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Synthesis of amphiphilic rod-coil ABC triblock copolymers with oligo(*para*-phenyleneethynylene) as the middle rigid block

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Abstract

An amphiphilic rod-coil ABC triblock copolymers using rigid oligo(*para*-phenyleneethynylene) (OPE) as the middle rod segment, poly(ethylene oxide)-*block*-oligo(*para*-phenyleneethynylene)-*block*-polystyrene (PEO-*b*-OPE-*b*-PS), was designed and successfully synthesized. In the synthetic route, a kind of macroinitiator, PEO-*b*-OPE-Br was achieved by stepwise coupling of iodo-terminated poly(ethylene oxide) and oligo(*para*-phenyleneethynylene) with amino end group, capping with 2-bromopropionyl bromide. Subsequently, from this macroinitiator atom transfer radical polymerization (ATRP) of styrene was performed to obtain PEO-*b*-OPE-*b*-PS. The resulting copolymers were characterized by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). All these novel copolymers were affirmed to have well-defined structures and narrow molecular weight distributions.

Keywords: ABC triblock copolymer; Atom transfer radical polymerization; Rod-coil polymer

1. Introduction

The supramolecular organization of rod-coil block copolymers, especially with π-conjugated rod segments, attracts a great deal of attention [1–4]. It not only can provide a rich variety of nanoscale morphologies due to the microphase separation caused by intensive immiscibility between blocks and the tendency of the rod segments to order into anisotropic structure [5–9], it also can incorporate the desirable chemical functionalities and physical properties that are associated with the blocks [10–14]. Of particular interest to us are the rod-coil block copolymers with poly(*para*-phenyleneethynylene) (PPE) or oligo(*para*-phenyleneethynylene) (OPE) rod segments, since they have unique optoelectronic properties and strong aggregation behavior [15–23]. Because the controlled length and low polydispersity, even monodispersity of the rod segment, as well as narrow molecular weight distribution of the coil, can help enhance the control over the self-organization morphology and determine the optoelectronic properties, many different synthetic techniques and approaches were used to achieve approving copolymers [15–20]. For example, premade coil blocks with low polydispersities were attached to rods [15,16], and living/controlled radical polymerization was used to obtain coil blocks from macroinitiators of rod blocks [17]. Compared to the former method, the later is more versatile in monomers and easier to operate, but the initiation efficiency of polymerization and the polydispersities are not satisfying.

Most of rod-coil polymers that have been synthesized and studied are AB diblock or ABA triblock copolymers. Linear ABC triblock copolymers [24–29], which have comparatively more independent parameters influencing their phase behavior, display a variety of different morphologies [30]. However, to the best of our knowledge, linear ABC triblock copolymers containing rod segment were only reported in a recent communication [31]. In this communication, the synthesis of an ABC triblock consisting of PEO, PMMA and rigid-rod PMPCS as A, B and C components respectively, was described. Herein, we report the synthesis of an amphiphilic rod-coil ABC triblock copolymer, which comprises rigid OPE as the middle rigid segment, a hydrophobic block polystyrene (PS) and a hydrophilic block poly(ethylene oxide) (PEO). The OPE block was monodisperse and no alkyl-substituent [32,33],

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and the triblock copolymers obtained have well-defined structure and narrow molecular weight distributions. These characters will help us to expect and observe interesting self-organization behaviors and supramolecular morphologies, as our ongoing work aims at.

2. Experimental part

2.1. Materials

1-Trimethylsilylethynyl-4-((4-iodophenyl)-ethynyl)benzene (**1**) and OPE1, 1-ethynyl-4-((4-aminophenyl)-ethynyl) benzene, were prepared according to the literature [32]. Poly(ethylene oxide) monomethyl ethers (PEO, Fluka) with $M_n = 750$ and 1900, PEO_{750} and PEO_{1900}, were dried by azeotropic distillation of their toluene solution. Tetrahydrofuran (THF) was distilled over potassium; triethylamine (NEt_3) was distilled over potassium hydroxide; and they both were degassed before use. Styrene was passed through a column of neutral alumina to remove inhibitor. All other chemicals were analytical grade and used as received without further purification.

2.2. Synthesis of amino-terminated OPEs

OPE1 was premade [32]. OPE1 (1.09 g, 5.0 mmol), $Pd(Ph_3)_2Cl_2$ (40 mg, 0.05 mmol, 1 mol%) and CuI (10 mg, 0.05 mmol, 1 mol%) were dissolved in a mixture of THF (20 ml) and NEt_3 (30 ml), and a solution of **1** (2.0 g, 5.0 mmol) in THF (10 ml) was added dropwise. The mixture was stirred 24 h under Ar atmosphere. After removing solvents, the resident was passed through an alumina column using dichloromethane as eluent to get trimethylsilyl-protected OPE2. This compound was dissolved in a solution of sodium hydroxide (0.2 g, 5.0 mmol) in a mixture of THF (10 ml) and methanol (10 ml), and was stirred 2 h at room temperature. After removal of solvents, the crude product was purified by column chromatography on alumina with dichloromethane as eluent and afforded a yellow needle solid of OPE2 (0.82 g, yield: 40%). ^1H NMR ($CDCl_3$): $\delta = 7.49$ (s, phenyl, 12H), 7.34 (d, $J = 8.6$ Hz, 2H), 6.62 (d, $J = 8.6$ Hz, 2H), 3.87 (broad, NH_2, 2H), 3.15 (s, $\equiv$CH, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 146.8$ (C–NH_2), 133.1, 132.0, 131.2, 112.8 (CH of C_6H_4), 124.1, 123.8, 121.4, 115.1 (C–C$\equiv$), 92.4, 87.0 (C$\equiv$C), 83.2, 78.7 (C$\equiv$CH). IR (KBr): 3465, 3375 (s, NH_2), 3272 (s, $\equiv$C–H), 2205 (m, C$\equiv$C), 2163 (m, C$\equiv$CH).

2.3. Synthesis of PEO-b-OPE with amino end group

A typical synthetic procedure was as follows. First, to a solution of water-freed PEO_{1900} (1.9 g 1.0 mmol) in benzene (18 ml) and pyridine (2 ml), 4-iodobenzoic chloride (0.8 g, 3.0 mmol) in benzene (5 ml) was added dropwise at 0 °C and stirred overnight at 40 °C. After filtration and precipitation in diethyl ether, the precipitate was dried to afford iodo-terminated PEO_{1900} (1.7 g, yield: 89%). Next, OPE1 (0.26 g, 1.2 mmol) was dissolved in THF (15 ml), and $Pd(PPh_3)_2Cl_2$ (40 mg, 5 mmol, 5 mol%), CuI (10 mg, 5 mmol, 5 mol%), NEt_3 (15 ml) and iodo-terminated PEO_{1900} (1.5 g, 0.8 mmol) were added. Under Ar atmosphere, the mixture was stirred overnight at 50 °C. After evaporating the solvents, the resident was extracted with a combination of THF and pyridine, and precipitated thrice in diethyl ether. The precipitate was collected and dried to afford PEO_{1900}-*b*-OPE1 with amino end group (1.36 g, yield: 78%). ^1H NMR: see Fig. 2. ^{13}C NMR ($CDCl_3$): $\delta = 165.8$ (C=O), 146.9 (C–NH_2), 133.1, 131.4, 129.6, 112.2 (CH of C_6H_4), 127.9, 124.5, 114.8 (C–C$\equiv$), 92.1, 90.5 (C$\equiv$C), 72.3, 70.4–71.6, 64.7, 59.4 (–CH_2–CH_2O–). IR (KBr): 3465, 3375 (w, NH_2), 1719 (m, C=O).

2.4. Synthesis of PEO-b-OPE-Br macroinitiator

In a typical protocol, to a solution of PEO_{1900}-*b*-OPE1 (2.2 g, 1 mmol), NEt_3 (0.310 g, 3.0 mmol) in THF (20 ml) cooled at 0 °C, 2-bromopropionyl bromide (0.65 g, 3 mmol) in THF (10 ml) was added dropwise and stirred for 2 h. Then the mixture was allowed to reach room temperature and stirred overnight. After filtration and precipitation in diethyl ether, the crude product was extracted with benzene and precipitated thrice in diethyl ether. The precipitate was dried to provide macroinitiator PEO_{1900}-*b*-OPE1-Br (1.96 g, yield: 83%). ^1H NMR: see Fig. 2. ^{13}C NMR ($CDCl_3$): $\delta = 167.9$, 165.8 (C=O), 138.7 (C–NH), 133.0, 131.5, 129.8, 121.1 (CH of C_6H_4), 127.9, 124.5, 119.6 (C–C$\equiv$), 92.1, 90.5 (C$\equiv$C), 72.0, 70.4–71.8, 64.7, 59.0 (–CH_2–CH_2O–), 46.2, 21.6 (BrCH–CH_3).

2.5. Synthesis of PEO-b-OPE-b-PS

The polymerization procedure was described as follows. A glass tube was charged with PEO_{1900}-*b*-OPE1-Br (0.235 g, 0.1 mmol), CuBr (15 mg, 0.1 mmol), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 15 mg, 0.1 mmol), styrene (0.92 ml, 8 mmol) and THF (0.92 ml). After being degassed by three freeze–vacuum–thaw cycles, the tube was sealed under vacuum and then immersed into an oil bath. The reaction mixture was thermostated at 90 °C for a certain time, then rapid cooled by ice water and diluted with THF. After passing the polymer solution through a column with neutral alumina and precipitating in an excess of hexane, the precipitate was dried to afford PEO_{1900}-*b*-OPE1-*b*-PS (0.735 g, yield: 61%). ^1H NMR: see Fig. 2.

2.6. Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker DMX-300 nuclear magnetic resonance (NMR) instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Vector-22 FT-IR instrument. Gel permeation chromatography (GPC) was performed at 30 °C using THF as eluent on a Waters 150C instrument equipped with microstyragel columns (10^3, 10^4, and 10^5 Å) and a Waters refractive index detector.

3. Results and discussion

The synthesis route of rod-coil ABC triblock copolymers is outlined in Fig. 1. The first step is to synthesize OPEs, OPE1 and OPE2, with different lengths. As shown in Fig. 1, **1** was connected to OPE1 under $Pd(Ph_3)_2Cl_2/CuI$ coupling condition and subsequently underwent desilylation to get OPE2. OPE1 and OPE2 both have one amino end group and one ethyne end group, as affirmed by IR and NMR spectroscopy. The signals at 3465 cm^{-1}, 3375 cm^{-1} in IR spectrum and signal at 3.87 ppm in ^1H NMR spectrum are attributed to $-NH_2$ of OPE2; signal at 2163 cm^{-1} of IR spectrum and signals at 3.15 ppm of H^1 NMR are attributed to the $\equiv C-H$ group. As the characteristic signals of OPE, a singlet at 7.49 ppm in ^1H NMR spectrum assigned to aromatic hydrogen of the main chain and signals at 87–93 ppm of $C\equiv C$ in ^{13}C NMR spectrum are afforded. The ^1H NMR spectrum of OPE2 also reveals a doublet at 6.62 ppm attributed to the two aromatic hydrogens at the *ortho*-position of $-NH_2$, and signals at 7.70 ppm in ^1H NMR spectrum of **1**, which were caused by the aromatic protons adjacent to iodo group, were absent in ^1H NMR spectrum of OPE2 indicating that the coupling reaction have done successfully. Longer rods can be envisaged as an extension of present route.

The second step is to condense OPE with iodo-terminated PEO via $Pd(Ph_3)_2Cl_2/CuI$ coupling reaction (Fig. 1). The iodo-terminated PEO was premade by replacing hydroxyl end groups of PEO with iodo groups using 4-iodobenzoic chloride. In the coupling reaction, a slight excess of OPE was used under more catalyst of $Pd(PPh_3)_2Cl_2/CuI$ compared to that used in the preparation of OPE2. After precipitating in diethyl ether, the surplus OPE could be complete removed by washing with diethyl ether several times. Four diblock copolymers, PEO_{1900}-*b*-OPE1, PEO_{1900}-*b*-OPE1, PEO_{750}-*b*-OPE2 and PEO_{750}-*b*-OPE2, were obtained and confirmed by NMR, IR. The representative formation of PEO_{1900}-*b*-OPE1 can be proven by the following evidence. By ^1H NMR analysis, signals at 7.75, 7.82 ppm ($AA'BB'$ system) corresponding to the aromatic protons in the spectrum of iodo-terminated PEO (Fig. 2) and signal at 3.15 ppm corresponding to $\equiv C-H$ of OPE1 completely disappear in the spectrum of PEO_{1900}-*b*-OPE1. Besides, new signals at 8.03, 7.58 ppm appear which are caused by aromatic protons at *ortho*- and *para*-position of ester group and the intensity of signal at 7.50 ppm

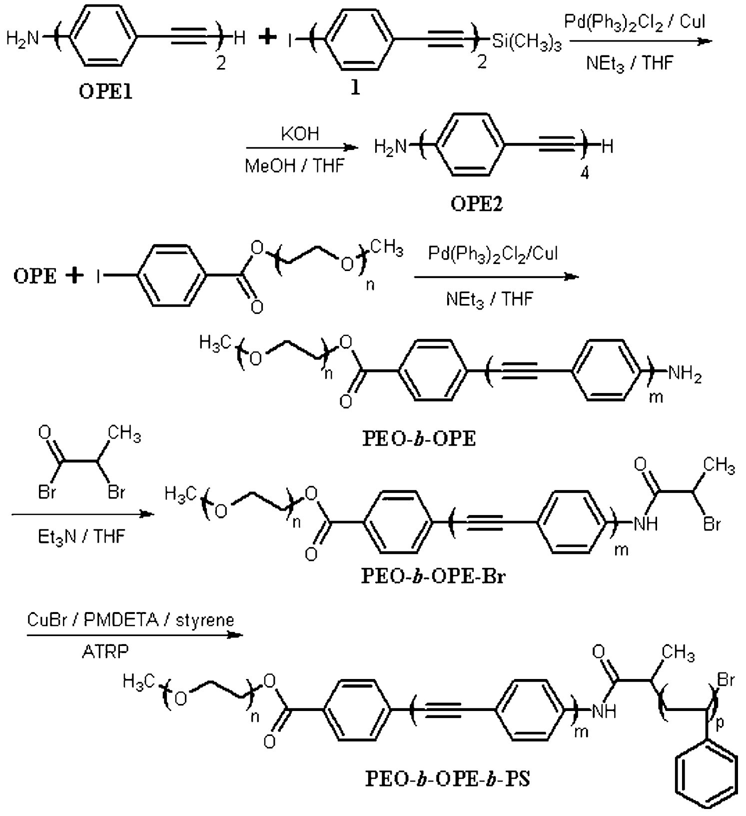

Fig. 1. Synthetic route of the PEO-*b*-OPE-*b*-PS triblock copolymers.

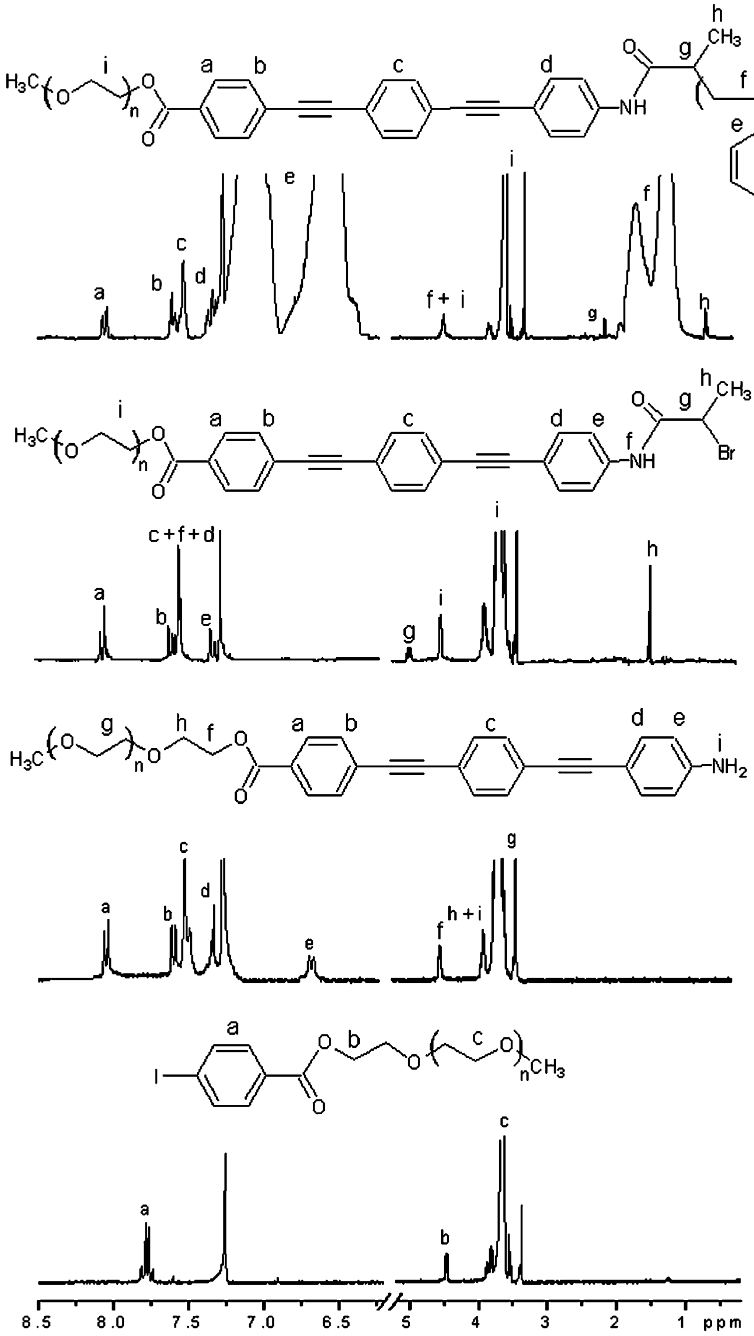

Fig. 2. ^{1}H NMR spectra of iodo-terminated PEO_{1900}, PEO_{1900}-*b*-OPE1, PEO_{1900}-*b*-OPE1-Br and PEO_{1900}-*b*-OPE-*b*-PS1.

increased. All signals in ^{13}C NMR are well attributed and IR spectrum proves that the amino group still exists by signals at 3375, 3465 cm^{-1}.

The next step is to prepare macroinitiators (PEO-*b*-OPE-Br, Fig.1) via condensation reaction of amino end group of PEO-*b*-OPE and 2-bromopropionyl bromide. The completely end capping can be proved by comparing ^{1}H NMR spectrum of macroinitiator with that of PEO-*b*-OPE. As shown in Fig. 2, signal at 6.64 ppm assigned to the two aromatic protons adjacent to –NH_2 of PEO_{1900}-*b*-OPE1 complete disappears. In ^{13}C NMR spectrum of PEO_{1900}-*b*-OPE1, signal at 147.5 ppm assigned to the aromatic carbon atom linked with –NH_2 is also absent in the spectrum of PEO_{1900}-*b*-OPE1-Br. New signals attributed to the ATRP initiate group appear, such as 4.94 ppm in ^{1}H NMR spectrum and 46.2 ppm in ^{13}C NMR spectrum caused by –CH–Br. Accordingly, four macroinitiators, PEO_{1900}-*b*-OPE1-Br, PEO_{1900}-*b*-OPE1-Br, PEO_{750}-*b*-OPE1-Br and PEO_{750}-*b*-OPE2-Br, are obtained and their molecular weight distributions of these diblock copolymers

Table 1
Conditions and results of ATRP of styrene using PEO-*b*-OPE-Br as initiator

Polymer	$[St]_o/[I]_o$	Time (h)	Conv. (%)[a]	$M_{n,theo}$[b]	$M_{n,NMR}$[c]	M_w/M_n[d]	f[e]
PEO_{750}-*b*-OPE1-Br					1200	1.05	
PEO_{750}-*b*-OPE1-*b*-PS1	40	3	54	3450	3850	1.28	0.85
PEO_{750}-*b*-OPE1-*b*-PS2	60	6	78	6050	6600	1.20	0.90
PEO_{1900}-*b*-OPE1-Br					2350	1.03	
PEO_{1900}-*b*-OPE1-*b*-PS1	80	4	61	7450	8150	1.16	0.88
PEO_{1900}-*b*-OPE1-*b*-PS2	80	6	83	9000	9650	1.14	0.91
PEO_{750}-*b*-OPE2-Br					1400	1.05	
PEO_{750}-*b*-OPE2-*b*-PS	60	5	69	5700	6350	1.18	0.87
PEO_{1900}-*b*-OPE2-Br					2550	1.03	
PEO_{1900}-*b*-OPE2-*b*-PS	100	4	59	8700	9100	1.16	0.94

[a] Conversion of styrene was calculated on the basis of gravimetric method.

[b] $M_{n,theo} = ([St]_o/[I]_o) \times conv. \times 104 + M_{n,PEO} + M_{OPE}$, where $[St]_o$ and $[I]_o$ are initial molar concentrations of styrene and macroinitiator; 104, $M_{n,PEO}$ and M_{OPE} are molecular weight of styrene, PEO and OPE, respectively.

[c] Calculated according to Eq. (1).

[d] Determined by gel permeation chromatography (GPC).

[e] Initiator efficiency of the polymerization of styrene from macroinitiator.

determined by GPC using polystyrene as standard and values of molecular weight checked by ^1H NMR analysis are listed in Table 1.

The polymerization of styrene from the macroinitiators was designed to be controlled under ATRP condition. According to the literature [17], which concluded that the carbon–carbon triple bond did not interfere with the ATRP, we no longer take account of the possibility of this problem. In our polymerization procedure, THF was used as solvent, the volume of which equals that of the monomer, and the polymerization was conducted at 90 °C with CuBr/PMDETA as catalyst system. The resulting copolymers were examined by ^1H NMR and GPC. A representative ^1H NMR spectrum of rod-coil ABC triblock copolymer, PEO_{1900}-*b*-OPE1-PS1, was analyzed (Fig. 2). Except the characteristic methylene protons signal at 3.61 ppm of PEO, the aromatic protons signals at 6.30–6.80, 6.80–7.30 ppm and methylene protons, methine protons signals of PS backbone at 1.10–2.25 ppm demonstrate that the macroinitiator initiated the polymerization of Styrene to form well-defined triblock copolymer. The molecular weights of copolymers are calculated on the basis of the integral values of signals at 3.61 ppm (I_a) and 6.30–6.80 ppm (I_b) according to Eq. (1).

$$M_{n,NMR} = \left[\frac{(I_b/2)}{(I_a/4)}\right](N_{PEO} - 1) \times 104 + M_{n,PEO} + M_{OPE} \quad (1)$$

Here N_{PEO} is the polymerization degree of PEO, and 104, $M_{n,PEO}$, M_{OPE} are molecular weights of styrene, PEO, OPE, respectively. The calculated results are listed in Table 1. GPC also characterized molecular weight values of PEO-*b*-OPE-*b*-PS copolymers. However, because no calibration simultaneously suitable to OPE rod block and PEO block existed, these values were not reliable and higher than their actual ones. For example, the M_n of PEO_{1900}-*b*-OPE1-*b*-PS1 given by GPC is 10800, while the theory value is 7450. The polydispersities of polymers determined by GPC are listed in Table 1 as well. All polymers obtained have low molecular weight distributions ($M_w/M_n \leq 1.20$ except for PEO_{750}-*b*-OPE1-*b*-PS1 $M_w/M_n = 1.28$). Fig. 3 shows GPC-RI traces of PEO_{1900}-*b*-OPE1-*b*-PS1, PEO_{1900}-*b*-OPE1-*b*-PS2 and their precursors which are all single and symmetrical, as further confirm the well-defined structure of the copolymers. From the polymerization data (Table 1), we can also find that the initiator efficiencies of macroinitiators are all higher than 0.85 by comparing the $M_{n,theo}$ and $M_{n,NMR}$ [34], and thus we consider that the initiator efficiencies are acceptable.

4. Conclusion

In sum, a new kind of macroinitiator of rod-coil diblock copolymer, PEO-*b*-OPE-Br, was designed and synthesized.

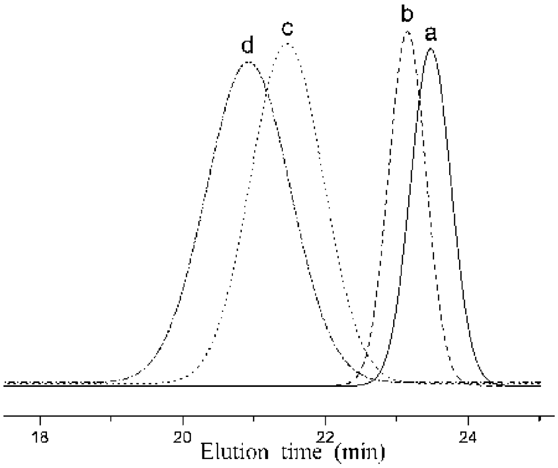

Fig. 3. GPC-RI traces of PEO_{1900} (a), PEO_{1900}-*b*-OPE1-Br (b), PEO_{1900}-*b*-OPE1-*b*-PS1 (c) and PEO_{1900}-*b*-OPE1-*b*-PS2 (d).

Then a novel amphiphilic rod-coil ABC triblock copolymer, PEO-*b*-OPE-*b*-PS, which had a rigid-rod segment in the middle, was obtained by ATRP process. The resulting copolymers all have well-defined structure and narrow molecular weight distributions, which were confirmed by NMR and GPC.

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