Block and Star Block Copolymers by Mechanism Transformation. 7. Synthesis of Polytetrahydrofuran/Poly(1,3-dioxepane)/Polystyrene ABC Miktoarm Star Copolymers by Combination of CROP and ATRP

Xiao-Shuang Feng and Cai-Yuan Pan*

Department of Polymer Science & Engineering, University of Science & Technology of China, Hefei, Anhui 230026, P. R. China

Received July 16, 2001

ABSTRACT: Polytetrahydrofuran (PTHF)/poly(1,3-dioxepane) (PDOP)/polystyrene (PSt) ABC miktoarm star copolymers were synthesized by combination of cationic ring-opening polymerization (CROP) and atom transfer radical polymerization. Two different functional groups, carboxylic acid and CHBr, were capped at one end of PTHF through the reaction of PTHF−OH with 2-bromosuccinic anhydride (BSA). After PTHF−OOCCHBrCH_2COOH reacted with thionyl chloride, block copolymer PTHF-*b*-PDOP was synthesized by CROP of DOP at −30 to −35 °C with PTHF−OOCCHBrCH_2COCl and $AgClO_4$ as catalyst. Finally, (PTHF) (PDOP)−Br was used to initiate the polymerization of St in the presence of CuBr and bipyridine at 110 °C, and ABC miktoarm star polymer, s-[(PTHF) (PDOP) (PSt)] was successfully prepared. The copolymers obtained were characterized by ^{1}H NMR and gel permeation chromatography measurements.

Introduction

Compared with linear block polymers, miktoarm star polymers exhibit dramatic differences in morphology[1−6] and solution properties,[7−10] etc. Recently, much interest has been directed to the research on miktoarm stars. The synthesis and properties of miktoarm star polymers were reviewed by Hadjichristidis.[11−13] Until now, three different procedures have been developed for the synthesis of ABC miktoarm stars. The first one is based on the macromonomer technique, where nonhomopolymerizable macromonomers at one chain end are incorporated at the block junction of diblock copolymers; the polymerization of the third monomer is then started from the additional active site to form the third arm. Fujimoto et al. reported for the first time the synthesis of ABC type miktoarm stars.[14] The lithium salt of *p*-(dimethylhydroxy)silyldiphenylethylene (DMS) was used as initiator for the polymerization of hexamethylcyclotrisiloxane (D_3). Living polystyrene (PSt) chains were reacted with the end double bond of the diphenylethylene, followed by the anionic polymerization of *tert*-butyl methacrylate (tBuMA). The target polymer [(PSt) (PDMS) (PtBuMA)] was obtained. However, poly(dimethylsiloxane) (PDMS) with a rather broad molecular weight distribution must be fractionated before the following synthetic steps. A similar synthetic route was adopted to synthesize ABC star copolymers containing PSt, polybutadiene (PB), poly(methyl methacrylate) (PMMA), PSt, PB, and poly(2-vinylpyridine) by Abetz et al.[2,15] Quirk et al. described a novel strategy to synthesize ABC terpolymer with nonpolymerizable monovinyl or divinyl linking agents.[16,17] The trichlorosilane method is the second one, which uses the selective, step-by-step substitution of the chlorine atoms in trichloromethylsilane with anionic living polymer chains to form star copolymers.[18−20]

The third method is based on heterofunctional macroinitiator bearing two chemically different functional groups which are able to initiate independently two different kinds of polymerizations. The 1,1-diphenylethylene derivative bearing a protected hydroxyl group was used as linking agent to produce a diblock copolymer. After deprotection, the copolymer with a hydroxyl group was used in the ring-opening polymerization of the third monomer such as ethylene oxide, ϵ-caprolactone, and lactides.[21,22] Huang et al. reported that the PSt chain terminated with *N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diaminodiphenylmethanol (TDDM) was obtained with PSt−Li capped with Michler's ketone. The ABC terpolymer of St, ethylene oxide, and methacrylic acid was synthesized by combination of anionic and photoinduced charge-transfer polymerization.[23]

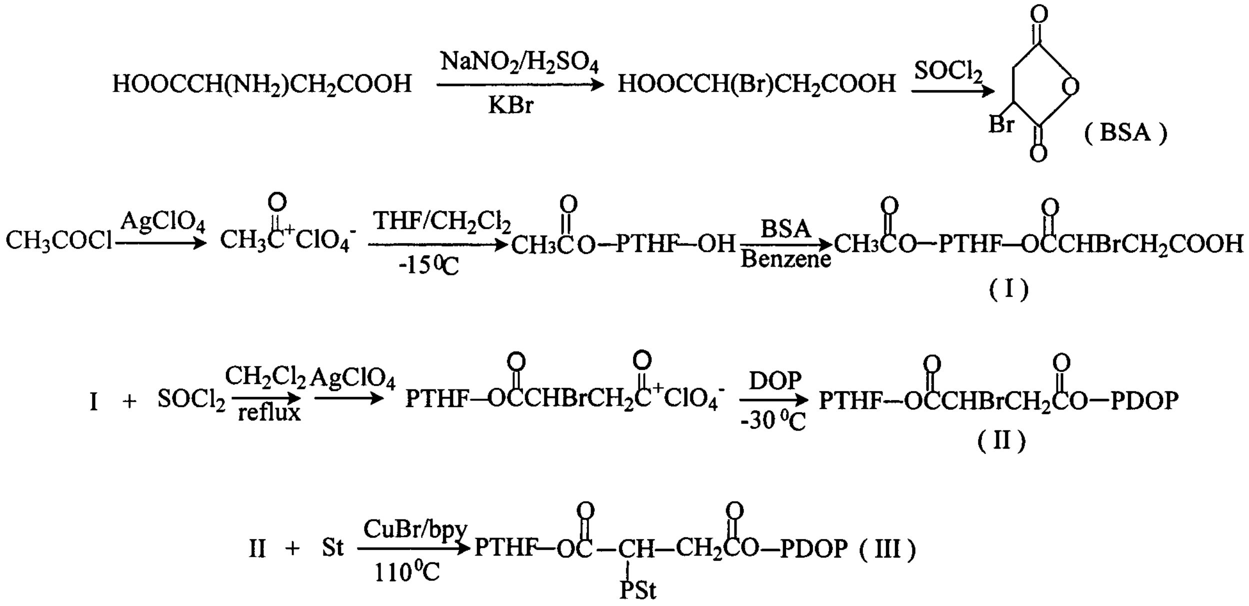
Recently, the development of living radical polymerization such as ATRP has opened a new route for the preparation of well-defined macromolecules because many monomers can undergo free-radical polymerization.[24] In previous articles,[25−27] our group successfully developed a new route to synthesize miktoarm stars of A_2B_2 and A_4B_4 by combination of ATRP and CROP. A tetrafunctional initiator, di(hydroxyethyl)-2,9-dibromosebate [$HOCH_2CH_2OOCCHBr(CH_2)_6CHBrCOOCH_2CH_2OH$], was used in ATRP of St with bipyridine (bpy) and CuBr as ligand and catalyst, and two-armed PSt with two primary hydroxyl groups sited at the center of macromolecule [s-$(PStBr)_2(OH)_2$] was first synthesized, followed by s-$(PStBr)_2(OH)_2$ which was used as a chain-transfer agent in the CROP of DOP with triflic acid as initiator; $(PSt)_2$ $(PDOP)_2$ miktoarm star was obtained.[26] Dioxacarbenium initiating species made from α,ω-dibromosebasinyl dichloride [$ClCOCHBr(CH_2)_6CHBrCOCl$] and $AgClO_4$ initiated CROP of THF to afford $(PTHF)_2Br_2$, followed by ATRP of St to form $(PSt)_2$ $(PTHF)_2$.[25] Similarly, $(PSt)_4$ $(PTHF)_4$ miktoarms were synthesized according to the above procedure when octafunctional initiator was employed.[27] Importantly, the experimental results indicate that the different types of initiating sites were not influenced by each other during the polymerization. In this article, we

---

* To whom correspondence should be addressed. E-mail: pcy@ustc.edu.cn.

10.1021/ma011243u CCC: $22.00

Scheme 1



present the synthesis of hitherto a new ABC miktoarm terpolymers, where A, B, and C arms are PTHF, PDOP, and PSt, respectively, by combination of CROP and ATRP. PDOP is easily decomposed in acidic conditions; the new morphology with hole or other structures can be formed when PDOP chains of the film prepared from this miktoarm copolymer are removed. As shown in Scheme 1, PTHF−OH reacted with BSA, resulting in macroinitiator with two different initiating sites standing at one end of the polymer chain. Following CROP of DOP and ATRP of St in sequence, the s-[(PTHF) (PDOP) (PSt)] miktoarm terpolymers were successfully prepared.

Table 1. Data for PTHF−OH and PTHF−OCOCHBrCH$_2$COOH

sample	M_n(NMR)[c]	M_n(GPC)[d]	M_w/M_n
PTHF−OH[a]	4670	6720	1.23
PTHF−OCOCHBrCH$_2$COOH[b]	5210	7590	1.17

[a] The polymerization of THF was performed in CH$_2$Cl$_2$ solution at −15 °C for 8 h with the feed molar ratio: [CH$_3$COCl]:[AgClO$_4$]:[THF] = 1/1/139.[29] [b] Esterification conditions: see Experiment Part. [c] PTHF−OH: M_n(NMR) = ($I_{3.42}/2I_{4.09}$) × 72 + 60; PTHF−OCOCHBrCH$_2$COOH: M_n(NMR) = ($I_{3.42}/2I_{4.09}$) × 72 + 60 + 179, where $I_{3.42}$ and $I_{4.09}$ are the integral values of the peaks at 3.42 and 4.09 ppm; 60, 72, and 179 are the molecular weights of acetic acid, THF, and BSA, respectively. [d] M_n(GPC) was measured on a Waters 150C with RI detector.

Experimental Section

Materials. DOP was prepared and purified as described in ref 28. Silver perchlorate (AgClO$_4$) was prepared in this laboratory and dried at 110 °C for 24 h before use. THF was distilled from a purple sodium ketyl solution. Dichloromethane and benzene were distilled from CaH$_2$. Thionyl chloride and acetyl chloride were distilled before use. St was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with water until neutralization. After drying with anhydrous magnesium sulfate, St was distilled at reduced pressure. All the chemical reagents were of analytical grade, purchased from Shanghai Chemical Reagents Co., and used as received without further purification. s-Bromosuccinic acid was prepared according to the procedure described in the literature;[30,31] mp 171−172 °C. IR (KBr, cm^{-1}): ν = 3500−3100 (OH), 1708 (C=O), 649 (C−Br). ^{1}H NMR (500 MHz, CF$_3$COOD) δ (TMS, ppm): 4.66 (t, 1H, BrC*H*COO), 3.30 (d, 2H, C*H*$_2$COO).

Synthesis of 2-Bromosuccinic Anhydride (BSA). L-Bromosuccinic acid (15 g, 76 mmol) and thionyl chloride (16 mL, 230 mmol) were added into a 100 mL round-bottom flask protected from moisture by an anhydrous calcium chloride tube. The mixture was refluxed for 3 h. Then, the remaining thionyl chloride was evaporated, and the residue was further dried at 40 °C under vacuum for 24 h. BSA was obtained in almost quantitative yield; mp 68−69 °C.

IR (KBr, cm^{-1}): ν = 1874, 1783 (−CO−O−CO−), 684 (C−Br).

^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 4.83 (dd, 1H, BrC*H*COO), 3.70 (dd, 1H, *H*CHCOO), 3.30 (dd, 1H, HC*H*COO).

Reaction of PTHF−OH with BSA. PTHF−OH was synthesized by CROP of THF with acetyl chloride in conjunction with silver perchlorate as initiator according to the procedure in the literature.[29] After trace water in PTHF−OH was removed by azeotropic distillation with anhydrous benzene, PTHF−OH (5.0 g, M_n = 5000, 1 mmol) was dissolved in anhydrous benzene (30 mL), and BSA (1.8 g, 10 mmol) was added. The mixture was stirred at 55 °C for 24 h. The mixture was washed with distilled water until it was neutral and then dried over anhydrous sodium sulfate. Benzene was removed with a rotary evaporator, the residue was dissolved in THF, and the solution obtained was added into methanol at −30 °C. The precipitate was filtered and finally dried at 40 °C under vacuum for 24 h. PTHFOOCCHBrCH$_2$COOH (I, 4.5 g) was obtained in 90% of yield.

Synthesis of s-[(PTHF) (PDOP)−Br] (II) by CROP of DOP (sample 3 in Table 2). A typical procedure was as follows: I (0.5 g, 0.1 mmol), thionyl chloride (0.3 mL, 5 mmol), and CH$_2$Cl$_2$ (5 mL) were added into a 25 mL two-neck flask equipped with anhydrous calcium chloride tube for protection of moisture. The mixture was refluxed overnight while stirring. After removal of volatile compounds at 60 °C under reduced pressure for several hours, a viscous liquid product was obtained. CH$_2$Cl$_2$ (2 mL) was added to dissolve PTHF−OOCCHBrCH$_2$COCl; 23 mg (0.11 mmol) of silver perchlorate was transferred into the solution of macroinitiator under nitrogen atmosphere at −30 to −35 °C. After stirring for 1 h, DOP was added with syringe and polymerized at this temperature for 4 h. The polymer solution was quenched by adding excess distilled water. The mixture was passed through a short column of neutral alumina for removing AgCl, and the solution was washed with distilled water until neutralization. The CH$_2$Cl$_2$ was removed with a rotary evaporator. The solution of the residue in THF was added into methanol at −30 °C. The precipitate was collected by filtration and finally dried at 40

Table 2. Conditions and Results of CROP of DOP Using Macromolecular Oxocarbenium Perchlorate as Initiator[a]

no.	sample	$[DOP]_0$ (mol L^{-1})	$[I]_0$ (mol L^{-1})	conv[b] (%)	M_n ($\times 10^4$) NMR[c]	th[d]	GPC[e]	M_w/M_n
1	$(PT)(PD)_1$	3.27	0.033	67	1.18	1.20	1.52	1.47
2	$(PT)(PD)_2$	4.90	0.025	78	2.12	2.08	1.94	1.48
3	$(PT)(PD)_3$	5.88	0.020	83	3.33	3.01	3.14	1.50

[a] Polymerization was performed in methylene chloride at −30 to −35 °C for 4 h. [b] Conversion was determined by gas chromatography. [c] Calculated according to eq 1. [d] The theoretical number-average $M_n(\mathrm{th}) = [102 \times \mathrm{conversion} \times ([DOP]_0/[I]_0)] + 5200$, where 102 and 5200 are molecular weights of DOP and PTHF macroinitiator and $[DOP]_0$ and $[I]_0$ are the initial molar concertrations of DOP and PTHF−OCOCHBrCH$_2$COCl macroinitiator. [e] M_n(GPC) was measured on Waters 515 with RI, RALLS, and DV detectors.

Table 3. Conditions and Results of ATRP of St Using (PTHF) (PDOP)−Br/CuBr/bpy as Initiating System[a]

no.	sample[b]	time (h)	conv[c] (%)	M_n ($\times 10^4$) NMR[d]	th[e]	GPC[f]	M_w/M_n
1	$(PT)(PD)(PS)_{11}$	1	2.4	1.39	1.43	1.83	1.49
2	$(PT)(PD)(PS)_{12}$	3	7.2	1.91	1.93	2.34	1.50
3	$(PT)(PD)(PS)_{21}$	2	4.2	2.54	2.56	3.05	1.50
4	$(PT)(PD)(PS)_{22}$	4	8.3	2.94	2.98	3.26	1.49
5	$(PT)(PD)(PS)_{31}$	2	4.5	3.76	3.80	4.40	1.54
6	$(PT)(PD)(PS)_{32}$	6	12.5	4.59	4.63	4.98	1.52

[a] St was polymerized in bulk at 110 °C with the molar ratio in feed: St/CuBr/bpy/PTHF-*b*-PDOPBr = 1000/1/3/1. [b] Samples 1 and 2, 3 and 4, and 5 and 6 were initiated respectively by (PT) $(PD)_1$, (PT) $(PD)_2$, and (PT) $(PD)_3$ in Table 2. [c] Conversion was calculated based on ^{1}H NMR data. [d] Calculated according to eq 2. [e] The theoretical number-average $M_n(\mathrm{th}) = ([St]_0/[I]_0) \times \mathrm{conversion} \times 104 + M_{n\mathrm{PTPD}}(\mathrm{NMR})$, where $[St]_0$ and $[I]_0$ are the initial molar concentrations of St and (PTHF) (PDOP)−Br respectively; 104 and $M_{n\mathrm{PTPD}}$ (NMR) are molecular weights of St and (PTHF) (PDOP)-Br. [f] M_n(GPC) was measured on a Waters 515 with RI, RALLS, and DV detectors.

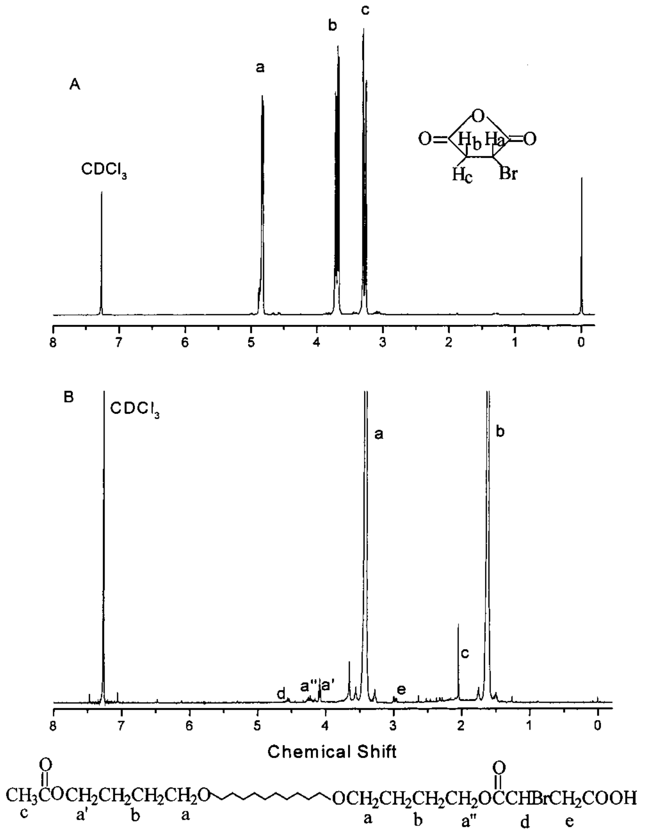
°C under vacuum for 24 h. Conversion: 83% (determined by gas chromatography), $M_n(\mathrm{NMR}) = 3.33 \times 10^4$, PDI = 1.50. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 4.65 (OC*H*$_2$O), 4.56 (C*H*BrC=O), 4.21 (2 C*H*$_2$OC=O), 4.07 (C*H*$_2$OOCCH$_3$, terminal), 3.54 (OCH$_2$OC*H*$_2$CH$_2$), 3.40 (CH$_2$C*H*$_2$OC*H*$_2$CH$_2$), 1.88−1.57 (C*H*$_2$CH$_2$OCH$_2$C*H*$_2$, and OCH$_2$OCH$_2$C*H*$_2$).

Synthesis of s-[(PTHF) (PDOP) (PSt)] (III) (sample 5 in Table 3). The ABC terpolymer **III** was synthesized by the bulk ATRP of St with the feed molar ratio St:II:CuBr:bpy = 1000:1:1:3. To a 5 mL glass tube, CuBr, bpy, **II**, and St were added successively. The heterogeneous mixture was degassed by three freeze−pump−thaw cycles. The tube was sealed under vacuum and then immersed in an oil bath thermostated at 110 °C. After the reaction was carried out for a prescribed time, the tube was rapidly cooled to room temperature by ice water, and the polymer solution in THF was passed through a short column of neutral alumina to remove the metal salt. By adding the polymer solution into an excess of methanol, the terpolymer was precipitated, filtered, and dried at 40 °C in a vacuum oven for 24 h. Conversion: 4.5% (based on ^{1}H NMR data), $M_n(\mathrm{NMR}) = 3.80 \times 10^4$, PDI = 1.54. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.08−6.60 (aromatic protons), 4.65 (OC*H*$_2$O), 4.49 (C*H*Br, terminal), 4.23 (2 C*H*$_2$OC=O), 4.09 (C*H*$_2$OOCCH$_3$, terminal), 3.54 (OCH$_2$OC*H*$_2$CH$_2$), 3.40 (CH$_2$C*H*$_2$OC*H*$_2$CH$_2$), 2.00−1.06 (C*H*$_2$CH$_2$OCH$_2$C*H*$_2$, OCH$_2$OCH$_2$C*H*$_2$ and C*H*$_2$C*H*Ph).

Characterization. ^{1}H NMR spectra were measured on a Bruker DMX-500 nuclear magnetic resonance instrument using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. FTIR spectra was recorded on a Vector-22 FTIR instrument. The melting point was determined on an Electrathermal digital melting point apparatus. The molecular weights of the polymers obtained were estimated on a Waters 515 fitted with Waters styragel HT3 and HT4 columns with a dual detector (Viscotek TDA 301), with right angle laser light scattering (RALLS) and differential viscometer (DV) detectors in series, combined on-line with a differential refractometer (RI, Waters 2410). The molecular weight distribution of the polymers was detected on a Waters 150C gel permeation chromatograph (GPC) equipped with Ultrastyragel columns (500, 10^3, and 10^4 Å) and RI detector. THF was used as eluent at a flow rate of 1.0 mL/min.

Results and Discussion

Esterification of PTHF−OH. BSA was synthesized according to ref 31 with slight modification. Instead of trifluoroacetic anhydride, thionyl chloride was employed. Figure 1A is its ^{1}H NMR spectrum. Because of inequality of three protons, all three peaks are splitted into a doublet. Peak a at 4.83 ppm and peaks b and c at 3.70 and 3.30 ppm are ascribed to the methine proton and the methylene protons.



$CH_3COCH_2CH_2CH_2CH_2O$〰〰$OCH_2CH_2CH_2CH_2OCCHBrCH_2COOH$

Figure 1. ^{1}H NMR spectra of 2-bromosuccinic anhydride (A) and reaction product of PTHF−OH with BSA (B).

PTHF−OH was synthesized by CROP of THF with acetyl chloride in combination with silver perchlorate as initiating system.[29] The molecular weight and poly-

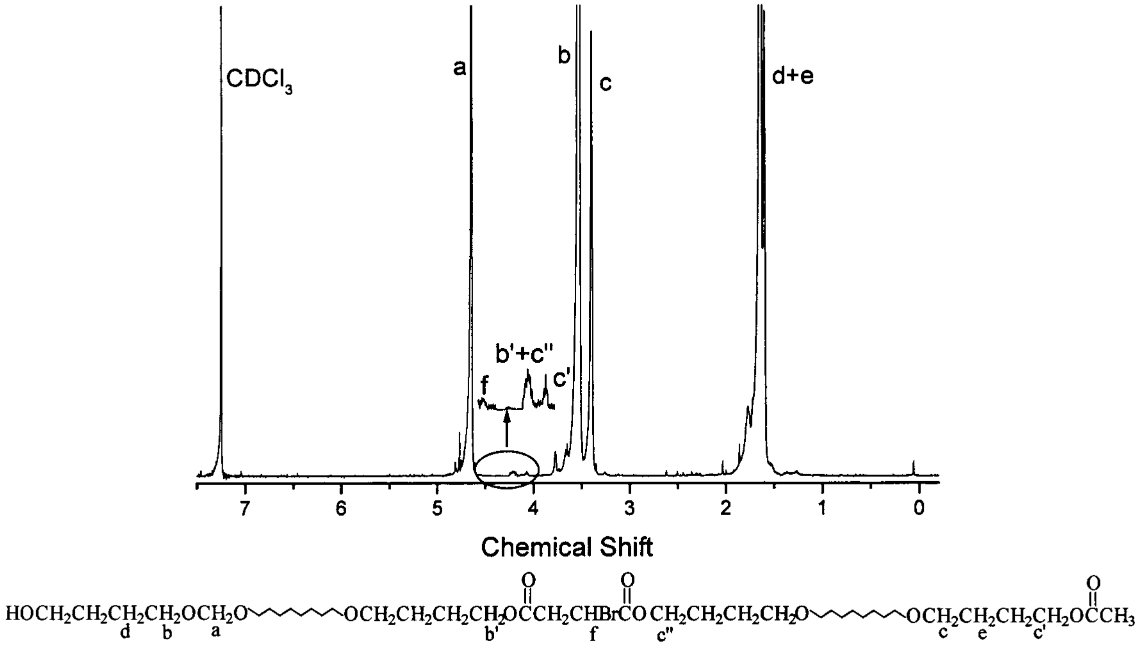


Figure 2. Typical ^{1}H NMR spectrum of PTHF-*b*-PDOPBr block copolymer (sample 3 in Table 2).

dispersity index are listed in Table 1. For preparing the well-defined ABC miktoarmed copolymer, no bromine loss and complete esterification of PTHF−OH are necessary in the reaction of PTHF−OH with BSA. It was reported that the esterification reaction of poly(ethylene glycol) with succinic anhydride was performed at 55 °C in $CHCl_3$ and pyridine;[32] some bromines were eliminated although complete esterification was achieved. Thus, the reaction of PTHF−OH with BSA was carried out without pyridine, but in benzene for 24 h, the ^{1}H NMR spectrum of the product is shown in Figure 1B. Peaks a and b at 3.42 and 1.62 ppm are assigned to methylene protons next to the ether oxygen and the protons of the two middle methylene groups in the tetramethylene unit, respectively. Peak c at 2.05 ppm belongs to the methyl protons of acetyl group standing at one end of polymer chain. Peaks a′ and a″ at 4.09 and 4.23 ppm correspond to the methylene protons connected to ester oxygens of acetate and bromosuccinate groups, respectively. Besides, peak d at 4.55 ppm is representative of a methine proton connected to bromine, peak e at 2.98 ppm is ascribed to one of methylene protons, and the other is overlapped by methylene protons of the PTHF main chain. Compared to the signals of BSA in Figure 1A, the signals of methine and methylene protons in BSA unit are shifted to high field, which is concurrent to its acyclic structure. In addition, the integration ratio of peaks of c, a′, a″, d, and e is nearly 3.5:2.2:1.9:1.0:1.0, indicating that the hydroxyl group of PTHF−OH reacted with BSA completely, and no debromination took place during the esterification; that is, the difunctional macroinitiator PTHF−$OCOCHBrCH_2COOH$ was successfully synthesized.

Synthesis of (PTHF) (PDOP)−Br by CROP of DOP. In our previous research on the preparations and characterizations of the A_2B_2 and A_4B_4 miktoarm stars,[26,27] the CHBr group in macroinitiator was not lost during CROP. As reported by our research group,[28] CROP of DOP was carried out at −30 to −35 °C using oxocarbenium perchlorate as initiator, and its polymerization rate is higher than that of THF using the same initiator. ^{1}H NMR data and GPC analysis demonstrate that the formation of cyclics can be neglected. The molecular weight of PDOP could be controlled by the molar ratio of DOP consumed to the initiator added. According to this polymerization procedure, we synthesized (PTHF) (PDOP)−Br using the macroinitiator PTHF−$OCOCHBrCH_2CO^+ClO_4^-$. The results are listed in Table 2, and the typical ^{1}H NMR spectrum and GPC curves are shown in Figures 2 and 3, respectively. Peaks a and b at 4.65 and 3.54 ppm in Figure 2 are assigned to the acetal methylene protons and the methylene protons next to ether oxygen, respectively, the methylene protons next to oxygen of THF units appear at 3.40 ppm (peak c in Figure 2), and the signals of the two middle methylene protons of tetramethylene groups in DOP and THF units are overlapped at 1.60 ppm. The results of ^{1}H NMR indicate the presence of the DOP unit in the copolymer. Peaks at 4.21 and 4.07 ppm are ascribed to the three methylene groups connected to the ester oxygen of bromosuccinate and acetate group, respectively. Peak f at 4.56 ppm corresponds to the methine proton connected to bromine. The integration

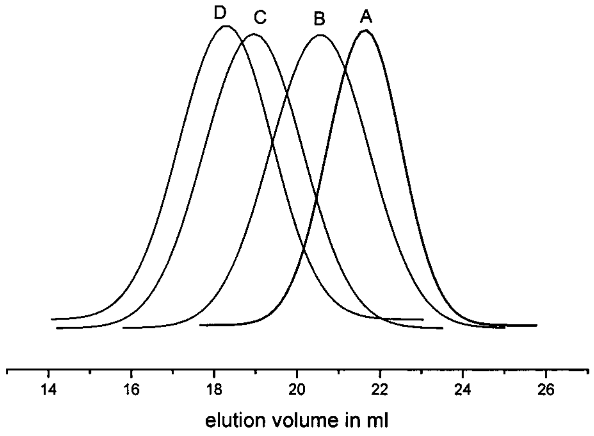


Figure 3. Stack GPC traces (RI detector) of PTHF and its copolymers with DOP PTHF-*b*-PDOBr (A is the macroinitiator PTHF sample 2 in Table 1; B, C, and D are samples 1, 2, and 3 in Table 2, respectively.

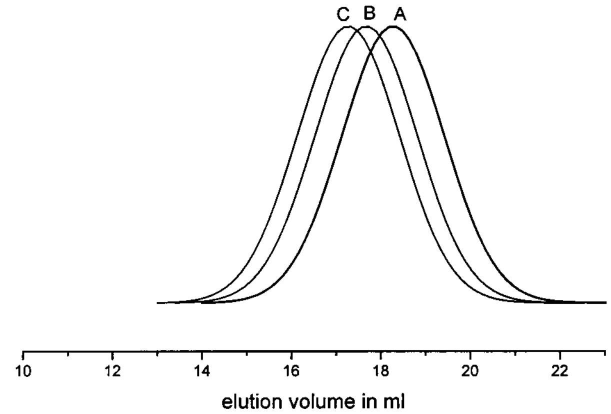


Figure 4. Typical GPC traces (RI detector) of PTHF-*b*-PDOPBr and its ABC terpolymers (A, sample 3 in Table 2; B and C, samples 5 and 6 in Table 3, respectively.)

ratio of peaks at 4.56, 4.21, and 4.07 ppm are approximately 1.0:4.3:1.8, demonstrating the complete initiation of macroinitiator, the formation of cyclics could be neglected, and almost no bromine was lost during CROP of DOP. The symmetrical GPC curves of (PTHF) (PDOP)−Br shown in Figure 3 manifest also these conclusions. The polydispersity indexes of polymers ranging from 1.47 to 1.50 listed in Table 2 are similar to our previous results of homopolymerization of DOP.[28]

Assuming that each macromolecule contains one PTHF chain and one PDOP chain, the number-average molecular weight M_{nPTPD}(NMR) can be calculated by eq 1, and the results are listed in Table 2.

$$M_{\mathrm{nPTPD}}(\mathrm{NMR}) = (I_{3.54}/I_{3.40}) \times \mathrm{DP_{PTHF}} \times 102 + 5200 \tag{1}$$

where $I_{3.54}$ and $I_{3.40}$ are the integral values of the peaks at 3.54 and 3.40 ppm, respectively, $\mathrm{DP_{PTHF}}$ is the degree of polymerization of PTHF segment, and 5200 and 102 are molecular weights of the PTHF segment and DOP, respectively. M_{nPTPD}(NMR) agrees well with M_{nPTPD}(th). The results listed in Table 2 demonstrate that molecular weight of PDOP segment could be controlled by the feed molar ratio of DOP consumed to the initiator added.

Synthesis of s-[(PTHF) (PDOP) (PSt)] Terpolymer. The s-[(PTHF) (PDOP) (PSt)] terpolymer was achieved by bulk polymerization of St at 110 °C using PTHF-*b*-PDOPBr/CuBr/bpy as initiating system. The conditions and results are listed in Table 3. The molecular weight of the polymer obtained is increased with the increasing conversion of St (see Table 3). The typical GPC curves shown in Figure 4 are symmetrical, indicating the macroinitiator PTHF-*b*-PDOPBr left in the polymer is not detected. Figure 5 is a typical ^{1}H NMR spectrum of ABC terpolymer. The characteristic peaks of the phenyl group in the PSt unit appear at 7.08−6.60 ppm; the signals at 1.06−2.00 ppm corresponding to the methylene and methine protons in the main chain of PSt segment are partially overlapped by the signals of two middle methylene protons of tetramethylene group in DOP and THF units. Compared with ^{1}H NMR of the macroinitiator PTHF-*b*-PDOPBr in Figure 2, the peak at 4.56 ppm of the methine proton connected to bromine is slightly shifted to high field at 4.49 ppm, which is the signal of end-standing methine proton next to bromine in PSt segment, but the integration ratio of the peak at 4.49 ppm to other two peaks at 4.23 and 4.09 ppm remains the same (the integration ratio of peaks at 4.49, 4.23, and 4.09 ppm is 1.0:4.4:1.8), indicating the complete initiation of CHBr group of PTHF-*b*-PDOPBr. The GPC and ^{1}H NMR facts verify that s-[(PSt) (PTHF) (PDOP)] terpolymer was formed. On the basis of the molecular weight of PTHF-*b*-PDOPBr, the number-average molecular weight, M_{nPTPDPSt}(NMR), can

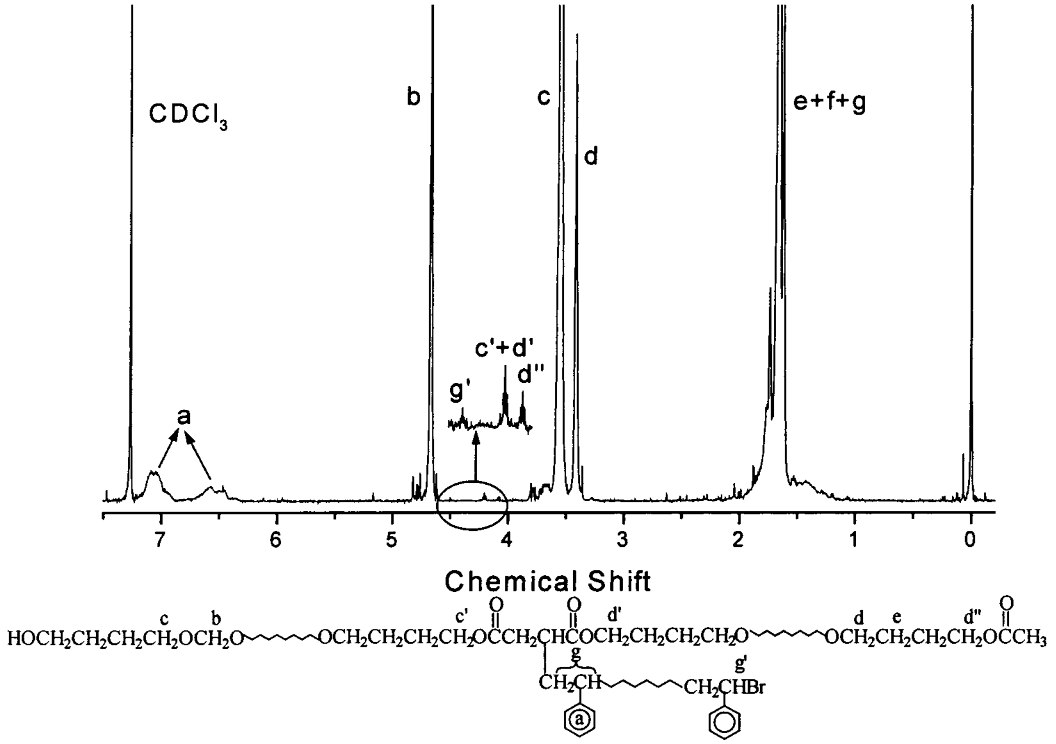


Figure 5. Typical ^{1}H NMR spectrum of s-[(PTHF) (PDOP) (PSt)] ABC terpolymer (sample 5 in Table 3).

be calculated by eq 2, and the results are listed in Table 3.

$$M_{\mathrm{nPTPDPSt}}(\mathrm{NMR}) = [(I_{7.08-6.60}/5)/(I_{3.40}/4)] \times \mathrm{DP}_{\mathrm{PTHF}} \times 104 + M_{\mathrm{nPTPD}}(\mathrm{NMR}) \quad (2)$$

where $I_{7.08-6.60}$ and $I_{3.40}$ are the integral values of the peaks at 7.08−6.60 and 3.40 ppm, respectively, $\mathrm{DP}_{\mathrm{PTHF}}$ is the DP of PTHF, and 104 and M_{nPTPD}(NMR) are molecular weights of St and (PTHF) (PDOP) macroinitiator, respectively. The good agreement of M_{nPTPDPSt}(NMR) and M_{nPTPDPSt}(th) and the symmetrical GPC traces suggest that the s-[(PTHF) (PDOP) (PSt)] miktoarm ABC stars are successfully synthesized.

Conclusions

An approach for synthesizing ABC miktoarm star coplymers by combination of CROP and ATRP has been developed. A macroinitiator containing two different functional groups, CHBr and carboxylic acid, can be prepared by the reaction of PTHF−OH with 2-bromosuccinic anhydride. Followed by CROP of DOP, the block copolymer PTHF-*b*-PDOPBr was obtained. The molecular weight of PDOP segment could be controlled by the molar ratio of DOP consumed to the initiator added. Its polydispersity index (1.47−1.5) is similar to the result of homopolymerization of DOP. Finally, the ATRP of St produced the ABC miktoarm stars, s-[(PTHF) (PDOP) (PSt)], using (PTHF) (PDOP)-Br/CuBr/bpy as the initiating system. By changing polymerization time, the terpolymers with different St segment chain length could be obtained. The well-defined ABC terpolymers obtained are supported by the results of the ^{1}H NMR characterization and GPC measurements (1.49−1.54).

Acknowledgment. The authors gratefully thank the support of the National Natural Science Foundation of China (Grant 50173025)

References and Notes

(1) Zioga, A.; Sioula, S.; Hadjichristidis, N. *Macromol. Symp.* **2000**, *157*, 239.
(2) Hückstädt, H.; Göpfert, A.; Abetz, V. *Macromol. Rapid Commun.* **2000**, *21*, 296.
(3) Beyer, F. L.; Gido, S. P.; Velis, G.; Hadjichristidis, N. *Macromolecules* **1999**, *32*, 6604.
(4) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 5272.
(5) Floudas, G.; Reiter, G.; Lambert, O.; Dumas, P. *Macromolecules* **1998**, *31*, 7279.
(6) Okamoto, S.; Hasegawa, H.; Hashimoto, T.; Fujimoto, T.; Zhang, H.; Kazama, T.; Takano, A.; Isono, Y. *Polymer* **1997**, *38*, 5275.
(7) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741.
(8) Pispas, S.; Avgeropoulos, A.; Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1329.
(9) Vlahos, C.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6691.
(10) Lambert, O.; Jada, A.; Dumas, P. *Colloids Surf., A* **1998**, *136*, 263.
(11) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(12) Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Vlahos, C.; Iatrou, H. *Adv. Polym. Sci.* **1999**, *142*, 71.
(13) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
(14) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208.
(15) Hückstädt, H.; Abetz, V.; Stadler, R. *Macromol. Rapid Commun.* **1996**, *17*, 599.
(16) Quirk, R. P.; Yoo, T.; Lee, B. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 911.
(17) Quirk, R. P.; Kim, Y. J. *Polym. Prepr.* **1996**, *37* (2), 643.
(18) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649.
(19) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromol. Symp.* **1997**, *117*, 167.
(20) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 1518.
(21) Lambert, O.; Dumas, P.; Hurtrez, G.; Riess, G. *Macromol. Rapid Commun.* **1997**, *18*, 343.
(22) Lambert, O.; Reutenauer, S.; Hurtrez, G.; Riess, G.; Dumas, P. *Polym. Bull. (Berlin)* **1998**, *40*, 143.
(23) Lu, Z.; Chen, S.; Huang, J. *Macromol. Rapid Commun.* **1999**, *20*, 394.
(24) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(25) Guo, Y.-M.; Pan, C.-Y. *Polymer* **2001**, *42*, 2863.
(26) Guo, Y.-M.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 437.
(27) Guo, Y.-M.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2134.
(28) Xu, Y.-J.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3401.
(29) Xu, Y.-J.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3391.
(30) Frick, J. A.; Klassen, J. B.; Bathe, A.; Abramson, J. M.; Rapoport, H. *Synthesis* **1992**, 621.
(31) Guerin, P.; Vert, M.; Braud, C.; Lenz, R. W. *Polym. Bull. (Berlin)* **1985**, *14*, 187.
(32) Ferruti, P.; Tanzi, M. C.; Rusconi, L.; Cecchi, R. *Makromol. Chem.* **1981**, *182*, 2183.

MA011243U