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Synthesis of asymmetric H-shaped block copolymer by the combination of atom transfer radical polymerization and living anionic polymerization

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Abstract

A new asymmetric H-shaped block copolymer $(PS)_2$–PEO–$(PMMA)_2$ has been designed and successfully synthesized by the combination of atom transfer radical polymerization and living anionic polymerization. The synthesized 2,2-dichloro acetate-ethylene glycol (DCAG) was used to initiate the polymerization of styrene by ATRP to yield a symmetric homopolymer $(Cl–PS)_2$–$CHCOOCH_2CH_2OH$ with an active hydroxyl group. The chlorine was removed to yield the $(PS)_2$–$CHCOOCH_2CH_2OH$ ($(PS)_2$–OH). The hydroxyl group of the $(PS)_2$–OH, which is an active species of the living anionic polymerization, was used to initiate ethylene oxide by living anionic polymerization via DPMK to yield $(PS)_2$–PEO–OH. The $(PS)_2$–PEO–OH was reacted with the 2,2-dichloro acetyl chloride to yield $(PS)_2$–PEO–$OCCHCl_2$ ($(PS)_2$–PEO–DCA). The asymmetric H-shaped block polymer $(PS)_2$–PEO–$(PMMA)_2$ was prepared via ATRP of MMA at 130 °C using $(PS)_2$–PEO–DCA as initiator and CuCl/bPy as the catalyst system. The architectures of the asymmetric H-shaped block copolymers, $(PS)_2$–PEO–$(PMMA)_2$, were confirmed by ^{1}H NMR, GPC and FT-IR.

Keywords: Atom transfer radical polymerization; Living anionic polymerization; Asymmetric H-shaped block copolymer

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1. Introduction

In recent years, the design and realisation of well-defined polymer architectures have become very important in polymer science as the polymers architectures determine the different properties of polymers with versatile application in somewhere. This strategy has been successfully used by the groups of researchers [1–3] to synthesize miktoarms star polymer and H-shaped symmetric block copolymers. Compared to the three miktoarms star polymers, the symmetric H-shaped block copolymers are more complex in structures and more difficult in synthesis. H-shaped copolymers (A_2BA_2) are based on two sidearms (A_2) attached to each end of the backbone (B), whereas the three miktoarm polymers (A_2B) connected at each end of the block (B) by chemical bond. In those H-shaped block copolymers, the blocks of A and B might have the different performances, and thus they would play some important roles as special materials from the theoretical as well as practical applications point of views [1–4]. Some properties like crystalline behaviors [1], nolinear stress relaxation [2] and rheology [3], etc. of H-shaped block copolymers have been reported elsewhere. Some other properties of H-shape block copolymers may also be studied by varying the blocks of the polymers [5–10], or like functionalized multiarm and miktoarm block copolymers have been studied extensively because they can have some interesting behaviors, such as microphase separation in bulk [5] and sol–gel states [6], and at interfaces and surfaces [7], the bulk behaviors [8], phase structures [9], and morphologies [10].

Nowadays, the well-defined and complex macromolecular architectures of polymers are synthesized by various methods like living anionic polymerization (AP) [11], living cationic polymerization (CP) [12], and controlled/living radical polymerization (CRP), namely, atom transfer radical polymerization (ATRP) [4f,g,13], nitroxide-mediated polymerization (NMP) [14], and reversible addition–fragmentation chain transfer (RAFT) [15], well-defined and complex macromolecular architectures. The methods provided powerful tools to

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synthesize star-shaped [4e,16], star-branched [17], comb-like [13h,i,18], dendrimer-like [19], exact graft polymers (π-shaped, H-shaped, super H-shaped) [1,3,21]. In general, those copolymers are synthesized by living ionic polymerization method. Besides these, some combinations of those methodologies like living anionic and cationic polymerization and controlled and living radical polymerizations have been widely used recently to prepare some complex polymers [16c,20,22].

Combinations of living anionic/cationic polymerization with other controlled polymerization methods have created a new horizon for the synthesis of more predictable macromolecular architectures and complex polymers [18b,21]. In this paper, we report a new asymmetric H-shaped block copolymer, $(PMMA)_2$–PEO–$(PS)_2$, by the combination of ATRP and living anionic polymerization using versatile macroinitiator, and the architectures of those polymers were confirmed by ^{1}H NMR, GPC and FT-IR.

2. Experiment section

2.1. Materials

2,2-Dichloro acetyl chloride (DCAC, 99%) was used as received without further purification. 2,2′-Bipyridine (bPy, 99.9%) was recrystallized from *n*-hexane and stored in dark under argon. Cuprous chloride (99%) was washed with acetic acid till colorless, and then washed with methanol, dried under vacuum at 40 °C for 24 h and stored in dark under argon. All materials of above were purchased from the China Medicine Group, Shanghai Chemical Reagent Co. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich 98%) was purchased from Aldrich. Styrene (Beijing Chemical Factory, 99.5%) and methyl methacrylate (Beijing Chemical Factory, 99%) were used. The monomers were distilled under reduced pressure to sealed ampules and stored in a refrigerator prior to use. THF (99.5%) and *n*-hexane (99.5%) were refluxed and distilled over sodium benzophenone to purple. Anionic polymerizations were carried out under argon atmosphere in a flame-dried glass reactor equipped with a high vacuum line; the solvent, initiator, and monomer were transferred to the reactor through a syringe. ATRP were carried out in a tube that was degassed by three or more freeze–vacuum–thaw cycles. The tube was sealed under vacuum and then immersed into an oil bath it 130 °C.

2.2. Instrumentation

^{1}H NMR spectra were obtained on a Bruker AV-600 NMR spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. The molecular weights and the polydispersity of the polymers were determined on a Waters GPC PL-GPC220 equipped with PL gel 10 μm MIXED×3 column and Waters RI detector at 30 °C, which was calibrated with PL EasiCal PS-1 standards. THF was used as an eluent with a flow rate of 1.0 mL/min. The data were calculated by the PL Caliber GPC Software. Fourier transform infrared spectra were recorded on a Bruker Vertex-70 FT-IR instrument equipped with the DTGS detector.

2.2.1. Synthesis of 2,2-dichloro acetate-ethylene glycol (DCAG)

Ethylene glycol (150 mL), sodium (4.6 g, 200 mmol) were added to a 250 mL dry three-necked flask equipped with a refluxing condenser and a constant pressure dropping funnel under the argon atmosphere and the ace water bath. After the sodium was reacted completely, 2,2-dichloro acetyl chloride (14.7 g, 100 mmol) were transferred to the constant pressure dropping funnel under argon atmosphere and added dropwise to the flask over 30 min. At first, the reaction mixture was kept at 0 °C for 1 h, and then at room temperature for 3 h. The mixture was dissolved in 150 mL dichloromethane, washed by 5% sodium carbonate aqueous solution to the aqueous solution till colorless and further washed by water till neutral. The solution of DCAG was dried over anhydrous magnesium sulfate for 12 h and filtered under vacuum. The solvent was removed under vacuum till colorless liquid. The DCAG was further purified by reduced pressure distillation. The yield of the initiator, DCAG was 98%. ^{1}H NMR δ (ppm): 6.01 [Cl_2HCCO–, 1H], 4.44 [–$COOCH_2$–, 2H], 3.92 [–CH_2OH, 2H], 2.13 [–OH, 1H]. FT-IR: the characteristic carbonyl-stretching band of ester at $\nu = 1760\ cm^{-1}$ and hydroxyl-stretching band of alcohol at $\nu = 3380\ cm^{-1}$.

2.2.2. Synthesis and determination of the concentration of diphenylmethylpotassium (DPMK)

The procedure for synthesis and determination of DPMK has been followed as described elsewhere et al. [22]. The concentration of DPMK determined was 4.216×10^{-4} mol/mL.

2.2.3. Synthesis of linear symmetric polymer, $HOCH_2CH_2OOCCH$–$(PSCl)_2$ (EG–$(PSCl)_2$) by ATRP

DCAG (0.1730 g, 1 mmol), CuCl (0.2970 g, 3 mmol), bPy (0.9371 g, 6 mmol), styrene (8.0 mL) and THF (4.0 mL) were added to a 20 mL polymerization tube that was degassed oxygen by three or more freeze–vacuum–thaw cycles. The tube was sealed under vacuum and no leakage was detected. The mixture was heated to 130 °C for 4 h. The resulted polymer was dissolved in 20 mL methylene chloride and the solution was passed through a 7 cm neutral alumina chromatography column (length diameter ratio, 10:1, cm) at least three times to remove the copper salt and the bPy. The polymer solution was precipitated into 300 mL methanol, and the polymer was collected by vacuum filtration. The solid product was dried under vacuum at 50 °C for 24 h. Yield of the linear symmetric polymer of $HOCH_2CH_2OOCCH$–$(PSCl)_2$ was 67%. ^{1}H NMR δ (ppm): 6.30–7.25 [aromatic protons], 4.73–4.75 [–CH(ph)Cl], 4.41–4.44 [–$COOCH_2CH_2OH$], 3.65 [–OCH_2CH_2OH], 1.31–1.98 [methylene and methine protons], 1.02–1.08 [–$OOCCH(CH_2$–$)_2$], 0.953–0.954 [–$OOCCH(CH_2$–$CH(ph)$–$)_2$]. $M_{n,NMR} = 14{,}000$ g/mol, $M_{n,GPC} = 9800$, $M_w/M_n = 1.12$. The data for other EG–$(PSCl)_2$ are listed in Table 1.

Table 1
Summary of molecular weight date for the linear symmetric polymers of $HOCH_2CH_2OOCCH–(PSCl)_2$ by ATRP using DCAG as an initiator

No.	Sample	Time (h)	$M_{n,NMR}$[a]	$M_{n,GPC}$	PDI
1[b]	EG–(PS1Cl)$_2$	4	14,000	9800	1.12
2[b]	EG–(PS2Cl)$_2$	5	18,500	13,400	1.14
3	EG–(PS3Cl)$_2$	6	21,100	14,900	1.18
4	EG–(PS4Cl)$_2$	7	24,200	18,600	1.09

All the polymers of EG–(PSCl)$_2$ were synthesized by the polymerization of styrene in THF at 130 °C. The molar ratio of the DCAG/CuCl/bPy = 1:3:6, DCAG (1 mmol), styrene (8 mL), THF (4 mL).

[a] The $M_{n,NMR}$ of the line-shaped copolymers was calculated by the Eq. (1).

[b] The T-shaped block copolymers were prepared by the samples.

2.2.4. Synthesis of linear symmetric chlorine free polymer $HOCH_2CH_2OOCCH–PS_2$ (EG–PS$_2$)

The removed of chloro-groups from the polymer was made by following the procedure as described elsewhere [23].

2.2.5. Synthesis of T-shaped block copolymers of HO–PEO–PS$_2$ (PEO–PS$_2$) by living anionic polymerization

0.1 mmol EG–PS$_2$ ($M_{n,NMR} = 14{,}000$ g/mol, 1.40 g,) was transferred into a 150 mL flame-dried Schlenk flask under vacuum. The flask was kept under argon environment before adding freshly distilled THF (50 mL) to dissolve the polymer. DPMK (0.26 mL, 0.11 mmol) was transferred by syringe into the flask and the solution of the mixture was stirred for 24 h at room temperature. The solution was cooled to −40 °C, and then ethylene oxide (EO) ($d = 0.88$ kg/m^3, 1.6 mL, 1.4 g) was added into the flask. Afterwards, the reaction was followed at −40 °C (2 h), 0 °C (2 h), and room temperature (6 h), respectively. The polymerization was terminated by addition of 1 mL deionized water. The polymer was obtained by removing the excess solvent after thorough washing with diethyl ether (3×20 mL), and deionized water (2×20 mL). ^{1}H NMR δ (ppm): 6.30–7.25 [aromatic protons], 4.41–4.44 [$–COOCH_2CH_2O–$], 3.65 [$–OCH_2CH_2O–$], 1.31–1.98 [methylene and methine protons], 1.02–1.08 [$–OOCCH(CH_2–CH(ph)–)_2$], 0.95–0.975 [$–OOCCH(–CH_2–CH(ph)–)_2$]. $M_{n,NMR} = 27{,}600$ g/mol, $M_{n,GPC} = 20{,}900$, $M_w/M_n = 1.14$.

2.2.6. Synthesis of T-shaped macroinitiator PS$_2$–PEO–DCA

Dioxane (50 mL), PEO–PS$_2$ (2.76 g, 0.1 mmol) and pyridine (0.79 g, 10 mmol) were added to a 100 mL three-necked dried flask equipped with a refluxing condenser and a constant pressure dropping funnel under argon atmosphere. The mixture was cooled to 0 °C, and 2,2-dichloro acetyl chloride (1.47 g, 10 mmol) were transferred to the constant pressure dropping funnel under argon atmosphere and added dropwise to the flask over a period of 1 h. The reaction mixture was kept at room temperature for at least 3 h. The solution was passed through a 7 cm neutral alumina chromatography column two times to remove the pyridine hydrochloride. The macroinitiator solution was precipitated into 300 mL petroleum ether (bp 60–90 °C), and the T-shaped macroinitiator was collected by vacuum filtration. The solid product was dried under vacuum at 50 °C for 24 h. Yield of T-shaped macroinitiator, PS$_2$–PEO–DCA was 89%. ^{1}H NMR δ (ppm): 6.30–7.25 [aromatic protons], 6.01 [$Cl_2HCCO–$, 1H], 4.40 [$–COOCH_2CH_2O–$, 2H], 3.65 [$–OCH_2CH_2O–$], 1.31–1.98 [methylene and methine protons], 1.02–1.08 [$–OOCCH(CH_2CH(ph)–)_2$], 0.953–0.954 [$–OOCCH(CH_2CH(ph)–)_2$].

2.2.7. Synthesis of symmetric linear block copolymers (ClPS)–PEO–(PSCl) by ATRP

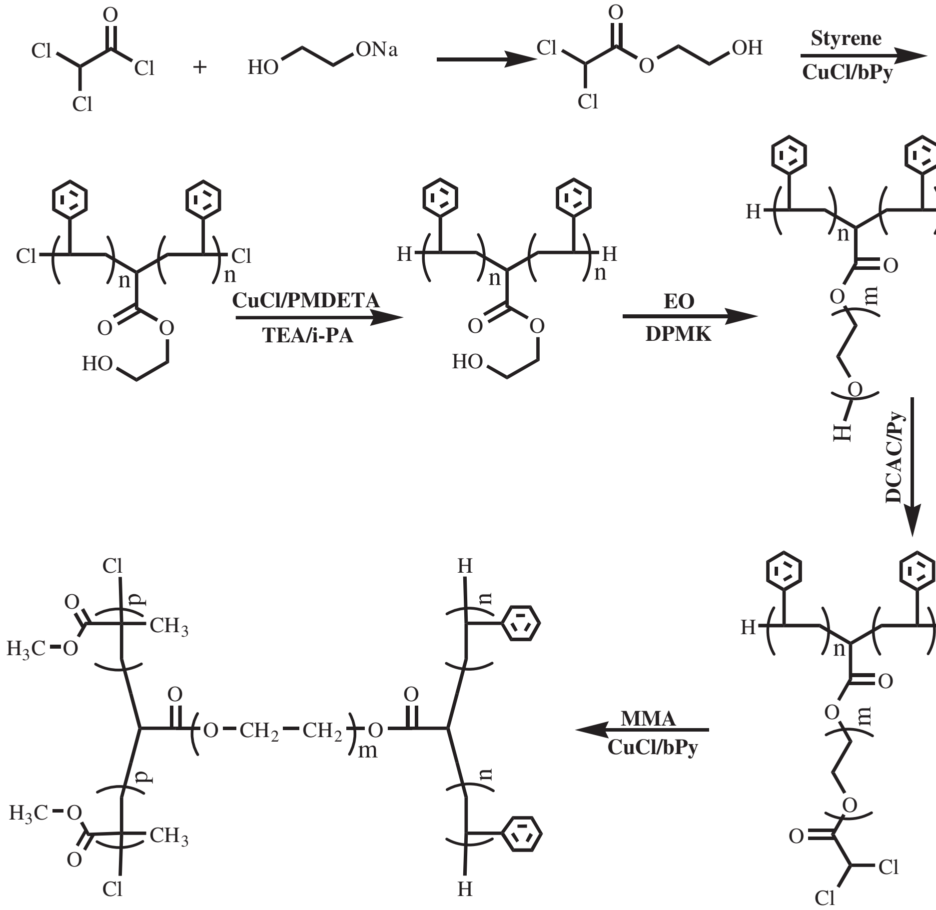
The macroinitiator CA–PEO–CA (0.05 mmol), CuCl (0.0198 g, 0.2 mmol), bPy (0.0937 g, 0.6 mmol), styrene (6.0 mL) and THF (8.0 mL) were added to a 20 mL polymerization tube and the procedure followed like synthesis of EG–(PSCl)$_2$. The reaction was continued for 30 min. The resulted polymer solution was precipitated into 300 mL petroleum ether (bp 60–90 °C), and the polymer was collected by vacuum filtration. The molecular weight of PEO based macrointiator, CA–PEO–CA is 1000 g/mol, M_n(L) = 2400 g/mol, PDI = 1.14.

2.2.8. Synthesis of symmetric H-shaped block copolymers (ClPS)$_2$–PEO–(PSCl)$_2$ and by ATRP

The macroinitiator DCA–PEO–DCA (0.05 mmol), CuCl (0.0198 g, 0.2 mmol), bPy (0.0937 g, 0.6 mmol), styrene (6.0 mL) and THF (8.0 mL) were added to a 20 mL polymerization tube and the procedure followed like synthesis of EG–(PSCl)$_2$. The reaction was continued for 30 min. The resulted polymer solution was precipitated into 300 mL petroleum ether (bp 60–90 °C), and the polymer was collected by vacuum filtration. The molecular weight of PEO based macrointiator, DCA–PEO–DCA is 1000 g/mol, and PDI is 1.04. M_n(H) = 3200 g/mol, PDI = 1.12; The H-shaped of ^{1}H NMR δ (ppm): 6.45–7.08 [aromatic protons], 3.65 [$–OCH_2.CH_2O–$], 1.31–1.98 [methylene and methane protons].

2.2.9. Synthesis of asymmetric H-shaped block copolymer, PS$_2$–PEO–PMMA$_2$ by ATRP

The macroinitiator PS$_2$–PEO–DCA ($M_{n,NMR} = 27{,}600$ g/ mol, 1.380 g, 0.05 mmol), CuCl (0.0198 g, 0.2 mmol), bPy (0.0937 g, 0.6 mmol), MMA (6.0 mL) and THF (8.0 mL) were added to a 20 mL polymerization tube and the procedure followed like synthesis of EG–(PSCl)$_2$. The reaction was continued for 70 min. The resulted polymer solution was precipitated into 300 mL petroleum ether (bp 60–90 °C), and the polymer was collected by vacuum filtration. The solid product was dried under vacuum at 50 °C for 24 h. Yield of the H-shaped asymmetric polymer of PMMA$_2$–PEO–PS$_2$ was 78%. ^{1}H NMR δ (ppm): 6.30–7.25 [aromatic protons], 3.65 [$–OCH_2CH_2O–$], 3.60 [$–OCH_3$],



Scheme 1. The synthesis strategy of the asymmetric H-shaped block copolymer $(PS)_2$–PEO–$(PMMA)_2$.

1.02–1.08 [–OOCC*H*(CH_2–CH(ph)–$)_2$], 0.83–1.98 [methylene and methine protons]. $M_{n,NMR}=41{,}000$ g/mol, $M_{n,GPC}=30{,}000$, $M_w/M_n=1.14$. The data for other asymmetric H-shaped block copolymers PS_2–PEO–$PMMA_2$ are listed in Table 3.

3. Results and discussion

H-shaped block copolymers were synthesized according to Scheme 1. The esterification reaction between DCAC and EG, DCAC and HO–PEO–PS_2, DCAC and PEO, CA and PEO produce versatile macroinitiators, namely DCAG, PS_2–PEO–DCA, DCA–PEO–DCA, CA–PEO–CA, respectively. The chemical structures of resulting initiators were characterized by IR, and H NMR. For example, DCAG, the formation of ester linkage ate 1210 cm^{-1}, and characterizations carbonyl-stretching band of ester at $\nu=1760$ cm^{-1} from FT-IR spectrum (Fig. 1), and peak are ratio of *a*/*b*/*c* from ^{1}H NMR spectroscopy (Fig. 2) confirmed the esterification reaction; thus, all the initiator/macroinitiators have characterization groups to participate in the ATRP reactions (Scheme 2).

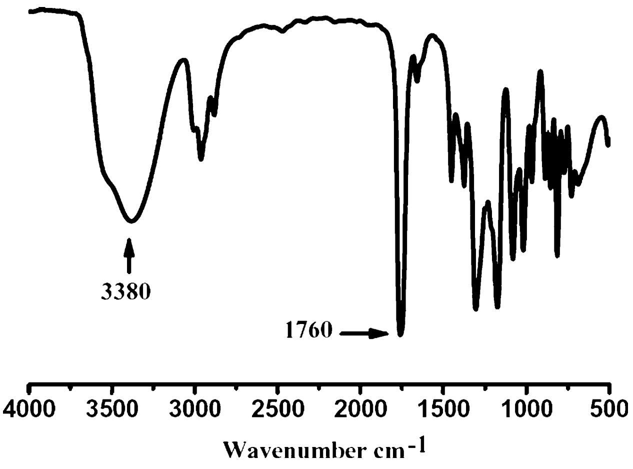


Fig. 1. The FT-IR spectrum of the DCAG.

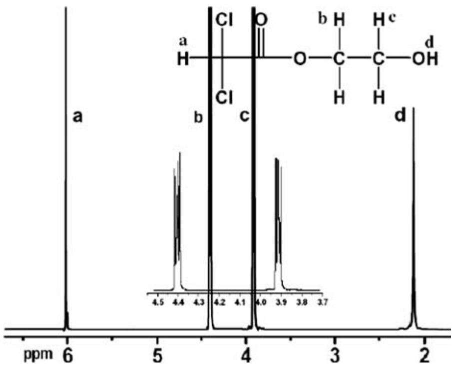
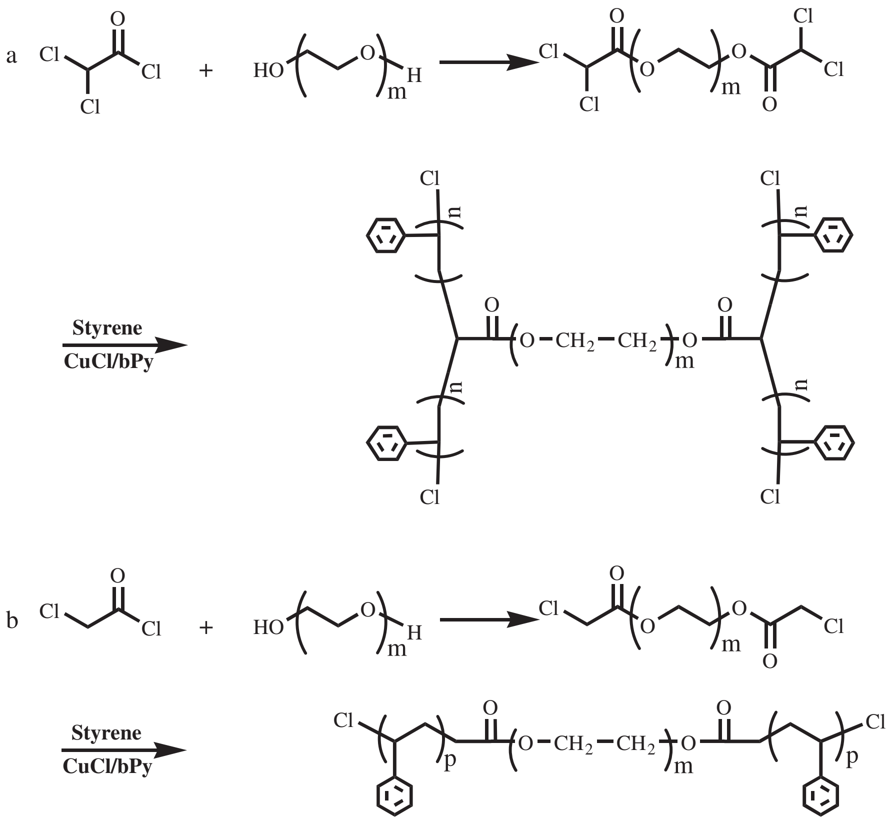


Fig. 2. The ^{1}H NMR spectrum of the DCAG.



Scheme 2. The synthesis strategy of symmetric H-shaped block copolymer, (ClPS)–PEO–(PSCl) and symmetric linear block copolymer, $(ClPS)_2$–PEO–$(PSCl)_2$.

3.1. Synthesis of the linear symmetric polymer, HO–CH_2CH_2-OOCCH–$(PSCl)_2$ by ATRP

The hydroxyl group and the carbonyl group of DCAG do not affect the polymerization of alpha vinyl monomers and thus the DCAG was used as initiator for the ATRP of styrene of CuCl/bPy as catalyst system. The characteristic parameters of the polymers are shown in Table 1. Parts 1–4 of Fig. 3 shows the GPC traces of linear symmetric polymers obtained via the different polymerization time as the other parameters remain constant. All the GPC curves in Fig. 3 are single and symmetrical, and those indicate that the pure linear symmetric polymers were obtained by ATRP. The ^{1}H NMR spectrum of the polymers included as Fig. 4. The ^{1}H NMR spectrum further confirms the structure of the polymers. The data of ^{1}H NMR spectrum indicates that the initiator of DCAG has two active species at the same alpha carbon atom, and the two active species initiate the ATRP of styrene using the CuCl/bPy as catalyst system at the same time, respectively. The molecule weight $M_{n,NMR}$, was calculated according to the Eq. (1).

$$M_{n,NMR} = [(I_a + I_b)/5]/(I_d/2)M_{St} + M_{DCAG} \quad (1)$$

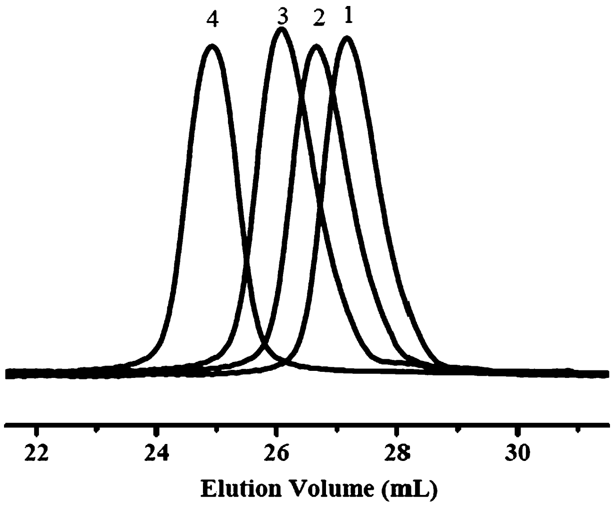


Fig. 3. GPC traces of the linear symmetric polymers EG–$(PS)_2$.

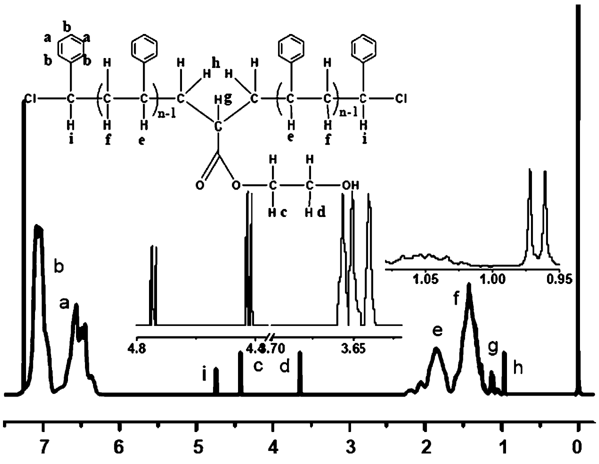


Fig. 4. The ^{1}H NMR spectrum of the linear symmetric polymer EG–$(PSCl)_2$.

Table 2
Summary of molecular weight date for the T-shaped polymers of HO–PEO–$(PS)_2$ by living anionic polymerization using DPMK as an initiator

No.	Sample	$M_{n,th}$[a]	$M_{n,NMR}$[b]		$M_{n,GPC}$	PDI
			$M_{n,PS}$	$M_{n,PEO}$		
5[c]	HO–PEO1–$(PS1)_2$	28,000	14,000	13,600	20,900	1.14
6[c]	HO–PEO2–$(PS2)_2$	37,000	18,500	17,100	35,600	1.16

All the polymers of HO–PEO1–$(PS1)_2$ was synthesized by EG–$(PS)_2$ initiated the polymerization of EO in THF using DPMK as the initiator. The ratio of DPMK and active species is 1.1. All the procedures for the anionic polymerization were carried out under absolutely anhydrous and degassed oxygen.

[a] $M_{n,th}$ was calculated by the integration ratio of the groups ($-OCH_2CH_2O-$) of PEO and the groups ($-OCH_3$) of PMMA in ^1H NMR.

[b] The proportion of the PEO and PS No. 5 and 6 was calculated by the integration ratio of the groups ($-OCH_2CH_2O-$) of PEO and the groups ($-OCH_3$) of PMMA in ^1H NMR, The $M_{n,NMR}$ of the T-shaped copolymers was calculated by the Eq. (2).

[c] The asymmetric H-shaped block copolymers were prepared by the polymers.

where, I_a+I_b is the integral of aromatic protons of benzene; I_d is the integral of the methylene protons of ethylene glycol at $\delta=3.63$–3.65 (d, HO–CH_2–); M_{St} is the molar mass of styrene, M_{DCAG} is the molecule weight of the DCAG. Herein, we define $N_{PS}=[(I_a+I_b)/5]/(I_d/2)$, i.e. the polymerization degree of polystyrene; $M_0=M_{DCAG}=173$ g/mol, i.e. constant.

3.2. Removal of terminal chlorine atoms from EG–$(PSCl)_2$

To synthesize the asymmetric H-shaped block copolymers the active species of EG–$(PSCl)_2$ was terminated by ATRP. An alternative approach to replace the chlorine termini with hydrogen atoms was reported by Bednarek et al. [23b]. The excess PMDETA was employed during ATRP, as the ligand can act as a radical chain transfer agent under monomer-starved conditions. The reaction had been successfully employed for the synthesis of halogen-free macromonomers [23]. The 10:1 molar ratio for PMDETA and CuCl was employed to terminate the chlorine atoms of EG–$(PSCl)_2$ with the hydrogen atoms.

3.3. Synthesis of the T-shaped block copolymers of HO–PEO–PS_2 (EG–PS_2) by living anionic polymerization

The polymer EG–PS_2 was used as the initiator of precursors for the anionic polymerization. Under absolutely anhydrous and degassed oxygen, the terminal hydroxyl groups were full deprotonated by DPMK as shown in Scheme 1. If the tendency to precipitate for the deprotonated EG–PS_2 in organic medium removed, the excess THF is very necessary during the procedure of anionic polymerization. After adding the DPMK to the reaction system, the solution turned pale yellow. The system turned colorless as the ethylene oxide introduced, and the viscosity increased with the growth of PEO blocks.

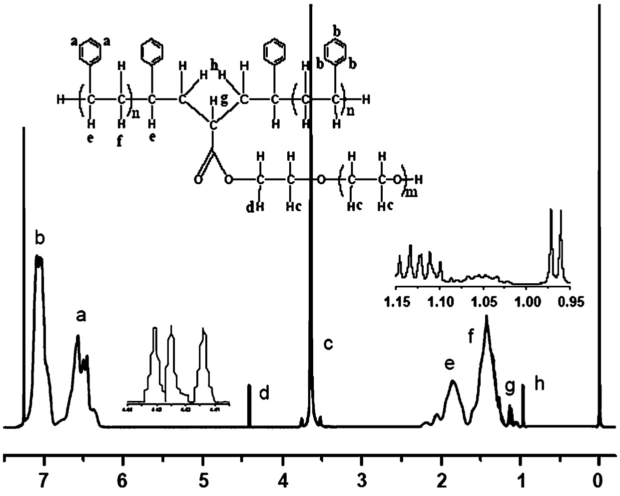


Fig. 6. The ^1H NMR spectrum of the T-shaped block copolymer HO–PEO–$(PS)_2$.

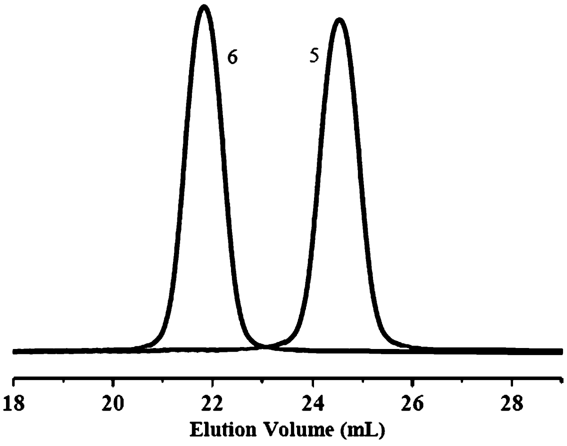


Fig. 5. GPC traces of the T-shaped block copolymers PEO–PS_2.

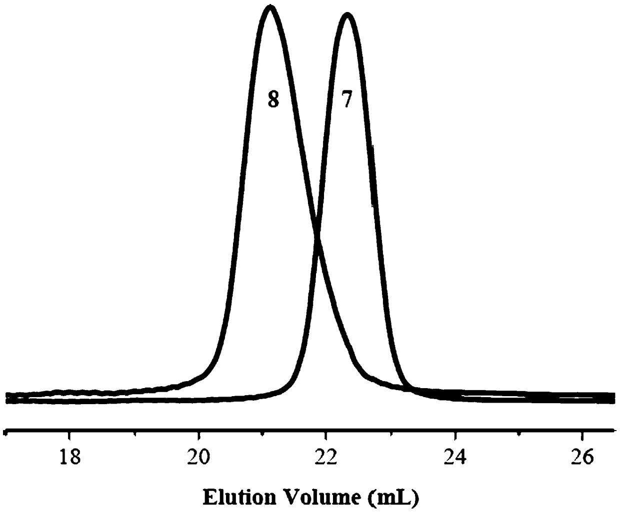


Fig. 7. GPC traces of the asymmetric H-shaped block copolymers $(PS)_2$–PEO–$(PMMA)_2$.

Table 3
Summary of molecular weight asymmetric H-shaped block copolymers $(PS)_2$–PEO–$(PMMA)_2$ by ATRP using $(PS)_2$–PEO–DCA as an initiator

No.	Sample	Time (min)	$M_{n,NMR}$[a]			$M_{n,GPC}$	PDI
			$M_{n,PS}$	$M_{n,PEO}$	$M_{n,PMMA}$		
7	$(PS1)_2$–PEO1–$(PMMA1)_2$	70	14,000	13,600	13,400	30,000	1.14
8	$(PS2)_2$–PEO2–$(PMMA2)_2$	90	18,500	17,100	17,600	39,000	1.16

All the polymers of $(PS)_2$–PEO–$(PMMA)_2$ were synthesized by the polymerization of MMA in THF at 130 °C. The molar ratio of the macroinitiator/CuCl/bPy = 1:4:12, macroinitiator (0.05 mmol), MMA (6 mL), THF (8 mL).

[a] The proportion of the PEO, PS and PMMA in the No. 8 and 9 was calculated by the ratio of its' integral in ^1H NMR, The $M_{n,NMR}$ of the H-shaped copolymers was calculated by the Eq. (3).

The characterization of the corresponding T-shaped block copolymer is shown in Table 2. Parts 5 and 6 of Fig. 5 shows the GPC traces of T-shaped miktoarm polymers obtained by the molar ratio of the EO and the initiator (Fig. 6). The GPC curves in Fig. 7 are single and symmetrical, and those indicate that the pure T-shaped miktoarm polymers of HO–PEO–PS_2 were obtained by ATRP. The ^1H NMR spectrum of T-shaped polymers included as Fig. 4. The fine conformation was determined by ^1H NMR spectrum. The molar ratio of the blocks and the actual $M_{n,NMR}$ were calculated by the Eq. (2).

$$M_{n,NMR} = (I_c/4)/[(I_a + I_b)/5]N_{PS}M_{EO} + M_{PS} \qquad (2)$$

where, I_a, I_b is the integral of aromatic protons of benzene; I_c is the integral of the chain segment of PEO protons; M_{EO} is the molar mass of ethylene oxide; N_{PS} and M_{PS} are same as in Eq. (1).

3.4. Synthesis of the asymmetric H-shaped block copolymers PS_2–PEO–$PMMA_2$ by ATRP

In the reaction of macroinitiator, PS_2–PEO–DCA, DCAC and pyridine form a complex compound $[Cl_2CHCO]^+[C_5H_5NCl]^-$, which accelerates the esterification reaction. PS_2–PEO–$PMMA_2$ was produced by ATRP of MMA using macroinitiator, PS_2–PEO–DCA as initiator and CuCl/bPy as catalyst system. The characterization parameters are listed in Table 3. The GPC traces of the resulting copolymers No. 7 and 8 in Fig. 7 are single, symmetrical and narrow distribution, those indicated that all the polymers are narrow distribution of molecular weight, i.e. we have obtained the designed pure copolymers. The ^1H NMR spectrum of copolymer thus obtained is shown in Fig. 8. The molar ratio of the blocks and the actual $M_{n,NMR}$ were calculated by the Eq. (3) (Fig. 9).

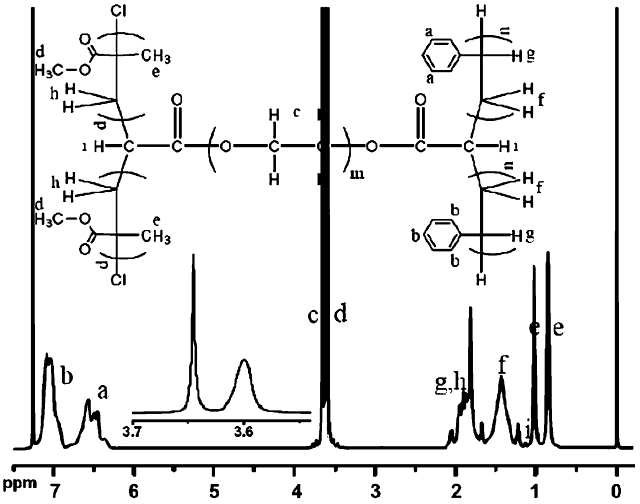


Fig. 8. The ^1H NMR spectrum of the asymmetric H-shaped block copolymer $(PS)_2$–PEO–$(PMMA)_2$.

$$M_{n,NMR} = (I_d/3)/[(I_a + I_b)/5]N_{PS}M_{MMA} + M_{PEO} + M_{PS} \qquad (3)$$

where I_d is the integral of CH_3O– protons of the chain segment PMMA; M_{MMA} is the molar mass of MMA; the other parameters have been defined previously. The $M_{n,GPC}$ of each block (PS, PEO and PMMA) was calculated by the molar ratio that was confirmed by the Eq. (3) (Table 4).

In those polymerization, both of the molar ratio of the initiator/CuCl/bPy = 1:3:6, and initiator (1 mmol), styrene (8 mL), THF (4 mL). The polymerization time of both is 30 min. Here, the degree of polymerization of H-shaped polymer is about equal to twice of linear block polymer.

The kinetics of ATRP is discussed previous using copper-mediated ATRP [13b,j], and the rate law for ATRP can be derived as follows.

$$R_p = k_p[M][I]_0 = k_pK_{ep}[M][I]_0[Cu^I]/[X-Cu^{II}]$$

According to the rate law and the relation of the degree of polymerization of H-shape and linear polymers, so the difunctional initiator of DCAG is proved and the H-shape architectures are accurate.

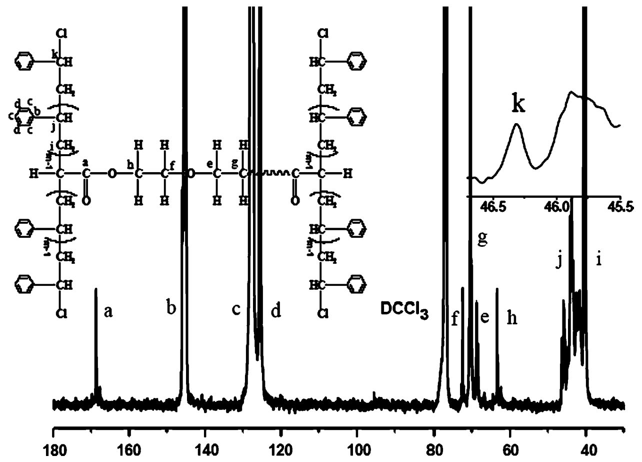


Fig. 9. The ^{13}C NMR spectrum of the symmetric H-shaped block copolymer $(ClPS)_2$–PEO–$(PSCl)_2$.

Table 4
Summary of molecular weight date for the H-shaped polymer of (ClPS)–PEO–(PSCl), and the linear shaped polymer of $(ClPS)_2$–PEO–$(PSCl)_2$

No.	Sample	Time (min)	$M_{n,GPC}$[a]	PDI
9	$(PS5)_2$–PEO3–$(PS5)_2$	30	3300	1.12
10	(PS6)–PEO3–(PS6)	30	2400	1.14

[a] Both of the molar ratio of the initiator/CuCl/bPy = 1:3:6, and initiator (1 mmol), styrene (8 mL), THF (4 mL). The polymerization time of both is 30 min. Here, the degree of polymerization of H-shaped polymer is about equal to twice of linear block polymer.

4. Conclusion

In this paper, a new asymmetric H-shaped block copolymer of $PMMA_2$–PEO–PS_2 has been designed and successfully synthesized by the combination of ATRP and living AP. The sidearms of the asymmetric H-shaped could be substituted by the other polymers, which will yield the different polymers with the corresponding properties. The symmetric linear ($HOCH_2CH_2OOCCH$–$(PS–Cl)_2$) was prepared by ATRP using the difunctional initiator DCAG and CuCl/bPy as the catalyst system. The T-shaped macroinitiator (Cl_2CHCOO–PEO–PS_2) was synthesized and used to initiate the polymerization of MMA by ATRP to yield the asymmetric H-shaped block copolymers $PMMA_2$–PEO–PS_2. To ensure complete reaction of the ended hydroxyl group of HO–PEO–PS_2 with the DCAC, the excess of 2,2-dichloro acetate is very necessary during the process of esterification reaction. The structures of DCAG and Cl_2CHCOO–PEO–PS_2 were confirmed by the data of those ^1H NMR. The molecular weights of the all polymers were verified by the data of ^1H NMR and GPC. The structures of the copolymers synthesized along the process have been examined by the ^1H NMR and GPC. The results show that the designed asymmetric H-shaped copolymer of $(PMMA)_2$–PEO–(PS_2) has been successfully synthesized by the controlled polymerizations.

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References

[1] (a) Gido SP, Lee C, Pochan DJ, Pispas S, Mays JW, Hadjichristidis N. Macromolecules 1996;29:7022–8.
(b) Li YG, Shi PJ, Pan CY. Macromolecules 2004;37:5190–5.
[2] Shie SC, Wu CT, Hua CC. Macromolecules 2003;36:2141–8.
[3] Perny S, Allgaier J, Cho D, Lee W, Chang T. Macromolecules 2001;34:5408–15.
[4] (a) Ball RC, McLeish TCB. Macromolecules 1989;22:1911–3.
(b) McLeish TCB, Allgaier J, Bick DK, Bishko G, Biswas P, Blackwell R, et al. Macromolecules 1999;32:6734–58.
(c) Radke W, Gerber J, Wittmann G. Polymer 2003;44(3):519–25.
(d) Moon B, Hoye TR, Macosko CW. Polymer 2002;43(20):5501–9.
(e) Wang X, Zhang H, Zhong G, Wang X. Polymer 2004;45(11):3637–42.
(f) Chatterjee U, Jewrajka SK, Mandal BM. Polymer 2005;46(24):10699–708.
(g) Yuan X, Lu J, Xu Q, Wang L. Polymer 2005;46(21):9186–91.
[5] (a) Lipic PM, Bates FS, Hillmyer MA. J Am Chem Soc 1998;120:8963–70.
(b) Garcia CBW, Zhang YM, Mahajan S, DiSalvo F, Wiesner U. J Am Chem Soc 2003;125:13310–1.
[6] (a) Batsberg W, Ndoni S, Trandum C, Hvidt S. Macromolecules 2004;37:2965–71.
(b) Lei L, Gohy J, Willet N, Zhang J, Varshney S, Jérôme R. Macromolecules 2004;37:1089–94.
[7] (a) Zhou Q, Fan X, Xia C, Mays J, Advincula R. Chem Mater 2001;13:2465–7.
(b) Harrak AE, Carrot G, Oberdisse J, Eychenne-Baron C, Boué F. Macromolecules 2004;37:6376–84.
[8] Xu H, Erhardt R, Abetz V, Müller AHE, Goedel WA. Langmuir 2001;17:6787–93.
[9] Ishizu K, Uchida S. Prog Polym Sci 1999;24:1439–80.
[10] Kong X, Kawai T, Abe J, Iyoda T. Macromolecules 2001;34:1837–44.
[11] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. Chem Rev 2001;101:3747–92.
[12] (a) Yan D, Jiang H, Dong H, Müller AHE. Macromolecules 1996;29(15):5065–71.
(b) Yan D, Dong H, Ye P, Müller AHE. Macromolecules 1996;29(25):8057–63.
[13] (a) Kamigaito K, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745.
(b) Matyjaszewski K, Xia J. Chem Rev 2001;101:2921–90.
(c) Xu K, Wang Y, Bai R, Lu W, Pan CY. Polymer 2005;46(18):7572–7.
(d) Sun X, Zhang H, Huang X, Wang X, Zhou QF. Polymer 2005;46(14):5251–7.
(e) Raghunadh V, Baskaran D, Sivaram S. Polymer 2004;45(10):3149–55.
(f) Zhang H, Jiang X, van der Linde R. Polymer 2004;45(5):1455–66.
(g) Huang CF, Lee HF, Kuo SW, Xu H, Chang FC. Polymer 2004;45(7):2261–9.
(h) Kurjata J, Chojnowski J, Yeoh CT, Rossi NAA, Holder SJ. Polymer 2004;45(18):6111–21.
(i) Wang G, Shi Y, Fu Z, Yang W, Huang Q, Zhang Y. Polymer 2005;46(23):10601–6.
(j) Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614–5.
[14] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661–88.
[15] (a) Rizzardo E, Chiefari J, Chong BYK, Ercole F, Krstina J, Jeffery J, et al. Macromol Symp 1999;143:291–307.
(b) Destarac M, Charmot D, Franck X, Zard SZ. Macromol Rapid Commun 2000;21:1035–9.
(c) Calitz FM, McLeary JB, McKenzie JM, Tonge MP, Klumperman B, Sanderson RD. Macromolecules 2003;36(26):9687–90.
(d) Adamy M, van Herk AM, Destarac M, Monteiro MJ. Macromolecules 2003;36(7):2293–301.
(e) Tsavalas JG, Schork FJ, de Brouwer H, Monteiro MJ. Macromolecules 2001;34:3938–46.
(f) Monteiro MJ, de Barbeyrac J. Macromolecules 2001;34:4416–23.
[16] (a) Baek KY, Kamigaito M, Sawamoto M. J Polym Sci, Part A: Polym Chem 2002;40:633–41.
(b) Li M, Jahed NM, Min K, Matyjaszewski K. Macromolecules 2004;37(7):2434–41.
(c) Tao L, Luan B, Pan CY. Polymer 2003;44(4):1013–20.
[17] Higashihara T, Nagura M, Inoue K, Haraguchi N, Hirao A. Macromolecules 2005;38(11):4577–87.
[18] (a) Schappacher M, Billaud C, Paulo C, Deffieux A. Macromol Chem Phys 1999;200:2377–86.

(b) Uhrig D, Mays JW. Macromolecules 2002;35:7182–90.
(c) Mijović J, Sun M, Pejanović S, Mays JW. Macromolecules 2003;36: 7640–51.

[19] (a) Washio I, Shibasaki Y, Ueda M. Macromolecules 2005;38(6):2237–46.
(b) Lepoittevin B, Matmour R, Francis R, Taton D, Gnanou Y. Macromolecules 2005;38(8):3120–8.
(c) Matsuo A, Watanabe T, Hirao A. Macromolecules 2004;37(17): 6283–90.

[20] (a) Tao L, Luan B, Pan CY. Polymer 2003;44:1013–20.
(b) Yuan J, Pan CY, Tang B. Macromolecules 2001;34:211–4.
(c) Feng X, Pan CY. Macromolecules 2002;35:4888–93.
(d) Johnson RM, Fraser CL. Macromolecules 2004;37:2718–27.
(e) Celik C, Hizal G, Tunca U. J Polym Sci, Part A: Polym Chem 2003; 41:2542–8.
(f) Lutz JF, Neugebauer D, Matyjaszewski K. J Am Chem Soc 2003;125: 6986–93.
(g) Tong JD, Zhou CL, Ni SR, Winnik MA. Macromolecules 2001;34: 696–705.

[21] (a) Roovers J, Toporowski PM. Macromolecules 1981;14:1174–8.
(b) Avgeropoulos A, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 1997;35:813–6.
(c) Velis G, Hadjichristidis N. Macromolecules 1999;32:534–6.
(d) Iatrou H, Mays JW, Hadjichristidis N. Macromolecules 1998;31: 6697–701.
(e) Paraskeva S, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2000;38:931–5.
(f) Beyer FL, Gido SP, Buschl C, Iatrou H, Uhrig D, Mays JW, et al. Macromolecules 2000;33:2039–48.

[22] (a) Normant H, Angelo B. Bull Soc Chim Fr 1960;354.
(b) Francis R, Taton D, Logan JL, Masse P, Gnanou Y, Duran RS. Macromolecules 2003;36:8253–9.

[23] (a) Schön F, Hartenstein M, Müller AHE. Macromolecules 2001;34: 5394–7.
(b) Bednarek M, Biedron T, Kubisa P. Macromol Chem Phys 2000;201: 58–66.
(c) Cai Y, Hartenstein M, Müller AHE. Macromolecules 2004;37: 7484–90.
(d) Cai Y, Armes SP. Macromolecules 2005;38(2):271–9.