbA-2	1.0	5.3	8.0	1.1	8.5/0/3.0/2.0/0.5	2.0	100
AbM-2	1.0	2.6	3.9	0.6	8.5/0/4.0/1.0/0.5	0.5	100
MbAbM	1.0	4.0	5.0	0.8	8.5/0/3.0/1.5/0.5	1.5	100
AbMbA	1.0	4.0	6.0	0.8	8.5/0/3.0/1.5/0.5	1.5	100
SbA-1	1.0	4.0	6.0	0.8	7.0/2.0/2.0/1.0/0.5	1.0	100
SbA-2	1.0	6.0	9.0	1.2	6.6/1.6/3.0/1.5/0.5	4.0	100
SbA-3	1.0	2.0	3.0	0.4	6.4/2.6/2.0/1.0/0.5	0.5	100
SbA-4	1.0	4.0	6.0	0.8	7.0/2.0/2.0/1.0/0.5	0.5	100

[a] The reaction was carried out with magnetic stirring, under the protection of nitrogen, at room temperature, for 24 h. 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 AMA component in the (co)polymer. [d] Molar amount of *N*-methylmorpholine *N*-oxide (NMO). [e] A 2.5 wt % solution in 2-methyl-2-propanol, which contained 2 mol % of OsO_4 compared to the molar amount of $C{=}C$ bonds in AMA segments, was employed. [f] To a polymerization solution, acetone, methanol, and water were sequentially added. [g] To keep the reaction proceeding homogeneously, methanol was dropwise added during the osmylation process. [h] Determined by ^1H NMR.

Table 6. Elemental Analyses of Poly(AMA) and Its Osmylated Product

		C (%)		H (%)		N (%)	
		theory	found	theory	found	theory	found
PAMA-2[a]	$C_7H_{10}O_2$	66.64	67.07	8.01	8.01		
o-PAMA-2[b]	$C_7H_{12}O_4 \cdot {}^1/_5H_2O$[c]	51.34	51.38	7.63	7.48	0.00	0.00

[a] See Table 1. [b] See Table 5. [c] Each repeating unit contains $^1/_5$ water molecule (see ref 3a).

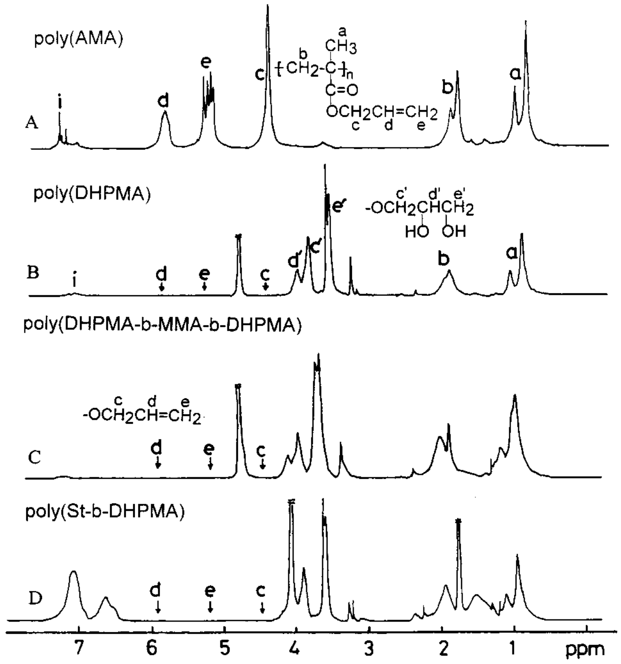


Figure 3. ^1H NMR spectra of PAMA-2 (A; in $CDCl_3$; Table 1, $M_n = 9800$, $M_w/M_n = 1.06$), osmylated PAMA-2 (B; in CD_3OD), osmylated triblock copolymer AbMbA [C; Table 3; in a mixture of CD_3OD and THF-d_8 (3:1 by weight)], and osmylated diblock copolymer SbA-1 (D; Table 4; in a mixture of CD_3OD and THF-d_8 (1:3 by weight)]. Peak i: phenyl groups of the initiator DPHL.

the reaction solution into a mixture of hexane and ethanol (1:1 by volume). The regenerated OsO_4, the excess of NMO, and the byproduct *N*-methylmorpholine were easily removed, because they are soluble in ethanol.

Figure 3A,B depicts the ^1H NMR spectra of poly(AMA) (PAMA-2 in Table 1) and of its osmylated product (Tables 5 and 6). After osmylation, the peaks c, d, and e corresponding to the allyl side groups of poly(AMA) disappeared completely, and the spectrum of the osmylated product became consistent with the molecular structure of poly(DHPMA). The osmylated homopolymer was also identified by ^{13}C NMR [o-PAMA-2 (Tables 5 and 6) in CD_3OD, δ 178.3, 178.1, 177.9 ($C{=}O$), 69.7, 66.3, 63.1 (CH_2CHCH_2), 54.7 (CH_2), 45.2, 44.9 ($-C-$), 18.6, 16.5 (CH_3)]. The complete disappearance of the absorptions (δ 131.8, 119.0, 65.8) due to the allyl group and the appearance of the absorptions (δ 69.7, 66.3, 63.1) corresponding to the dihydroxypropyl indicate that after osmylation a complete change from poly(AMA) to poly(DHPMA) took place.

The ^1H and ^{13}C NMR results are also supported by the FT-IR measurements. Parts A and B of Figure 4 present the FT-IR spectra of PAMA-2 and of its osmylated product, respectively. After osmylation, the peak A-a due to the $C{=}C$ double bond of poly(AMA) disappeared completely, and the two strong bands, B-b and B-c corresponding to the hydroxyl groups emerged. For the osmylated block copolymers, similar NMR and FT-IR results were obtained. Parts C and D of Figure 3 display the ^1H NMR spectra of the osmylated products of AbMbA and SbA-1, respectively. Obviously, the poly(AMA) segments were completely changed to the poly(DHPMA) ones. As shown in Figure 4C,D, the formation of the diol side groups in these block copolymers is confirmed by the appearance of the strong absorptions of C-b, C-c and D-b, D-c.

As shown in Table 6, the elemental analysis results of homopoly(AMA) and its osmylated product are consistent with the calculated values. The calculations have indicated that each repeating unit of poly(DHPMA) contained $^1/_5$ water molecule. It is of interest to notice that when poly(DHPMA) was prepared by polymerizing a protected monomer followed by deprotection,[3a] the same amount of water per repeating unit was found. On the other hand, even though a nitrogen-containing compound, NMO, was employed in the osmylation process, the elemental analysis did not indicate the

Table 7. Solubilities of the (Co)polymers before and after Osmylation[a]

no.[b]	hexane	Bz	$CHCl_3$	DMF	pyridine	1,4-dioxane	THF	acetone	C_2H_5OH	CH_3OH	H_2O
PAMA-2	I	S	S	S	S	S	S	S	I	I	I
o-PAMA-2	I	I	I	S	S	I	I	I	I	S	S
o-PAMA-1	I	I	I	S	S	I	I	I	I	S	S
o-PAMA-4	I	I	I	S	S	I	I	I	I	D	S
PHEMA[c]	I	I	I	S	S	I	I	I	S	S	I
MbA-1	I	S	S	S	S	S	S	S	I	I	I
o-MbA-1	I	I	SW	S	S	I	I	SW	I	S	SW
o-MbA-2	I	I	I	S	S	I	I	I	I	S	SW
o-AbM-2	I	I	SW	S	S	I	I	SW	I	S	SW
o-MbAbM	I	I	SW	S	S	I	I	I	I	D	SW
o-AbMbA	I	I	I	S	S	I	I	I	I	S	P
SbA-1	I	S	S	S	S	S	S	S	I	I	I
o-SbA-1	I	I	SW	S	S	D	S	SW	I	SW	SW
o-SbA-2	I	I	I	S	S	I	I	I	I	P	P
o-SbA-3	I	D	D	S	S	D	S	I	I	I	SW
o-SbA-4	I	SW	SW	S	S	SW	SW	I	I	SW	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; W = wetting; SW = swollen; I = insoluble. [b] o-: the (co)polymers after osmylation. [c] Poly(2-hydroxyethyl methacrylate) prepared in a previous paper.[2d]

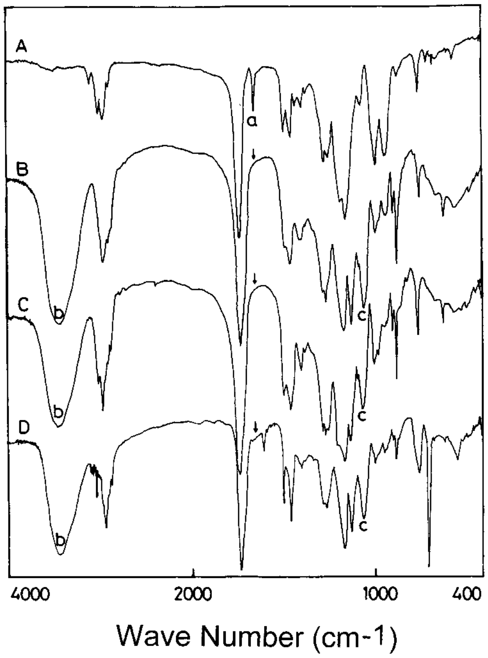


Figure 4. FT-IR spectra of PAMA-2 (A, Table 1) and of the osmylation products of PAMA-2 (B, Table 5), MbA-1 (C, Tables 2 and 5), and SbA-1 (D, Tables 4 and 5).

presence of nitrogen in the resulting polymer. Consequently, the reagents were completely removed during the purification process, and very pure poly(DHPMA) was obtained.

To verify by GPC whether cross-linking and/or chain damage occurred during osmylation, the dihydroxylate of poly(AMA) was reprotected by reacting the formed hydroxyl groups with benzoic anhydride (see Experimental Section). As shown in Figure 5b, the GPC chromatogram of the polymer thus obtained exhibits a single peak, and its MWD ($M_n = 20\,500$, $M_w/M_n = 1.08$) is as narrow as that of its precursor (PAMA-2 in Table 1, $M_n = 9800$, $M_w/M_n = 1.06$). Consequently, no cross-linking occurred during osmylation, and this process did not affect the chain structure of the polymer.

Solubilities of the (Co)polymers before and after Osmylation. The poly(AMA) and its osmylated product exhibit different solubilities. For instance, as shown in Table 7, PAMA-2 is soluble in benzene, chloroform, DMF, pyridine, 1,4-dioxane, THF, and acetone but insoluble in hexane, ethanol, methanol, and water. However, its osmylated product is soluble in DMF, pyridine, methanol, and water but insoluble in any of the other solvents. The molecular weight affects the solubility of the dihydroxylate of poly(AMA). When the molecular weight is small, such as PAMA-1 ($M_n = 5900$) and PAMA-2 ($M_n = 9800$), their osmylated products dissolved in methanol more rapidly than in water. However, the dissolution of dihydroxylate of PAMA-4, which has a large molecular weight ($M_n = 170\,000$), is much faster in water than in methanol. For comparison, solubility experiments for poly(HEMA) were also carried out. This polymer possesses only one hydroxyl in each of its repeating units. As shown in Table 7, in contrast to poly(DHPMA), it is soluble in ethanol and methanol but insoluble in water. As expected, the molecular architectures of the triblock copolymers, poly(DHPMA-*b*-MMA-*b*-DHPMA) and poly(MMA-*b*-DHPMA-*b*-MMA), affected their hydrophilicities. The former is completely soluble in methanol and partially soluble in water. In contrast, the latter triblock copolymer, which possesses a poly(DHPMA) hydrophilic segment in the middle of the polymer chain, is only swollen by water and dissolved very slowly in methanol. The composition of the block copolymers has also an effect on their solubility. For instance, o-SbA-1 ($W_{St}/W_{AMA} = 51/49$) is soluble in THF and 1,4-dioxane but only swollen in methanol and water; o-SbA-2 ($W_{St}/W_{AMA} = 26/74$) is partially soluble in water and methanol but insoluble in THF and 1,4-dioxane; o-SbA-3 ($W_{St}/W_{AMA} = 77/23$) is insoluble in polar solvents but soluble in benzene and $CHCl_3$. Consequently, the molecular weight,

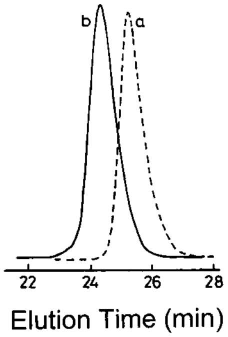


Figure 5. GPC traces of PAMA-2 (a; Table 1, $M_n = 9800$, $M_w/M_n = 1.06$) and of the reprotected product (b; $M_n = 20\,500$, $M_w/M_n = 1.08$) of its dihydroxylate.

molecular architecture, and the copolymer composition can affect the hydrophilicity of the osmylated (co)polymers, and all these factors can be accurately controlled in the (co)polymerization step.

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