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Synthesis of symmetric H-shaped block copolymer by the combination of ATRP and living anionic polymerization

Xifei Yu [a,b], Guo Zhang [a,*], Tongfei Shi [b], Yanchun Han [b], Lijia An [b,**]

[a] *College of Chemistry, Ministry of Education Key Laboratory of Automobile Materials, Jilin University, Changchun 130012, PR China*
[b] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*

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Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

A novel fluorescent dye labeled H-shaped block copolymer, $(PMMA\text{-}Fluor\text{-}PS)_2\text{-}PEO\text{-}(PS\text{-}Fluor\text{-}PMMA)_2$, is synthesized by the combination of atom transfer radical polymerization (ATRP) and anionic polymerization (AP). To obtain the designated structure of the copolymer, a macroinitiator, 2,2-dichloro acetyl-PEO-2,2-dichloro acetyl (DCA-PEO-DCA), was prepared from DCAC and poly(ethylene oxide). The copolymer was characterized by ^1H NMR, GPC and fluorescence spectroscopy.

Keywords: Atom transfer radical polymerization; Anionic polymerization; H-shaped block copolymer

1. Introduction

Polymers with well-designed structures are generally prepared by controlled polymerization methods [1–4], which can yield polymers with precisely defined molecular weight, polydispersity, and terminal functionalities. These methods include: living anionic polymerization (AP) [2,5], atom transfer radical polymerization (ATRP) [1,6], nitroxide-mediated polymerization (NMP) [3], reversible addition-fragmentation chain transfer (RAFT) [7], and combinations of these methods [8–10]. Star-shaped polymers are interesting macromolecules due to their spatial architectural shapes, and those have been synthesized by several methods, which include living polymerization with a multifunctional initiator [11,12], coupling of living linear polymers with a multifunctional coupling agent (terminator) [13,20], and the linking of living linear polymers by reaction with difunctional or multifunctional vinyl compounds [14] via microgel formation. Controlled polymerization is a versatile effective method to synthesizing complex polymers with interesting properties [15].

Functionalized multiarm block copolymers have been studied extensively because of their interesting behaviors [16,17], like microphase separation in different states to the bulk behavior, phase structures, and morphologies. This understanding inspires us to design an H-shaped copolymer labeled fluorescent dyes, $(PMMA\text{-}Fluor\text{-}PS)_2\text{-}PEO\text{-}(PS\text{-}Fluor\text{-}PMMA)_2$, and to study its properties. The fluorescent dyes behave like the direct nonradiative energy transfer (DET) [18] between donors and acceptors in an efficient way to the interface of the incompatible polymers. Recently, the H-shaped copolymers, $(PS)_2\text{-}PEO\text{-}(PS)_2$, have been successfully synthesized by Hadjichristidis' groups, Hizal's groups and Pan's groups et al. [19], and an asymmetric H-shaped block copolymer, $(PS)_2\text{-}PEO\text{-}(PMMA)_2$, and a double H-shaped amphiphilic block copolymer, $(PMMA)_2\text{-}PEO\text{-}(PS)_2\text{-}PEO\text{-}(PMMA)_2$, has been successfully synthesized by Yu et al. [21]. Anionic polymerization is the most effective method to make a labeled polymer, and ATRP provides a very easy approach to obtain complex H-shaped polymers with well-defined molecular weight and low polydispersity. Combinations of AP with other polymerization methods have created

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* Corresponding author.
** Corresponding author.
E-mail addresses: guozhang@jlu.edu.cn (G. Zhang), ljan@ciac.jl.cn (L. An).

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a new horizon for the synthesis of more predictable macromolecular architecture and more complex polymers.

2. Experimental 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 above purchased from the China Medicine Group, Shanghai Chemical Reagent Co. Styrene (Beijing Chemical Factory, 99.5%) and methyl methacrylate (Beijing Chemical Factory, 99.5%) were washed with 5% sodium hydroxide aqueous solution for three times, followed by water washes to neutrality, and then dried with anhydrous magnesium sulfate overnight and calcium hydroxide for 72 h. The monomers were distilled under reduced pressure to sealed ampules and stored in a refrigerator prior to use. Anthracene (Beijing Chemical Factory, 98%) and 9-bromophenanthrene (Aldrich, 99%) were used without further purification. THF (99.5%) and *n*-hexane (99.5%) were refluxed and distilled over sodium benzophenone to a purple color. Triethylaluminium (Aldrich, 99%) was diluted with *n*-hexane to 2% (v/v) and sealed in ampules prior to use. Poly(ethylene oxide) ($M_n = 20{,}000$ g/mol, PDI = 1.06, The Shanghai First Chemical Reagent Co.) was freed of water by azeotropic distillation using benzene. Anionic polymerizations were carried out under argon atmosphere in a flame-dried glass reactor equipped with a vacuum line; the solvent, initiator, and monomer were transferred to the reactor through stainless steel cannula or a syringe. ATRP polymerizations 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 at 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 410 GPC equipped with Waters Styragel HT6E column and Waters RI detector at 35 °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 fluorescence spectra were produced on a Shimadzu RF-5301 PC Spectrofluorophotometer. The UV–vis spectra were produced on a Shimadzu UV-2450 Spectrofluorophotometer.

2.3. Synthesis of 1-(9-phenanthryl)-1-phenylethylene and 1-(2-anthryl)-1-phenylrthylene

The fluorescent dye molecule, 1-(9-phenanthryl)-1-phenylethylene (PPE) and 1-(2-anthryl)-1-phenylrthylene (APE), was synthesized and purified following a procedure reported in the literature [18a,20]. ^{1}H NMR δ (ppm): PPE, 8.73–7.21 [aromatic, 14H], 6.02 [$=CH_2$, 1H], 5.49 [$=CH_2$, 1H] and APE, 8.39–7.35 [aromatic, 14H], 5.67 [$=CH_2$, 1H], 5.56 [$=CH_2$, 1H].

2.4. Synthesis of macroinitiator: 2,2-dichloro acetate-PEO-2,2-dichloro acetate (DCA-PEO-DCA)

40.0 g PEO ($M_n = 20{,}000$ g/mol, PDI = 1.06, 2 mmol), 140 mL of anhydrous methylene chloride, and 7.9 g (100 mmol) of anhydrous pyridine were added into a 250 mL dry three-necked flask equipped with a refluxing condenser and a constant pressure dropping funnel under argon atmosphere. When the PEO was dissolved completely, the flask was cooled into an ice-water bath, and then 14.6 g of (100 mmol) 2,2-dichloro acetyl chloride was transferred to the constant pressure dropping funnel under argon atmosphere and added dropwise into the flask over a period of 1 h. The reaction mixture was warmed and kept at room temperature for additional 3 h at least, and refluxed for 12 h. The mixture was filtered to remove the $C_5H_5NH^+Cl^-$, and the filtrate was passed through a 10 cm neutral alumina chromatography column (length diameter ratio, 10:1 cm) at least three times. The resulted solution was precipitated into 300 mL of anhydrous diethyl ether, and filtered. The product obtained was dried under vacuum at 50 °C for 24 h. The yield of the macroinitiator, DCA-PEO-DCA, was 83%. ^{1}H NMR δ (ppm): 6.01 [$Cl_2\mathit{H}CCO-$, 1H], 4.43 [$-COOC\mathit{H_2}CH_2-$, 2H], 3.63 [$-OC\mathit{H_2}C\mathit{H_2}O-$, 900H]. $M_{n,NMR} = 20{,}000$ g/mol.

2.5. Synthesis of H-shaped block copolymers: $(ClPS)_2$-PEO-$(PSCl)_2$

The procedure for synthesis of sample No. 1 (see Table 1) is given here as an example. 0.40 g (0.02 mmol) of macroinitiator, DCA-PEO-DCA ($M_{n,NMR} = 20{,}000$ g/mol), 0.049 g (0.50 mmol) of CuCl, 0.418 g (0.30 mmol) of bPy, 5.0 mL of styrene, and 2.0 mL of THF were added into a 20 mL polymerization tube which was degassed to remove oxygen by three or more freeze–vacuum–thaw cycles. The tube was sealed under vacuum and no leakage was detected. The mixture was heated at 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 at least three times to remove the copper salt and the bPy. The polymer solution was precipitated into 200 mL petroleum ether (b.p. 30–60 °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 block copolymer, $(ClPS)_2$-PEO-$(PSCl)_2$, was 67%. ^{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]. $M_{n,NMR} = 104{,}000$ g/mol, $M_{n,GPC} = 88{,}000$, $M_w/M_n = 1.12$. The data for other $(ClPS)_2$-PEO-$(PSCl)_2$ copolymers are listed in Table 1.

Table 1
Synthesis of H-shaped $(PS1)_2$-PEO-$(PS1)_2$ polymers by ATRP using DCA-PEO-DCA as macroinitiator[a]

No.	Sample	Time (h)	$M_{n,NMR}$[b]	$M_{n,GPC}$	PDI
PEO				20,000	1.06
1[c]	$(PS1)_2$-PEO-$(PS1)_2$	4	104,000	88,000	1.12
2	$(PS2)_2$-PEO-$(PS2)_2$	5	116,000	96,000	1.10
3	$(PS3)_2$-PEO-$(PS3)_2$	6	126,000	113,000	1.08
4	$(PS4)_2$-PEO-$(PS4)_2$	7	137,000	117,000	1.09
5	$(PS5)_2$-PEO-$(PS5)_2$	8	142,000	129,000	1.12
6	$(PS6)_2$-PEO-$(PS6)_2$	9	153,000	138,000	1.15
7[c]	$(PS7)_2$-PEO-$(PS7)_2$	14	202,000	182,000	1.07

[a] All the polymers of $(PS)_2$-PEO-$(PS)_2$ were synthesized by the ATRP of styrene in THF at 130 °C. The molar ratio of the DCA-PEO-DCA:CuCl:bPy = 1:5:15, DCA-PEO-DCA ($M_{n,NMR} = 20{,}000$ g/mol, 0.4 g, 0.02 mmol), styrene (5 mL), THF (2 mL, Nos. 1–6; 10 mL, No. 7). The $M_{n,NMR}$ of macroinitiator, DCA-PEO-DCA, can be calculated by Eq. (1)

$$M_{n,NMR} = [(I_c/4)/(I_a/2)] \times 44.05 + 111.93 \times 2 + 16.00 \tag{1}$$

where the number 44.05 is the molar mass of the group $-CH_2OCH_2-$; the number 111.93 is the molar mass of the group Cl_2HCCO-; the number 16.00 is the atomic weight of oxygen; $(I_c/4)/(I_a/2) = 450 = N_{PEO}$ is the effective number of ethylene oxide repeat unit in the macroinitiator, DCA-PEO-DCA (as determined by ^1H NMR).

[b] The $M_{n,NMR}$ of the obtained copolymer, $(ClPS)_2$-PEO-$(PSCl)_2$ was calculated by Eq. (2)

$$M_{n,NMR} = [(I_a + I_{a'})/5]/(I_b/4) \times N_{PEO} \times 104.15 + 20{,}000 \tag{2}$$

where, $I_a + I_{a'}$ is the integral of aromatic protons of benzene; I_b is the integral of the chain segment of PEO protons; 104.15 is the molar mass of styrene, 20,000 is the $M_{n,NMR}$ of DCA-PEO-DCA (for N_{PEO} see the Eq. (1)).

[c] The ended polymers were prepared by the samples.

2.6. Synthesis of fluorescent labeled H-shaped block copolymers: (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$

The procedure for synthesis of sample No. 9 (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ block copolymer is given here as an example. The other polymers are shown in Table 2. 2.02 g (0.01 mmol) of macroinitiator, $(ClPS)_2$-PEO-$(PSCl)_2$, No. 7 ($M_{n,NMR} = 202{,}000$ g/mol), 0.5 g of lithium, and 3 mL of triethylaluminium solution (diluted by *n*-hexane to 2% v/v) were transferred into a flame-dried Schlenk flask with 28/15 spherical o-ring joint glass equipped with a high vacuum line (10^{-4} Pa). The mixture was cooled to 5 °C, and then THF (50.0 mL) was added to the Schlenk flask and was allowed to react for 5 h. The mixture was cooled to −78 °C, and then 5 mL (0.01 mol/L) of 1-(9-phenanthryl)-1-phenylethylene in THF was added into the flask. After 10 min, MMA (0.76 g, 0.81 mL, 7.3 mmol) was added, and the reaction was allowed to proceed for 3 h. The polymerization was terminated by addition of 1 mL methanol. The polymer solution was warmed to room temperature and passed through a neutral alumina column twice to remove the lithium salt and then precipitated into 300 mL petroleum ether (b.p. 30–60 °C). The solid product was dried under vacuum at 50 °C for 24 h, and the designed H-shaped block copolymer, (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ was obtained. ^1H NMR δ (ppm): 6.45–7.08 [aromatic protons], 3.65 [$-OCH_2CH_2O-$], 3.60 [$-OCH_3$], 1.31–1.98 [methylene and methane protons], 0.834–1.02 [$-CH_3$]. $M_{n,NMR} = 278{,}000$, $M_{n,GPC} = 258{,}000$, $M_w/M_n = 1.16$.

3. Results and discussion

Scheme 1 shows the synthesis route for the designed H-shaped block copolymers. The macroinitiator, DCA-PEO-DCA, was synthesized by esterification between PEO and DCAC catalyzed by pyridine. DCAC and pyridine form a complex compound $[Cl_2CHCO]^+[C_5H_5NCl]^-$ to accelerate the esterification reaction. The ^1H NMR spectrum of the macroinitiator is shown in Fig. 1A. The chemical shifts and the intensities of the respective peaks of the compound are: 6.01 [Cl_2HCCO, 1H] $I_a = 0.099$; 4.43 [$COOCH_2$, 2H], $I_b = 0.205$; 3.63 [$-OCH_2CH_2O-$, 900H], $I_c = 89.114$. $I_a:I_b = 0.483 \approx 1:2$. The presence of the resonance peaks at 6.01 and 4.33 clearly indicates the formation of the macroinitiator.

The H-shaped block copolymer, $(ClPS)_2$-PEO-$(PSCl)_2$, was synthesized by ATRP [21]. The characteristic parameters of these copolymers are shown in Table 1. For example, the copolymer No. 7 was synthesized with 10 mL THF for 14 h. The mixture becomes solid if no THF is added. At this stage the reaction passes through a heterogeneous stage and PEO forms the complex with the copper ion, and thus, affects the measurement results of GPC. The resulted polymer was passed through neutral alumina chromatography column to completely remove the copper salt. The ^1H NMR spectrum of

Table 2
Synthesis of H-shaped (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ polymers by AP[a]

No.	Sample	$M_{n,th}$[b]	$M_{n,NMR}$[c]			$M_{n,GPC}$	PDI
			$M_{n,PEO}$	$M_{n,PS}$	$M_{n,PMMA}$		
8	(PMMA1-*b*-PS1)$_2$-PEO-(PS1-*b*-PMMA1)$_2$	180,000	20,000	84,000	76,000	161,000	1.19
9	(PMMA1-*b*-PS7)$_2$-PEO-(PS7-*b*-PMMA1)$_2$	278,000	20,000	182,000	76,000	258,000	1.16

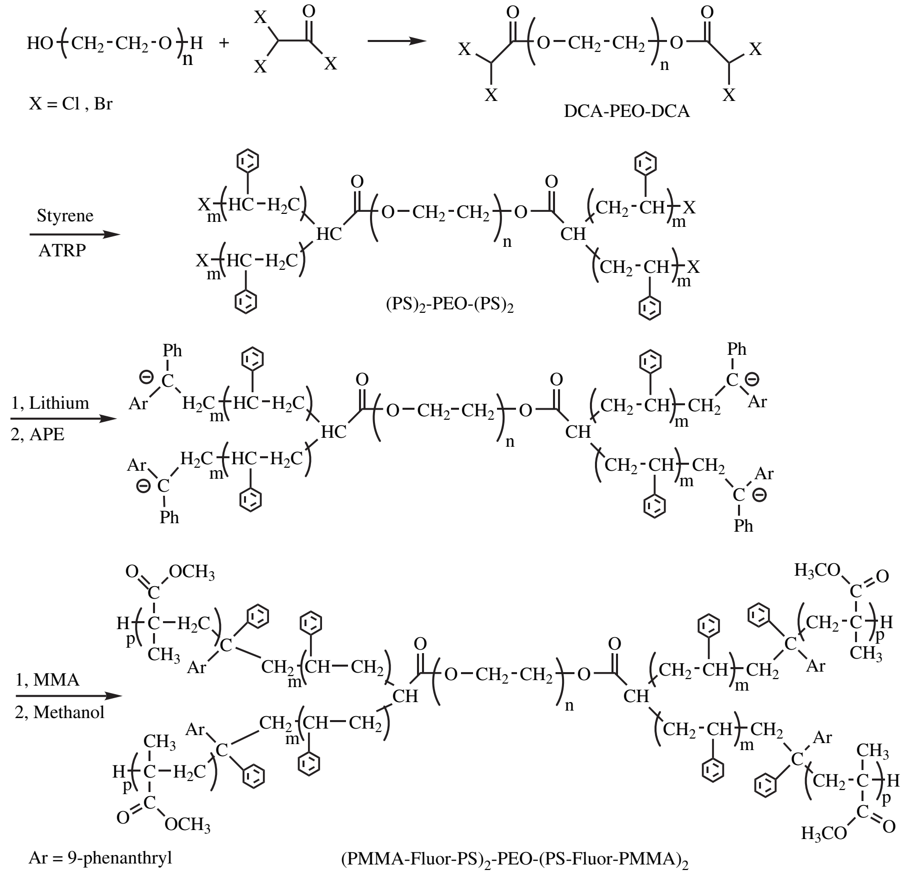
[a] All the polymers of (PMMA-*b*-PS)$_2$-PEO-(PS-*b*-PMMA)$_2$ were synthesized by $(PS)_2$-PEO-$(PS)_2$ that initiated the polymerization of MMA in THF at −78 °C. The molar ratio of the (PMMA-*b*-PS)$_2$-PEO-(PS-*b*-PMMA)$_2$:dye = 1:5. Triethylaluminium solution (diluted by *n*-hexane to 2% v/v, 5 mL), THF (80 mL).

[b] $M_{n,th}$ was calculated by the molar ratio of the polymer anion and MMA.

[c] The proportion of the PEO, PS and PMMA in Nos. 8 and 9 was calculated by the ratio of its integral in ^1H NMR. The $M_{n,NMR}$ of (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ is calculated by Eq. (3)

$$M_{n,NMR} = [(I_a + I_{a'})/5]/(I_b/4) \times N_{PEO} \times 104.15 + [(I_c/3)/(I_b/4)] \times N_{PEO} \times 100.11 + 20{,}000 \tag{3}$$

where I_c is the integral of CH_3O- protons of the chain segment PMMA; 100.11 is the molar mass of an MMA unit; the other parameters have been defined previously.



Scheme 1. The strategy of synthesis of the H-shaped $(PMMA\text{-}Fluor\text{-}PS)_2\text{-}PEO\text{-}(PS\text{-}Fluor\text{-}PMMA)_2$.

the polymer is shown in Fig. 1B. The peaks at 6.45–7.08 assigned to aromatic protons indicate the presence of PS blocks in the copolymers. Therefore, the polymer we obtained is a PS-*b*-PEO copolymer. ^{1}H NMR δ (ppm): 6.45–7.08 [aromatic protons], $I_a + I_{a'} = 1.272$; 3.65 [$-OCH_2CH_2O-$], $I_b = 0.710$; 1.31–1.98 [methylene and methane protons], $I_c = 1.331$, $I_{c'} = 0.769$. $(I_a + I_{a'}):(I_c + I_{c'}) = 1.651 \approx 5:3$. The degree of polymerization of styrene, $m = [(I_a + I_{a'})/I_b \times (4/5) \times N_{PEO}]/4 = 163$ was confirmed by ^{1}H NMR. The GPC traces (Nos. 1, 7) for all the copolymers are mono-nodal,

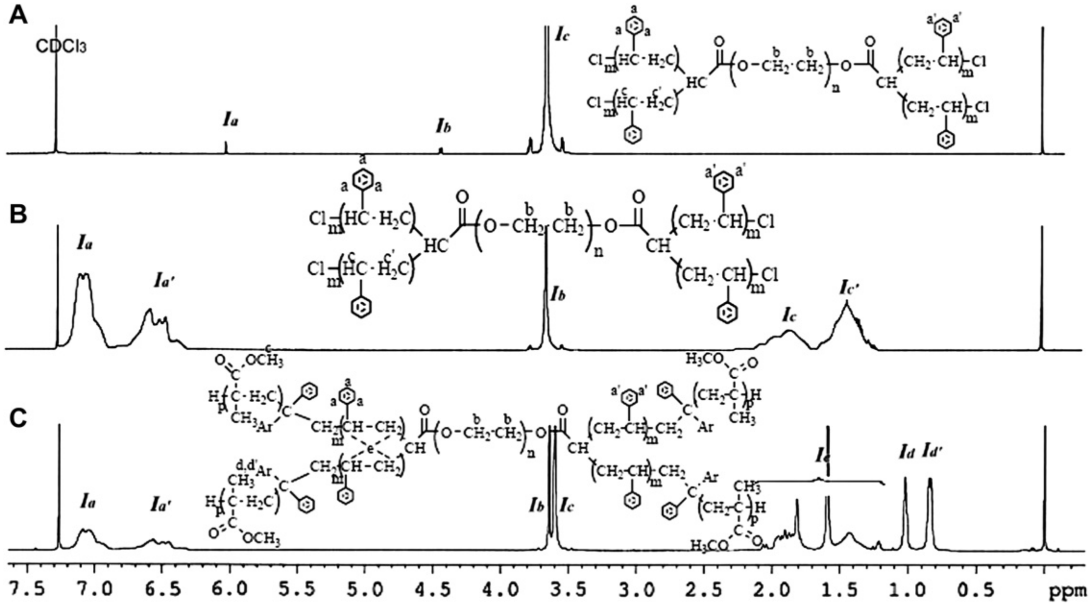


Fig. 1. ^{1}H NMR spectra of the macroinitiator and polymers. A. The ^{1}H NMR spectrum of the macroinitiator 2,2-dichloro acetyl-PEO-2,2-dichloro acetyl. B. The ^{1}H NMR spectrum of $(PS)_2\text{-}PEO\text{-}(PS)_2$. C. The ^{1}H NMR spectrum of $(PMMA\text{-}Fluor\text{-}PS)_2\text{-}PEO\text{-}(PS\text{-}Fluor\text{-}PMMA)_2$.

symmetrical and narrow, which indicate that the polymers formed have same degree of polymerization in the PEO based initiator participation in the ATRP of styrene. The molecular weights determined by GPC are apparent values.

$(ClPS)_2$-PEO-$(PSCl)_2$ was used to synthesize the fluorescent labeled H-shaped block copolymer (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ by living AP. The PEO block in the macroinitiator $(ClPS)_2$-PEO-$(PSCl)_2$ is very hydrophilic and can associate with H_2O by H-bonding, therefore extra caution has been taken to make the initiator anhydrous. The macroinitiator was dissolved in freshly distilled anhydrous THF and the 5% (w/w) solution of it was passed through a 10 cm neutral alumina chromatography column (length diameter ratio, 20 cm/2 cm) three times. The polymer was precipitated into anhydrous *n*-hexane and collected by vacuum filtration. The $(ClPS)_2$-PEO-$(PSCl)_2$ polymers were dried under vacuum at 110 °C for 96 h before they were used as AP initiator. The chain ends of the copolymer $(ClPS)_2$-PEO-$(PSCl)_2$ contain the alpha-halogens which react with the lithium in THF to produce the polymeric anions. The addition of triethylaluminium into the system before MMA anionic polymerization is only additional in situ purification of the mixture, because the PEO could complex with H_2O with hydrogen bonding. The anionic complex first reacts with 1-(2-anthryl)-1-phenylethylene or 1-(9-phenanthryl)-1-phenylethylene and finally produces dye anions at junctions. The dye anion further reacts with MMA [22]. The dye anions cannot react with their own dye molecules, and therefore only a single dye molecule is attached to each active site. The molecular weight of copolymers of (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ are listed in Table 2. The ^{1}H NMR spectrum of the copolymer is shown in Fig. 1C. ^{1}H NMR δ (ppm): 6.45–7.08 [aromatic protons], $I_a + I_{a'} = 8.043$; 3.65 $[-\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}-]$, $I_b = 4.921$; 3.60 $[-\mathrm{OC}H_3]$, $I_c = 8.324$; 1.31–1.98 [methylene and methane protons]; 0.83–1.02 $[-\mathrm{C}H_3$ protons], $I_d + I_{d'} = 7.854$. The results of ^{1}H NMR confirmed that the copolymer consists of PS, PEO, and PMMA blocks.

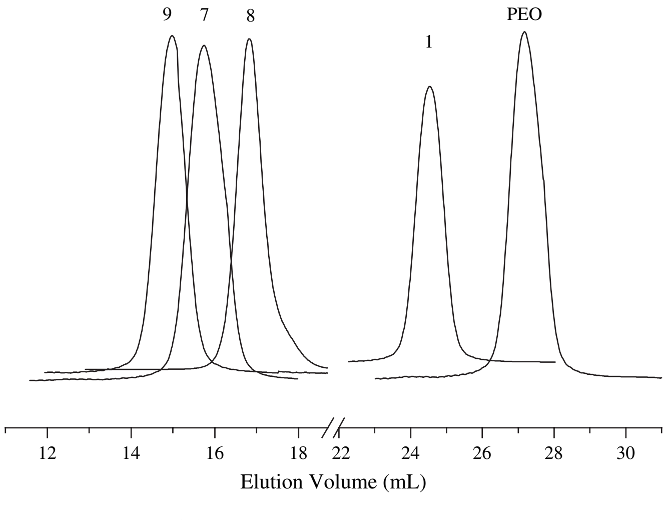


Fig. 2. GPC traces of the PEO $(PS)_2$-PEO-$(PS)_2$ (Nos. 1, 7) and the (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ (Nos. 8, 9).

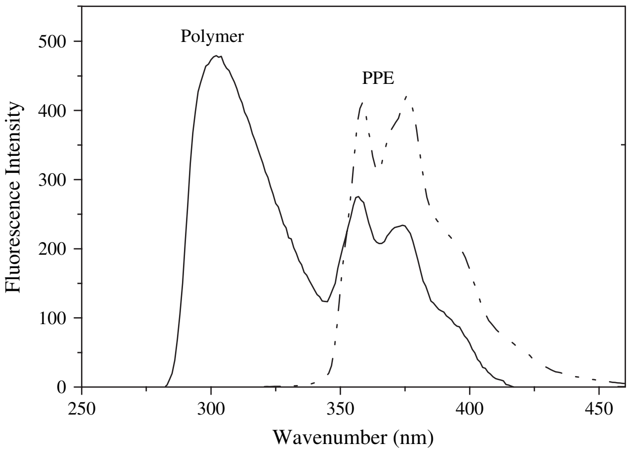


Fig. 3. Fluorescence spectrum of (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ (No. 9) and 1-(9-phenanthryl)-1-phenylethylene (PPE).

The GPC traces (Nos. 8, 9 in Fig. 2) of the block copolymers resemble $(ClPS)_2$-PEO-$(PSCl)_2$. The metal–halogen exchange reaction is accompanied by coupling of alkylhalide and alkyllithium leading to products with higher molar weight. These chains could be ''hidden'' in the product of block copolymerization and overlapped with block copolymers in GPC eluograms from the GPC curves also. If there is significant coupling of alkylhalide (or carbonyl groups of (Cl-PS)$_2$-PEO-(PS-Cl)$_2$) and alkyllithium during the anionic production and anionic polymerization, the GPC curve of block copolymer should have a tail at lower molecular weight position at least. The GPC curves in Fig. 2 (from No. 1 to No. 8 and from No. 7 to No. 9) are single (mono-nodal) and symmetrical, indicating that pure H-shaped block copolymer was obtained, and also indicate that the chains are not ''hidden'' in product of block copolymerization.

The fluorescence spectrum and the UV–vis spectrum of solution of sample No. 9 (Table 2) is compared with that of 1-(9-phenanthryl)-1-phenylethylene (PPE) solution and shown in Figs. 3 and 4, respectively. The curves of PPE and fluorolabeled block copolymer both posses the emission peaks in between 358 and 375 nm. The curves of PPE and fluorolabeled

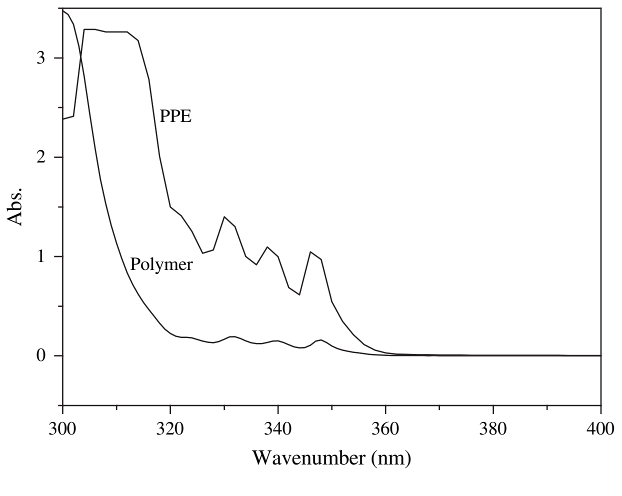


Fig. 4. UV–vis spectrum of (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ (No. 9) and 1-(9-phenanthryl)-1-phenylethylene (PPE).

block copolymer both posses the absorption peak at 346, 338 and 330 nm. The fluorescent spectrum and the UV–vis spectrum confirm the presence of fluorescent molecule in the main chain of the H-shaped block copolymer, (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$.

4. Conclusion

In this paper, a novel symmetric fluorescent labeled H-shaped block copolymer (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$ has been designed and successfully synthesized by combination of ATRP and living AP. The macroinitiator DCA-PEO-DCA was designed and synthesized, and then was used to prepare the H-shaped block copolymer (PS)$_2$-PEO-(PS)$_2$ by ATRP. The fluorescent dye labeled H-shaped block copolymer, (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$, was prepared by the combination of living AP from the block copolymer (PS)$_2$-PEO-(PS)$_2$. In conclusion, we can say that the study of ^{1}H NMR, GPC and fluorescence spectroscopy and UV–vis spectroscopy confirms the designed H-shaped block copolymer.

Acknowledgment

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References

[1] (a) Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614–5;
(b) Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745;
(c) Matyjaszewski K, Xia J. Chem Rev 2001;101:2921–90.

[2] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. Chem Rev 2001;101: 3747–92.

[3] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661–88.

[4] Hirao A, Matsuo A, Morifuji K, Tokuda Y, Hayashi M. Polym Adv Technol 2001;12:680–6.

[5] (a) Rempp P, Franta E, Herz JE. Adv Polym Sci 1988;86:145;
(b) Baskaran D. Prog Polym Sci 2003;28:521;
(c) Vlček P, Lochmann L. Prog Polym Sci 1999;24:793;
(d) McGrath JE. ACS Symp Ser 1981;166:441.

[6] (a) Kong H, Gao C, Yan DY. J Am Chem Soc 2004;126:412–3;
(b) Sarbu T, Lin KY, Ell J, Siegwart DJ, Spanswick J, Matyjaszewski K. Macromolecules 2004;37:3120–7;
(c) Postma A, Davis TP, Moad G, Michael S. React Funct Polym 2006; 66(1):137–47;
(d) Haddleton DM, Crossman MC, Dana BH, Duncalf DJ, Heming AM, Kukulj D, et al. Macromolecules 1999;32:2110–9.

[7] (a) Zhai GQ, Yu WH, Kang ET, Neoh KG. Ind Eng Chem Res 2004;43: 1673–80;
(b) Coote ML, Radom L. J Am Chem Soc 2003;125:1490–1;
(c) He T, Zheng GH, Pan CY. Macromolecules 2003;36:5960–6.

[8] (a) Xu YJ, Pan CY. Macromolecules 2000;33:4750–6;
(b) Yuan JY, Pan CY, Tang BZ. Macromolecules 2001;34:211–4;
(c) Feng XS, Pan CY. Macromolecules 2002;35:2084–9;
(d) Feng XS, Pan CY. Macromolecules 2002;35:4888–93;
(e) He T, Li DJ, Sheng X, Zhao B. Macromolecules 2004;37:3128–35;
(f) Johnson RM, Fraser CL. Macromolecules 2004;37:2718–27.

[9] (a) Lutz JF, Neugebauer D, Matyjaszewski K. J Am Chem Soc 2003; 125:6986–93;
(b) Francis R, Taton D, Jennifer LL, Masse P, Gnanou Y, Duran RS. Macromolecules 2003;36:8253–9;
(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;
(h) Sun X, Zhang H, Huang X, Wang X, Zhou QF. Polymer 2005;46(14): 5251–7.

[10] (a) Celik C, Hizal G, Tunca U. J Polym Sci Part A Polym Chem 2003;41: 2542–8;
(b) Miura Y, Narumi A, Matsuya S, Satoh T, Duan Q, Kaga H, et al. J Polym Sci Part A Polym Chem 2005;43:4271–9.

[11] (a) Francis R, Taton D, Jennifer LL, Masse P, Gnanou Y, Duran RS. Macromolecules 2003;36:8253–9;
(b) Hou SJ, Chaikof EL, Taton D, Gnanou Y. Macromolecules 2003;36: 3874–81;
(c) Tsitsilianis C, Lutz JP, Graff S, Lamps JP, Rempp P. Macromolecules 1991;24:5897–902;
(d) Shen Z, Chen Y, Barriau E, Frey H. Macromol Chem Phys 2006;207: 57–64.

[12] (a) Feng XS, Pan CY, Wang J. Macromol Chem Phys 2001;202: 3403–9;
(b) Klok HA, Becker S, Schuch F, Pakula T, Müllen K. Macromol Chem Phys 2002;203:1106–13;
(c) Angot S, Taton D, Gnanou Y. Macromolecules 2000;33: 5418–26;
(d) Beil JB, Zimmerman SC. Macromolecules 2004;37:778–87;
(e) Matsuo A, Watanabe T, Hirao A. Macromolecules 2004;37: 6283–90;
(f) Bernaerts KV, Du Prez FE. Prog Polym Sci 2006;31:671–722.

[13] (a) Ishizu K, Takeda H. Eur Polym J 2001;37:2073–8;
(b) Knauss DM, Huang TZ. Macromolecules 2002;35:2055–62;
(c) Audouin F, Renouard T, Schmaltz B, Nuffer R, Mathis C. Polymer 2005;46(19):8519–27;
(d) Hadjichristidis N, Iatrou H, Pitsikalis M, Pispas S, Avgeropoulos A. Prog Polym Sci 2005;30(7):725–82;
(e) Hirao A, Hayashi M, Loykulnant S, Sugiyama K, Ryu SW, Haraguchi N, et al. Prog Polym Sci 2005;30(2):111–82.

[14] (a) Chojnowski J, Cypryk M, Fortuniak W, Ścibiorek M, Rózga-Wijas K. Macromolecules 2003;36:3890–7;
(b) Quirk RP, Tsai Y. Macromolecules 1998;31:8016–25.

[15] (a) Knauss DM, Huang TZ. Macromolecules 2002;35:2055–62;
(b) Knauss DM, Huang TZ. Macromolecules 2003;36:6036–42;
(c) Hirao A, Tokuda Y. Macromolecules 2003;36:6081–6;
(d) Mahajan S, Cho BK, Allgaier J, Fetters LJ, Coates GW, Wiesner U. Macromol Rapid Commun 2004;25:1889–94;
(e) Khelfallah N, Gunari N, Fischer K, Gkogkas G, Hadjichristidis N, Schmidt M. Macromol Rapid Commun 2005;26:1693–7.

[16] (a) Xu H, Erhardt R, Abetz V, Müller AHE, Goedel WA. Langmuir 2001;17:6787–93;
(b) Mutsuda M, Omae H. Macromolecules 2004;37:3346–52;
(c) Zhou QY, Fan XW, Xia CJ, Mays J, Advincula R. Chem Mater 2001;13:2465–7;
(d) Zhou DS, Li L, Xue G. Langmuir 2002;18:4559–61;
(e) Ishizu K, Uchida S. Prog Polym Sci 1999;24:1439–80;
(f) Harrak AE, Carrot G, Oberdisse J, Christophe EB, Boué F. Macromolecules 2004;37:6376–84;
(g) Kong XX, Kawai T, Abe J, Iyoda T. Macromolecules 2001;34: 1837–44.

[17] (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;
(c) Johnson MA, Iyer J, Hammond PT. Macromolecules 2004;37:2490–501;
(d) Batsberg W, Ndoni S, Trandum C, Hvidt S. Macromolecules 2004; 37:2965–71;
(e) Krishnan R, Srinivasan KSV. J Appl Polym Sci 2005;97:989–1000;
(f) Mao BW, Gan LH, Gan YY, Tam KC, Tan OK. Polymer 2005; 46(23):10045–55;
(g) Kuo SW, Huang CF, Tung PH, Huang WJ, Huang JM, Chang FC. Polymer 2005;46(22):9348–61.

[18] (a) Tong JD, Zhou CL, Ni SR, Winnik MA. Macromolecules 2001;34: 696–705;
(b) Ni SR, Zhang P, Wang YC, Winnik MA. Macromolecules 1994;27: 5742–50.

[19] (a) Li YG, Shi PJ, Pan CY. Macromolecules 2004;37:5190–5;
(b) Gido SP, Lee C, Pochan DJ, Pispas S, Mays JW, Hadjichristidis N. Macromolecules 1996;29:7022–8;
(c) Gungor E, Cote G, Erdogan T, Durmaz H, Demirel AL, Hizal G, et al. J Polym Sci Part A Polym Chem 2007;45:1055–65;
(d) Durmaz H, Karatas F, Tunca U, Hizal G. J Polym Sci Part A Polym Chem 2006;44:3947–57.

[20] Hruska Z, Vuillemin B, Riess G. Makromol Chem 1992;193: 1987–94.

[21] (a) Yu XF, Shi TF, Zhang G, An LJ. Polymer 2006;47:1538–46;
(b) Yu XF, Shi TF, An LJ, Zhang G, Dutta PK. J Polym Sci Part A Polym Chem 2007;45:147–56.

[22] (a) Freyss D, Rempp P, Benoît H. J Polym Sci Part B Polym Lett 1964;2(2):217–22;
(b) Ballard DGH, Bowles RJ, Haddleton DM, Richards SN, Sellens R, Twose DL. Macromolecules 1992;25:5907–13;
(c) Davis TP, Haddleton DM, Richards SN. J Macromol Sci Rev Macromol Chem Phys 1994;C34(2):232–43;
(d) Feldthusen J, Iván B, Müller AHE. Macromolecules 1998;31: 578–85;
(e) Radke W, Müller AHE. Macromolecules 2005;38(9):3949–60.