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

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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-Fluor-PS)\textsubscript{2}-PEO-(PS-Fluor-PMMA)\textsubscript{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 $^1$H 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-Fluor-PS)\textsubscript{2}-PEO-(PS-Fluor-PMMA)\textsubscript{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)\textsubscript{2}-PEO-(PS)\textsubscript{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)\textsubscript{2}-PEO-(PMMA)\textsubscript{2}, and a double H-shaped amphiphilic block copolymer, (PMMA)\textsubscript{2}-PEO-(PS)\textsubscript{2}-PEO-(PMMA)\textsubscript{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...
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) (99%) was diluted with THF, 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 C₂H₆NH⁺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 product obtained was dried under vacuum and then immersed into an oil bath at 130 °C.

2.2. Instrumentation

1H NMR spectra were obtained on a Bruker AV-600 NMR spectrometer using CDCl₃ 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]. 1H NMR δ (ppm): PPE, 8.73–7.21 [aromatic, 14H], 6.02 [=CH₂, 1H], 5.49 [=CH₂, 1H] and APE, 8.39–7.35 [aromatic, 14H], 5.67 [=CH₂, 1H], 5.56 [=CH₂, 1H].

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

40.0 g PEO (Mₙ = 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 C₂H₆NH⁺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%. 1H NMR δ (ppm): 6.01 [Cl₂HCCO–, 1H], 4.43 [–COOCH₂CH₂–, 2H], 3.63 [–OCH₂CH₂O–, 900H]. Mₙ,NMR = 20,000 g/mol.

2.5. Synthesis of H-shaped block copolymers: (CIPS)₀-PEO-(PSCl)₀

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 (Mₙ,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, (CIPS)₀-PEO-(PSCl)₀, was 67%. 1H NMR δ (ppm): 6.45–7.08 [aromatic protons], 3.65 [–OCH₂CH₂–], 1.31–1.98 [methylene and methane protons]. Mₙ,NMR = 104,000 g/mol, Mₙ,GPC = 88,000, Mₙ/M₀ = 1.12. The data for other (CIPS)₀-PEO-(PSCl)₀ copolymers are listed in Table 1.
The molar ratio of the (PMMA-fluorinated PMMA)2-PEO-(PS-fluorinated PMMA)2 block copolymers can be calculated by Eq. (1)

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

(1)

where the number 44.05 is the molar mass of the group CH2OCH2-; the number 111.93 is the molar mass of the group Cl2HCCO-; the number 16.00 is the atomic weight of oxygen; \((I_a/4)/(I_a/2) = 450 - N_{PEO}\) is the effective number of ethylene oxide repeat unit in the macroinitiator, DCA-PEO-DCA (as determined by \(^1\)H NMR).

The \(M_{n,NMR}\) of the obtained copolymer, [(P(S)Cl)2-PEO-(PSCl)2], was calculated by Eq. (2)

\[
M_{n,NMR} = [(I_a + I_c)/S]/(I_a/4) \times N_{PEO} + 104.15 + 20.000
\]

(2)

where, \(I_a + I_c\) is the integral of aromatic protons of benzene; \(I_a\) is the integral of the chain segment of PEO protions; 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)).

The procedure for synthesis of sample No. 9 (PMMA-Fluor-PS2-PEO-(PS-Fluor-PMMA)2) is given here as an example. The other polymers are shown in Table 1. 2.02 g (0.01 mmol) of macroinitiator, (CIPS)2-PEO-(PSCI)2, No. 7 \((M_{n,NMR} = 202,000\text{ g/mol})\), 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-PS2-PEO-(PS-Fluor-PMMA)2), was synthesized by esterification between PEO and DCAC catalyzed by pyridine. DCAC and pyridine form a complex compound \([Cl_2CHCO][Cl_2H_2NCl]\) to accelerate the esterification reaction. The \(^1\)H 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 \([Cl_2HCO, 1H]\) \(I_a = 0.099\); 4.43 \([COOCH_2, 2H]\), \(I_a = 0.205\); 3.63 \([-OCH_2CH_2O-, 90H]\), \(I_a = 89.114\). \(I_a/I_b = 0.483 \approx 1.2\). The presence of the resonance peaks at 6.01 and 4.33 clearly indicates the formation of the macroinitiator.

The H-shaped block copolymer, (CIPS)2-PEO-(PSCI)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 \(^1\)H NMR spectrum of

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Time (h)</th>
<th>(M_{n,NMR})</th>
<th>(M_{n,GPC})</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(PMMA1-PS1)-PEO-(PS1-PMMA1)2</td>
<td>4</td>
<td>104,000</td>
<td>88,000</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>(PS2)-PEO-(PS2)2</td>
<td>5</td>
<td>116,000</td>
<td>96,000</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>(PS3)-PEO-(PS3)2</td>
<td>6</td>
<td>126,000</td>
<td>113,000</td>
<td>1.08</td>
</tr>
<tr>
<td>4</td>
<td>(PS4)-PEO-(PS4)2</td>
<td>7</td>
<td>137,000</td>
<td>117,000</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>(PS5)-PEO-(PS5)2</td>
<td>8</td>
<td>142,000</td>
<td>129,000</td>
<td>1.12</td>
</tr>
<tr>
<td>6</td>
<td>(PS6)-PEO-(PS6)2</td>
<td>9</td>
<td>153,000</td>
<td>138,000</td>
<td>1.15</td>
</tr>
<tr>
<td>7*</td>
<td>(PS7)-PEO-(PS7)2</td>
<td>14</td>
<td>202,000</td>
<td>182,000</td>
<td>1.07</td>
</tr>
</tbody>
</table>

* All the polymers of (PS2)-PEO-(PS2)2 were synthesized by (PS2)-PEO-(PS2)2 that initiated the polymerization of MMA in THF at -78 °C. The molar ratio of the (PMMA-Fluor-PS2-PEO-(PS-Fluor-PMMA)2) was 1:5. Triethylaluminium solution (diluted by n-hexane to 2% v/v, 5 mL), THF (80 mL).

The \(M_{n,NMR}\) was calculated by the molar ratio of the polymer anion and MMA.

The proportion of the PEO, PS and PMMA in Nos. 8 and 9 was calculated by the ratio of its integral in \(^1\)H NMR. The \(M_{n,NMR}\) of (PMMA-Fluor-PS2)-PEO-(PS-Fluor-PMMA2) is calculated by Eq. (3)

\[
M_{n,NMR} = [(I_a + I_c)/S]/(I_a/4) \times N_{PEO} + 104.15 + [(I_a)/3]/(I_a/4)] \times N_{PEO} \times 100.11 + 20.000
\]

(3)

where \(I_a\) is the integral of CH3O- protons of the chain segment PMMA; 100.11 is the molar mass of an MMA unit; the other parameters have been defined previously.

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 \([Cl_2CHCO][Cl_2H_2NCl]\) to accelerate the esterification reaction. The \(^1\)H 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 \([Cl_2HCO, 1H]\) \(I_a = 0.099\); 4.43 \([COOCH_2, 2H]\), \(I_a = 0.205\); 3.63 \([-OCH_2CH_2O-, 90H]\), \(I_a = 89.114\). \(I_a/I_b = 0.483 \approx 1.2\). The presence of the resonance peaks at 6.01 and 4.33 clearly indicates the formation of the macroinitiator.

The H-shaped block copolymer, (CIPS)2-PEO-(PSCI)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 \(^1\)H NMR spectrum of Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>(M_{n,th}) (M_{n,NMR})</th>
<th>(M_{n,GPC})</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>(PMMA1-b-PS1)-PEO-(PS1-b-PMA1)2</td>
<td>180,000</td>
<td>20,000</td>
<td>84,000</td>
</tr>
<tr>
<td>9</td>
<td>(PMMA1-b-PS7)-PEO-(PS7-b-PMA1)2</td>
<td>278,000</td>
<td>20,000</td>
<td>182,000</td>
</tr>
</tbody>
</table>

* All the polymers of (PMMA-b-PS2)-PEO-(PS-b-PMA2) were synthesized by (PS2)-PEO-(PS2) that initiated the polymerization of MMA in THF at -78 °C.

The \(M_{n,NMR}\) of (PMMA-Fluor-PS2)-PEO-(PS-Fluor-PMMA2) is calculated by Eq. (3)
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. $^1H$ NMR δ (ppm): 6.45–7.08 [aromatic protons], $I_a + I'_a = 1.272$, $l_b = 0.710$, 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, $m = [(I_a + I'_a)/l_b] \times (4/5) \times N_{PEO}/4 = 163$ was confirmed by $^1H$ NMR. The GPC traces (Nos. 1, 7) for all the copolymers are mono-nodal.

**Scheme 1.** The strategy of synthesis of the H-shaped (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-PMMA)$_2$.

**Fig. 1.** $^1H$ NMR spectra of the macroinitiator and polymers. A. The $^1H$ NMR spectrum of the macroinitiator 2,2-dichloro acetyl-PEO-2,2-dichloro acetyl. B. The $^1H$ NMR spectrum of (PS)$_2$-PEO-(PS)$_2$. C. The $^1H$ NMR spectrum of (PMMA-Fluor-PS)$_2$-PEO-(PS-Fluor-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-(PSCI)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-(PSCI)2 is very hydrophilic and can associate with H2O 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-(PSCI)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-(PSCI)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 H2O 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 1H NMR spectrum of the copolymer is shown in Fig. 1C. 1H NMR δ (ppm): 6.45–7.08 [aromatic protons], Ia + Ia0 = 8.043; 3.65 [–OCH2CH2O–], Ib = 4.921; 3.60 [–OCH3], Ic = 8.324; 1.31–1.98 [methylene and methane protons]; 0.83–1.02 [–CH3 protons], Id + Id0 = 7.854. The results of 1H NMR confirmed that the copolymer consists of PS, PEO, and PMMA blocks.
block copolymer both possesses the absorption peak at 346, 338 and 330 nm. The fluorescent spectrum and the UV—vis spec-
trum 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. In conclusion, we can say that the 
study of 1H NMR, GPC and fluorescence spectroscopy and 
UV—vis spectroscopy confirms the designed H-shaped block 
copolymer.

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