Synthesis of Novel Amphiphilic and pH-Sensitive ABC Miktoarm Star Terpolymers

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ABSTRACT: Novel amphiphilic ABC miktoarm star terpolymers were synthesized that consist of hydrophilic poly(ethylene oxide) (PEO), hydrophobic poly(ϵ-caprolactone) (PCL), and pH-sensitive poly(2-vinylpyridine) (P2VP), thus a water-soluble block upon protonation. In the first step, poly(ethylene oxide monomethyl ether) (MPEO) was capped by one ω-epoxy end group by reaction of the original hydroxy end group with epichlorohydrin. MPEO-*b*-P2VP diblock copolymers were prepared by nucleophilic addition of living P2VP$^-$Li$^+$ chains onto the epoxy group of MPEO's. Finally, the hydroxy group formed at the junction of the MPEO and P2VP blocks was used to initiate the ring-opening polymerization of ϵ-caprolactone in the presence of tin octoate. The ABC star-shaped triblocks were characterized by ^{1}H NMR spectroscopy and size exclusion chromatography.

Introduction

Star-shaped copolymers with three or more arms, at least two of which are molecularly and chemically different, are called miktoarm star copolymers. In ABC miktoarm star terpolymers, three different polymer chains emanate from a central junction point. Steadily increasing attention is paid now to ABC miktoarm star terpolymers because of unique properties compared to the linear ABC triblock copolymers. For example, dramatic differences are observed in morphology[1−7] and solution properties,[7,8] including formation of novel multicompartment micelles.[9] Synthesis and properties of linear and nonlinear (miktoarm) ABC terpolymers were reviewed recently by Hadjichristidis et al.[7,10,11] Three synthetic methods have been devised to synthesize ABC miktoarm star terpolymers. The first strategy uses a multifunctional termination agent for living linear chains.[3,10,12−14] For example, Hadjichristidis and Iatrou[13] prepared an ABC miktoarm star terpolymer of polystyrene (PS), polybutadiene, and polyisoprene by the sequential deactivation of the parent anionically growing chains onto methyltrichlorosilane. Because the incorporation of a polymethacrylate block by this method was a problem, Sioula et al. added first living polyisoprene chains followed by living polystyrene chains to trichloromethylsilane (one type of polyanion per chloride). In the last step, they converted the third SiCl group to a sterically hindered anionic species, diphenylalkyl anion, that initiated the polymerization of a methacrylate with formation of the third arm.[12]

The second method relies on the 1,1-diphenylethylene (DPE) approach,[2,10,15−18] i.e., on the deactivation of a living macroanion onto the DPE (or 1,4-bis(1-phenylethenyl)benzene (DDPE)) end group of a second polymer, which results in the formation of a diblock with an anionic species at the junction point. Again the anionic polymerization of the third monomer was initiated from this central position. Similarly, Fujimoto et al.[16] synthesized ABC miktoarm star terpolymers of PS, polydimethysiloxane (PDMS), and poly(*tert*-butyl methacrylate) (P*t*BMA) by reaction of PS$^-$Li$^+$ with 1,1-diphenylethylene-terminated PDMS, followed by the anionic polymerization of *tert*-butyl methacrylate.

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The third method requires the use of a "bifunctional macroinitiator", i.e., a polymer chain capped at one chain-end by two functional groups able to initiate independently the polymerization of two distinct monomers. Lambert et al. prepared a bifunctional macroinitiator by end-capping a living polymer with 1,1-diphenylethylene bearing two different initiating groups.[19,20] ABC terpolymers of styrene, ethylene oxide, and methacrylic acid or ϵ-caprolactone were then synthesized by anionic polymerization. Pan et al. prepared a series of ABC miktoarm star terpolymers by combination of cationic ring-opening polymerization (CROP) and reversible addition−fragmentation transfer polymerization with a maleic anhydride linking agent.[21,22] Some of us developed an ABC star-shaped block terpolymer of poly(ethylene oxide), poly(benzyl β-malolactonate), and poly(ϵ-caprolactone), thus three biocompatible/bioresorbable arms.[23] Recently, ABC miktoarm star terpolymers were synthesized by using a trifunctional initiator that allowed three "living"/controlled polymerization techniques (ring-opening polymerization (ROP), atom transfer radical polymerization (ATRP), and nitroxide-mediated polymerization (NMP))[24] to be combined.

This paper reports the synthesis of novel amphiphilic pH-sensitive ABC miktoarm star that combined poly(ϵ-caprolactone) (PCL), poly(ethylene oxide) (PEO), and poly(2-vinylpyridine) (P2VP) blocks. To the best of our knowledge, this is the first time that these three blocks are combined together. The strategy to build this architecture (Scheme 1) was inspired by the second method (cf. supra). Living P2VP$^-$Li$^+$ macroanions were added to the epoxy end group of MPEO chains, with formation of a diblock copolymer, MPEO(OH)-*b*-P2VP, that contains a hydroxyl group at the junction point. ROP of ϵ-caprolactone was initiated by this hydroxyl mid-group in the presence of tin octoate to produce the expected [(MPEO)(P2VP)(PCL)] miktoarm star terpolymer.

Experimental Section

Materials. Poly(ethylene oxide monomethyl ether) (MPEO) (MPEO1: M_n = 2050, MWD = 1.05; MPEO2: M_n = 6050, MWD = 1.05) was purchased from Fluka. NaH (dry, 95%, Aldrich) was used without further purification. Epichlorohydrin (ECH) (99%, Janssen Chemical) and ϵ-caprolactone (99%, Aldrich) were purified by distillation from calcium hydride under reduced pressure. *tert*-Butyllithium (Aldrich, 1.7 M in pentane), tin 2-ethylhexanoate

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Scheme 1. Synthesis of the ABC Miktoarm Star Terpolymer

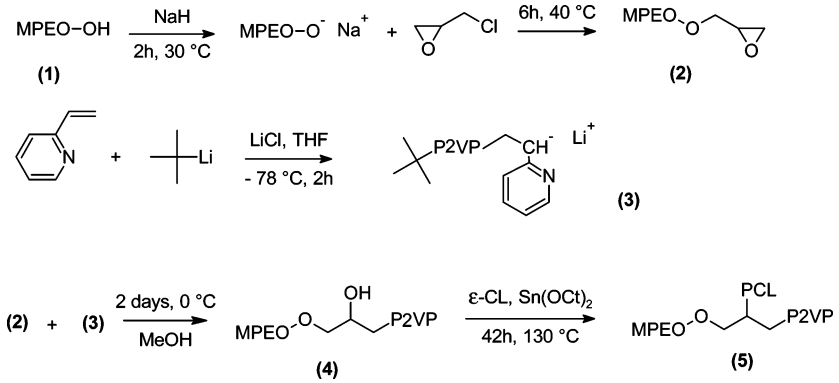

Table 1. Macromolecular Characteristics of the α-Methoxypoly(ethylene oxide) Chains (MPEO) and of the Poly(2-vinylpyridine) Chains (P2VP)[a]

no.	name	yield[b] (%)	M_n (NMR)[c]	M_w/M_n (SEC)[d]
1a	MPEO1		2050	1.10
2a	ω-epoxy-MPEO1	97	2250	1.05
1b	MPEO2		6050	1.05
2b	ω-epoxy-MPEO2	99	6200	1.05

no.	name	$[M]_0/[I]_0$	M_n(th)[e]	M_n (NMR)[f]	M_w/M_n (SEC)[d]
3a	P2VP1	14	1450	1750	*g*
3b	P2VP2	43	4500	3900	1.10
3c	P2VP3	57	6000	5200	1.10

[a] 2VP was polymerized in tetrahydrofuran at −78 °C, with *t*-BuLi as an initiator. [b] Yield was calculated by ^{1}H NMR spectroscopy from the relative intensity of peaks c and a (Figure 1). [c] M_n was calculated by ^{1}H NMR spectroscopy according to eq 1. [d] M_w/M_n was determined by SEC calibrated by PEO and P2VP standards. [e] $M_n(\text{th}) = ([M]_0/[I]_0) \times \text{conversion} \times 105$, where $[M]_0$ and $[I]_0$ are the initial molar concentrations of 2VP and *t*-BuLi, respectively; 105 is the molecular weight of 2VP. [f] M_n was calculated by ^{1}H NMR spectroscopy. $M_n(\text{NMR}) = [I_{8.3}/(I_{0.55}/9)] \times 105$, where $I_{8.3}$ and $I_{0.55}$ are the peak intensities at 8.3 ppm (P2VP) and 0.55 ppm (*t*Bu end group), respectively. [g] Inaccurate data.

($SnOct_2$, 95%, Aldrich, 0.06 M solution in toluene), and 1,1-diphenylethylene (97%, Aldrich, 0.76 M solution in toluene) were used as received. Lithium chloride (99.99%, Aldrich) was oven-dried at 300 °C for 30 min. 2-Vinylpyridine (97%, Aldrich) was purified by distillation first over calcium hydride and then over triethylaluminum. Toluene and tetrahydrofuran (THF) were distilled from sodium and sodium/ benzophenone purple complex, respectively. All other chemicals were used as received.

Synthesis of α-Methoxy-ω-epoxypoly(ethylene oxide) ((2) Scheme 1) (MPEO). MPEO (**1a**, in Table 1; 10 g, 5 mmol) was dissolved in 50 mL of anhydrous toluene and dried by azeotropic distillation of the solvent. The ω-hydroxy end group of MPEO was then converted into sodium alkoxide by reaction with sodium hydride (0.18 g, 7.5 mmol) at 30 °C for 2 h. ECH (1.6 mL, 20 mmol) was added to the solution and reacted at 40 °C for 6 h. The polymer was precipitated in diethyl ether, filtered off, washed with diethyl ether, dried, and redissolved in dichloromethane (200 mL). The CH_2Cl_2 solution was extracted twice with water, followed by drying over anhydrous magnesium sulfate, filtration, and elimination of dichloromethane. Yield = 97%, M_n(NMR) = 2250, M_w/M_n = 1.05. ^{1}H NMR, δ (TMS, ppm): 3.62 (m, 4H, OCH_2CH_2), 3.36 (t, 3H, OCH_3, terminal), 3.15 (m, 1H, $CHOCH_2$), 2.78 (d, 1H, CH_2-OCH), 2.59 (d, 1H, CH_2OCH).

Synthesis of Living Poly(2-vinylpyridine) ((3) Scheme 1). Dry THF (250 mL) and LiCl (1 g, 26 mmol) were added into a 500 mL one-neck round flask. After cooling to −78 °C, three drops of DPE (0.76 M) were added. Then, *tert*-butyllithium was added first dropwise until a permanent red color was observed, followed by rapid addition of 2 mL (3.4 mmol). Then, 2-vinylpyridine (**3a**, in Table 1; 5 mL, 46 mmol) was added, which resulted in a color change from bright red to dark red. After 2 h, an aliquot was analyzed by size exclusion chromatography. M_n(NMR) = 1750.

Table 2. Characteristics of the PEO−P2VP Diblocks and the ABC Miktoarm Terpolymers

no.	name	M_n(NMR) PEO-epoxide	M_n(NMR) P2VP⁻	M_n(th)[a]	M_n(NMR)[b]	M_w/M_n (SEC)[c]
4a	(MPEO1)(P2VP1)	2250	1750	4000	3990	1.10
4b	(MPEO2)(P2VP2)	6200	3900	10100	9750	1.05
4c	(MPEO2)(P2VP3)	6200	5200	11400	11850	1.05

no.	name	$[M]_0/[I]_0$	M_n(th)[d]	M_n(NMR)[b]	M_w/M_n (SEC)[c]
5a	(MPEO1)(P2VP1)(PCL1)	6	4700	4500	1.10
5b	(MPEO2)(P2VP2)(PCL2)	6	10450	10000	1.05
5c	(MPEO2)(P2VP3)(PCL3)	47	17200	19000	1.10

[a] $M_n(\text{th}) = M_{n,\omega-\text{epoxy}-\text{MPEO}} + M_{n,\text{P2VP}}$. [b] M_n was calculated by ^{1}H NMR spectroscopy according to eqs 2 and 3. [c] M_w/M_n was determined by SEC calibrated by PS standards. [d] $M_n(\text{th}) = (([M]_0/[I]_0) \times \text{conversion} \times 114) + 3990$ (or 9750 or 11850), where $[M]_0$ and $[I]_0$ are the initial molar concentrations of ϵ-Cl and MPEO(OH)-*b*-P2VP, respectively; 114, 3990, 9760, and 11830 are the molecular weights of ϵ-Cl, (MPEO1)(P2VP1), (MPEO2)(P2VP2), and (MPEO2)(P2VP3), respectively.

Synthesis of MPEO-*b*-P2VP Diblock Copolymer ((4) Scheme 1). α-Methoxy-ω-epoxy-PEO (**2a**, in Table 1; 5 g, M_n = 2250, 2.2 mmol) was dried by azeotropic distillation of toluene, dissolved in anhydrous THF (30 mL), and added to a solution of living $P2VP^-Li^+$ anions used in excess (**3a**, in Table 1; 3.3 mmol). The mixture was stirred at 0 °C for 2 days until a residual pale red color was observed. Residual anions were deactivated by degassed methanol, THF was removed with a rotary evaporator, and the solid residue was dissolved in aqueous HCl (10^{-2} M). This solution was dialyzed (porosity: 3500 Da) against HCl (10^{-2} M) for 10 h in order to remove the unreacted P2VP, followed by neutralization with a solution of NaOH (10^{-2} M) and lyophilization. The copolymer was dissolved in dichloromethane; the solution was twice extracted with water and dried over anhydrous magnesium sulfate. After filtration, dichloromethane was removed with a rotary evaporator. M_n(NMR) = 3990, M_w/M_n = 1.10. ^{1}H NMR, δ (TMS, ppm): 8.3 (m, 1H, CHNC), 7.3−6.3 (m, 3H, aromatic protons), 3.62 (m, 4H, OCH_2CH_2), 3.36 (t, 3H, OCH_3, terminal), 2.2−1.8 (m, 3H, CH_2CH), 0.55 (m, 9H, $(CH_3)_3C$, terminal). IR, υ (cm^{-1}): 3383 (OH, polymers junction), 1600−1430 (C=C and C=N, P2VP), 1100 (C−O−C, PEO).

Synthesis of ABC Miktoarm Star Terpolymer [(MPEO)-(P2VP)(PCL)] ((5) in Scheme 1). MPEO-*b*-P2VP (**4a**, in Table 2; 3.46 g, 0.86 mmol) was dissolved in dry toluene in a 50 mL dry glass reactor containing a magnetic bar. It was dried by azeotropic distillation of toluene, added with a solution of $SnOct_2$ in dry toluene (0.1 mL, 0.06 M), and heated in an oil bath at 130 °C under stirring for 10 min. ϵ-Caprolactone (0.55 mL, 4.9 mmol) was then added and reacted at 130 °C for 42 h. The reactor was cooled to room temperature, and one drop of acetic acid was added. The terpolymer was collected by precipitation in petroleum ether, filtration, and

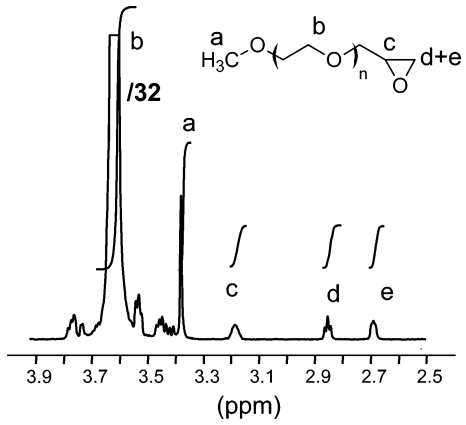

Figure 1. ^{1}H NMR spectrum of α-methoxy-ω-epoxypoly(ethylene oxide), sample **2a** in Table 1.

drying in vacuo overnight. M_n(NMR) = 4500, M_w/M_n = 1.10. ^{1}H NMR, δ (TMS, ppm): 8.3 (m, 1H, CHNC), 7.3−6.3 (m, 3H, aromatic protons), 4.02 (t, 2H, CH_2OCO), 3.62 (m, 4H, OCH_2-CH_2), 3.36 (t, 3H, OCH_3, terminal), 2.27 (t, 2H, CH_2COO), 2.2−1.3 (m, 3H, CH_2CH, t, 4H, CH_2), 0.55 (m, 9H, $(CH_3)_3C$, terminal).

Characterization Methods. ^{1}H NMR (400 MHz) spectra were recorded in $CDCl_3$ at 25 °C with a Bruker AM 400 apparatus. Size-exclusion chromatography (SEC) was carried out in dimethylformamide/LiBr at 55 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector (columns HP PL gel 5 μm (10^4, 10^3, 100 Å)) and calibrated with PS, P2VP, and PEO standards. The flow rate was 1 mL/min. FTIR analysis was carried out with a Bio-Rad Excalibur FTIR spectrometer (resolution: 0.2 cm^{-1}). Spectra were recorded (from 4000 to 700 cm^{-1}) with a single-reflection crystal system (Split PEA from Harrick) and a DTGS detector. Films of ω-epoxy-MPEO and PEO-*b*-P2VP (previously dried by azeotropic distillation of toluene and dissolved in dry dichloromethane) were solvent-cast onto a NaCl disk and analyzed with a Perkin-Elmer FTIR 1720x spectrometer.

Results and Discussion

End-Capping of α-Methoxy-PEO (MPEO) by an Epoxy Group ((2) Scheme 1). In the first step (Scheme 1), α-methoxy-PEO (MPEO) was end-capped by an epoxy group at the ω-position. For this purpose, the ω-hydroxyl end group of commercially available MPEO was metalated by sodium hydride and then reacted with epichlorohydrin as reported elsewhere by Ikeda et al.[25] Toluene was however used instead of THF to precipitate sodium chloride formed as a byproduct and to shift the reaction equilibrium toward the expected α-methoxy-ω-epoxy-PEO. Two MPEO samples of a different molecular weight (M_n = 2050 and 6050 g/mol) were epoxidized. Figure 1 shows the ^{1}H NMR spectrum for the lower M_n PEO after epoxidation and purification. The signals at δ = 3.15, 2.78, and 2.59 ppm were assigned to the protons of the epoxide end group, in agreement with the expected structure. The signal at 3.62 ppm is characteristic of the methylene protons of the ethylene oxide units, whereas the peak at 3.36 ppm is typical of the methyl α-end group. The epoxidation yield could be estimated from the relative integral value of the peaks c and a. This ratio was close to 1:3, consistent with a quasi-quantitative conversion of the hydroxyl end group of MPEO into an epoxy one (Table 1). M_n of the two α-methoxy-ω-epoxy-PEO samples (**2a** and **2b**, in Table 1) was calculated according to eq 1

$$M_n(\text{NMR}) = (3I_b/4I_a) \times 44 + 31 + 57 \qquad (1)$$

in which I_b and I_a are the integral values of the peaks at 3.62 ppm (PEO) and 3.36 ppm (methoxy end group), respectively,

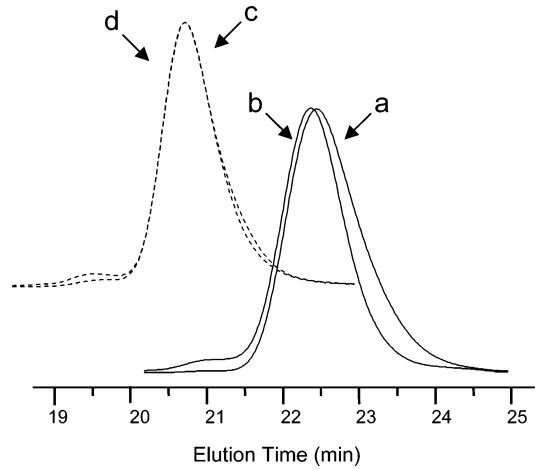

Figure 2. Size exclusion chromatography curves of (a) α-methoxy-ω-hydroxypoly(ethylene oxide) (**1a**, in Table 1), (b) α-methoxy-ω-epoxypoly(ethylene oxide) (**2a**, in Table 1), (c) α-methoxy-ω-hydroxypoly(ethylene oxide) (**1b**, in Table 1), and (d) α-methoxy-ω-epoxypoly(ethylene oxide) (**2b**, in Table 1).

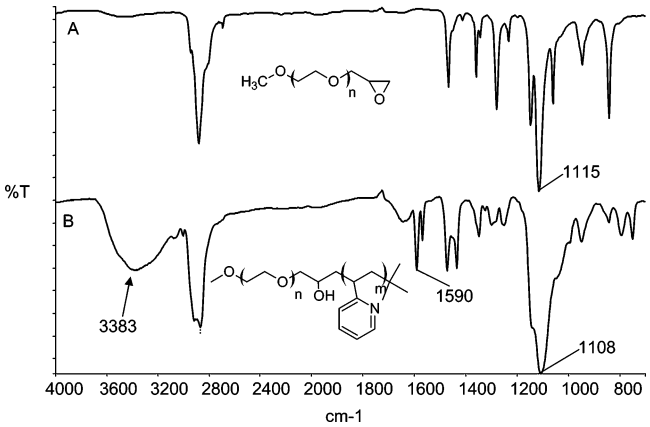

Figure 3. IR spectra of (A) α-methoxy-ω-epoxypoly(ethylene oxide) (**2a**, in Table 1) and (B) diblock copolymer (**4a**, in Table 2).

31, 57, and 44 being the molecular weight of the CH_3O-, $-CH_2-$epoxide, and $-CH_2-CH_2-O$ moieties, respectively. M_n of the original MPEO (**2a**, in Table 1) increased by ∼10% after epoxidation and purification, which indicates that the shorter MPEO chains were lost, as illustrated in Figure 2 (traces a and b) by the SEC curves before and after epoxidation.

Synthesis of Living Poly(2-vinylpyridine) Chains ((3) Scheme 1). 2-Vinylpyridine was anionically polymerized in THF at −78 °C, with *tert*-butyllithium as the initiator as reported elsewhere.[26,27] LiCl was added in order to decrease the reactivity of the active species and to restrict side reaction on the pyridine ring.[26,27] Data reported in Table 1 confirm that the polymerization is controlled, with a low polydispersity index and experimental molecular weight dictated by the monomer-to-initiator ratio and monomer conversion.

Synthesis of the MPEO-*b*-P2VP Diblock Copolymers ((4) Scheme 1). The living $P2VP^-Li^+$ chains were reacted with the α-methoxy-ω-epoxy-MPEO in order to prepare the MPEO-*b*-P2VP diblock. Simultaneously to this coupling reaction, a hydroxyl group is formed at the junction of the blocks. Figure 3 compares the IR spectra for the α-methoxy-ω-epoxy-PEO and the coupling product, which emphasizes the formation of a hydroxyl group at 3383 cm^{-1}. The experimental conditions and the molecular characteristics of the diblocks are listed in Table 2. SEC curves and a typical ^{1}H NMR spectrum are shown in Figures 4 and 5, respectively. Figure 4 compares the SEC traces

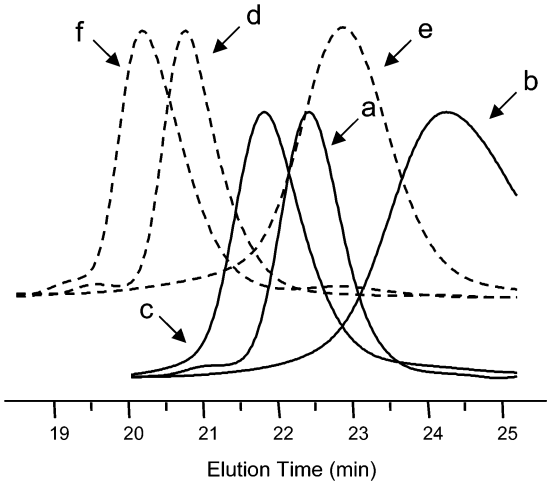

Figure 4. Size exclusion chromatography curves of (a) α-methoxy-ω-epoxypoly(ethylene oxide) (**2a**, in Table 1), (b) poly(2-vinylpyridine) (**3a**, in Table 1), (c) diblock copolymer (**4a**, in Table 2), (d) α-methoxy-ω-epoxypoly(ethylene oxide) (**2b**, in Table 1), (e) poly(2-vinylpyridine) (**3b**, in Table 1), and (f) diblock copolymer (**4b**, in Table 2).

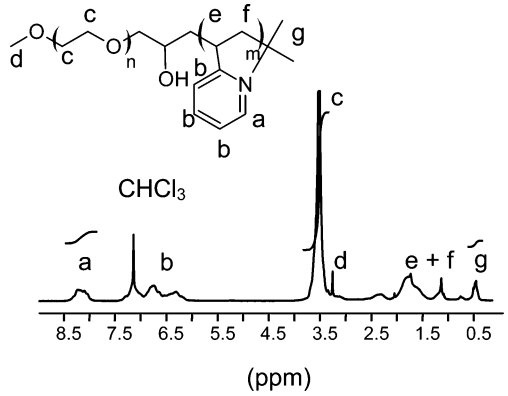

Figure 5. ^{1}H NMR spectrum of PEO−P2VP diblock copolymer, sample **4a** in Table 2.

for the mutually reactive polymers (MPEO and P2VP) and for the diblocks purified by dialysis. For each of the MPEO samples (M_n = 2050 and 6050), the reaction product clearly shifts toward shorter elution times compared to the constitutive homopolymers. It also appears that the excess of P2VP chains and unreacted PEO, if any, were eliminated by dialysis, leaving a diblock with high purity and low polydispersity (Table 2). The NMR spectrum for sample **4a** (Table 2) is shown in Figure 5 for the aromatic protons of the P2VP block in the 6.3−7.3 ppm range, except for the hydrogen atom adjacent to nitrogen which is observed at 8.3 ppm. Peaks at 3.62 and 3.36 ppm are characteristic of the inner methylene protons and the terminal methyl protons of the PEO block, respectively. The aliphatic protons of the P2VP block appear at 1.8−2.2 ppm, and the methyl protons of the *tert*-butyl end group of P2VP are observed at 0.55 ppm. M_n(NMR) of the MPEO-*b*-P2VP diblocks was calculated by eq 2 on the basis of M_n(NMR) of the PEO block

$$M_n(\mathrm{NMR})_{\mathrm{MPEO}-b-\mathrm{P2VP}} = (4I_a/I_c) \times \mathrm{DP}_{\mathrm{PEO}} \times 105 + M_{n,\mathrm{PEO}} \quad (2)$$

in which I_a and I_c are the integral values of the peaks at 8.3 and 3.62 ppm; $\mathrm{DP}_{\mathrm{PEO}}$ and $M_{n,\mathrm{PEO}}$ are the degree of polymerization and molecular weight of α-methoxy-ω-epoxy-MPEO determined by ^{1}H NMR spectroscopy (cf. supra), and 105 is the molecular weight of the 2VP monomer unit. These data are listed in Table 2. The good agreement between M_n(NMR) and M_n-(th) ($M_{n,\mathrm{MPEO}} + M_{n,\mathrm{P2VP}}$) is an additional evidence that the diblock copolymer was effectively rid of homopolymers, particularly the excess of P2VP. The coupling reaction was quasi-quantitative not only for low $M_{n,\mathrm{MPEO}}$ (∼2000) but also for the longer chains (∼6000).

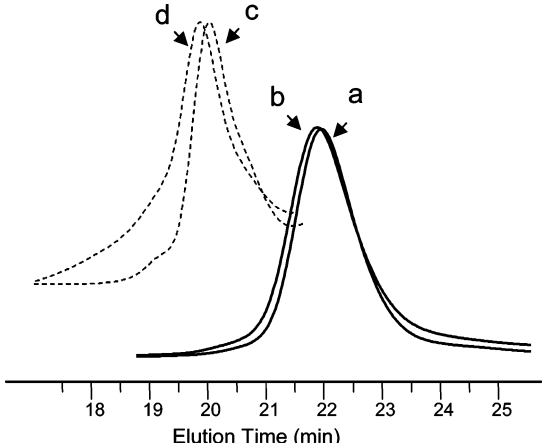

Figure 6. Size exclusion chromatography curves of (a) diblock copolymer (**4a**, in Table 2), (b) miktoarm terpolymer (**5a**, in Table 2), (c) diblock copolymer (**4c**, in Table 2), and (d) miktoarm terpolymer (**5c**, in Table 2).

Synthesis of the ABC Miktoarm Star Terpolymers ((5) Scheme 1). In the last step, the MPEO(OH)-*b*-P2VP diblock was used as a macroinitiator for the ring-opening polymerization of ϵ-CL, under the conditions listed in Table 2. This polymerization was closed to completeness. Figure 6a,b shows the SEC traces for the ABC miktoarm star terpolymer **5a** (Table 2) and its precursor. The SEC profiles are identical except for a shift toward lower elution volumes for the terpolymer compared to the diblock. This shift is however more important in the case of the triarm **5c** (Table 2) because DP of the PCL block (47) is higher (curves c and d, Figure 6), which confirms the success of the 3-arm terpolymer synthesis. M_n of the PCL block directly depends on M_n of MPEO in order to have an appropriate hydrophilic/lipophilic balance (HLB). The successful synthesis of the ABC miktoarm star terpolymers was confirmed by ^{1}H NMR analysis (Figure 7a,b). In addition to the peaks characteristic of the diblock copolymers, peaks typical of PCL are observed at 2.27 ppm (methylene protons adjacent to the carbonyl) and at 4.1 ppm (−CH_2−O protons). The signals for the other protons of the PCL block (h and i) and the aliphatic protons of the P2VP block overlap each other. On the assumption that each macromolecule contains one MPEO, one P2VP, and one PCL block, the number-average molecular weight of the ABC miktoarm star terpolymer should fit eq 3

$$M_n(\mathrm{NMR})_{(\mathrm{MPEO})(\mathrm{P2VP})(\mathrm{PCL})} = (4I_f/2I_d) \times \mathrm{DP}_{\mathrm{PEO}} \times 114 + M_{n,\mathrm{PEO}-b-\mathrm{P2VP}} \quad (3)$$

in which 114 is the molecular weight of the ϵ-CL monomer unit and I_f and I_d are the integral values of the peaks at 2.27 and 3.62 ppm, respectively. $\mathrm{DP}_{\mathrm{PEO}}$ and $M_{n,\mathrm{PEO}-b-\mathrm{P2VP}}$ are the degree of polymerization of α-methoxy-ω-epoxy-MPEO and the molecular weight of the PEO-*b*-P2VP diblock copolymer, respectively. The experimental molecular weights are reported in Table 2. Again, M_n(th) agrees well with M_n(NMR), which confirms that the expected ABC miktoarm star terpolymer was formed and that the polymerization of the third block from the junction of the PEO−P2VP diblocks was controlled.

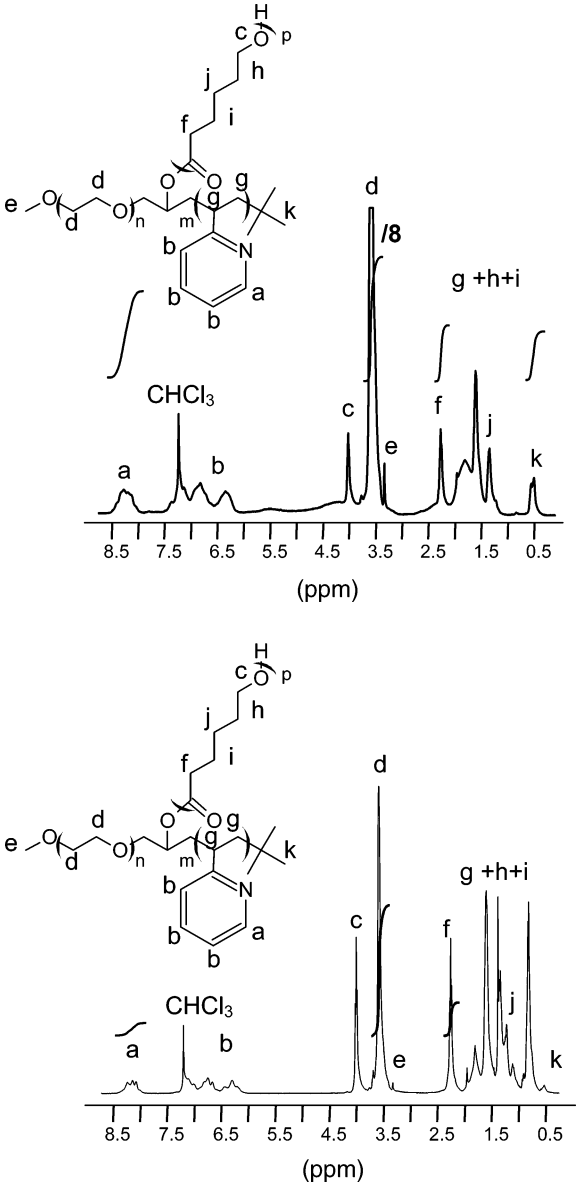

Figure 7. ^{1}H NMR spectrum of miktoarm terpolymers of (a, top) lower molecular weight (**5a**, in Table 2) and (b, bottom) upper molecular weight (**5c**, in Table 2).

Conclusions

New ABC miktoarm star terpolymers of PEO, P2VP, and PCL were successfully synthesized by the combination of anionic and ring-opening polymerizations. α-Methoxy-ω-epoxy-MPEO is reactive toward living $P2VP^-$ chains, which leads to a very efficient coupling of the chains with formation of a hydroxyl group at the junction of the two blocks. This coupling is quasi-quantitative, with M_n as high as 5000 in this work. In the presence of tin octoate, the hydroxyl group is a well-known initiator for the ROP of ϵ-CL, which, in this case, leads to the synthesis of the ABC star-shaped terpolymer. Because all the blocks are prepared by living/controlled polymerization techniques, the length of each arm is easily tuned. The supramolecular self-assembly in water of the well-defined ABC miktoarm star terpolymers prepared in this work is under current investigation, with the purpose develop pH-triggered drug delivery systems.

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