



Polymer Communication

Synthesis and characterization of ABC ternary segregated H-shaped copolymers

Kui Xu^a, Yun Wang^a, Yanxue Wang^a, Tao Yu^a, LiJia An^b, Caiyuan Pan^a, Ruke Bai^{a,*}^a Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China^b State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 13 February 2006; received in revised form 28 April 2006; accepted 28 April 2006

Available online 19 May 2006

Abstract

The synthesis of a novel ABC ternary segregated H-shaped copolymer is described, of which a central poly(ethylene glycol) (PEG) chain is terminated on both sides by polystyrene (PS) and poly(*tert*-butylacrylate) (PtBA) chains. The synthetic procedure involves functionalization of PEG by 2-bromosuccinic anhydride followed by esterification of 1,6-hexanediol, which gives its ends the bifunctional nature that allows sequential growth of two PS, then two PtBA arms via atom transfer radical polymerization (ATRP). The resulting segregated H-shaped copolymers were characterized by NMR spectroscopy and gel permeation chromatography (GPC). All these copolymers were affirmed to have well-defined structures and narrow molecular weight distributions.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: ABC ternary copolymer; Atom transfer radical polymerization; Segregated H-shaped polymer**1. Introduction**

ABC ternary block copolymers have attracted a great deal of attention in the realm of polymer science [1–8]. One of the main reasons is that they have more independent parameters influencing the phase behavior, in comparison with AB binary block copolymers, and display a variety of morphologies [9–13]. However, most of the large quantity of reported work is focused on linear ABC ternary copolymers. Only a few of publications are concerning other topologies like branched macromolecular architectures due to synthetic difficulties, and the majority of these publications are on the synthesis and properties of ABC miktoarm star polymers. Toward star-like ABC miktoarm copolymers, three synthetic methods are often used. The first one is based on macromonomer technique, where non-homopolymerizable macromonomers are incorporated at one polymer chain end and from this block junction the polymerization of the third monomer is then started [14–16]. The second one uses the selective, step-by-step substitution of the chlorine atoms in trichloromethylsilane with anionic living

polymer chains to form star copolymers [17,18]. The third method is based on heterofunctional macroinitiator bearing two chemically different functional groups to initiate independently two different kinds of polymerizations [19–22].

The synthesis of polymer materials with well-defined complex macromolecular architectures is a particularly challenging aspect of polymer chemistry concerning the development of techniques [23–25]. To well establish structure/properties relationships, polymers with narrow molecular and compositional dispersity and with well-defined architecture are essential. Recently, more and more synthesis and studies of block copolymers with complex polymer architectures, including star, H- and π -shaped, and dendrimer-like copolymers, have been reported [26–32]. An important motivation for the increasing number of publications is the advance in the area of controlled radical polymerization (CRP), namely, atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT), which allows better definition and ease in the synthesis procedure [33–35].

In this contribution, we report the synthetic procedure of a novel ABC ternary segregated H-shaped copolymer (Fig. 1(a)), which comprises hydrophilic PEG as the middle block, hydrophobic blocks PS and PtBA as side chains. It is necessary to emphasize that through the same synthetic method we also have successfully achieved another kind of ABC

* Corresponding author. Tel.: +86 551 3600722; fax: +86 551 3631760.
E-mail address: bairk@ustc.edu.cn (R. Bai).

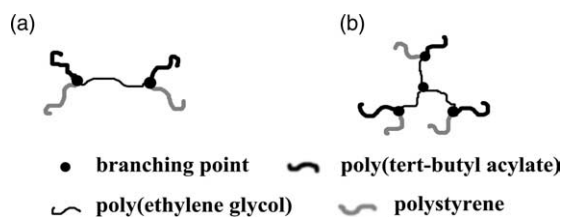


Fig. 1. Molecular architectures of ABC ternary copolymers with segregated H-shaped (a) and dendrimer-like architecture (b).

dendrimer-like copolymer (Fig. 1(b)). To the best of our knowledge, ABC ternary block copolymers with segregated H-shaped and dendrimer-like molecular architectures have not reported before. Further work is ongoing in our lab concerning the synthesis and properties of these unique structural copolymers, which may find important applications in the fields such as controlled drug delivery, macromolecular self-assembly and the preparation of advanced materials.

2. Experimental part

2.1. Materials

tert-Butylacrylate (*t*BA) and styrene were stirred over CaH_2 and distilled at reduced pressure before use. PEG (Fluka, $M_n = 4000$, $M_w/M_n = 1.02$) were dried by azeotropic distillation of their toluene solution. Triarm star-shaped PEG was synthesized according to the literature [36]. 2-Bromosuccinic anhydride (BSA) was prepared according to the procedure described in the literature [22]. 4-(*N,N*-Dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared by mixing saturated THF solutions of DMAP (1 equiv.) and *p*-toluenesulfonic acid monohydrate (1 equiv.) at room temperature. All other chemicals were analytical grade and used as received without further purification.

2.2. Reaction of PEG with BSA

PEG (4.0 g, $M_n = 4000$, 1.0 mmol) was dissolved in anhydrous benzene (30 mL), and BSA (1.8 g, 10 mmol) was added. The mixture was stirred at 55 °C for 24 h. The mixture was added into diethyl ether and the precipitate was collected. After resolved in CH_2Cl_2 , the precipitation cycle was repeated twice more. The resulting product **1** was dried in vacuum oven at 40 °C for 24 h. The yield of **1**, Br-COOH-PEG-COOH-Br (3.9 g) is 91%. ^1H NMR (CDCl_3): see Fig. 2. ^{13}C NMR (CDCl_3): $\delta = 173.4$, 169.6, 168.9, (C=O) 70.2–71.8, 68.8, 64.3 ($\text{OCH}_2\text{CH}_2\text{O}$), 40.3, 38.7 (CH_2CHBr).

2.3. Synthesis of Br-HO-PEG-OH-Br macroinitiator

A solution of 1,6-hexanediol (1.18 g, 10 mmol) in CH_2Cl_2 (10 mL) and a solution of dicyclohexylcarbodiimide (DCC) (0.516 g, 2.5 mmol) in 5 mL of CH_2Cl_2 were added simultaneously at room temperature under a nitrogen flow into a stirred solution of compound **1** (4.40 g, 2.0 mmol) and 4-(*N,N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (0.6 g,

2.0 mmol) in CH_2Cl_2 (13 mL). After 24 h, the precipitated dicyclohexylurea was filtered off and the solvents were removed under reduced pressure. The residue was extracted with acetone and precipitated into excess diethyl ether. The precipitation cycle was repeated twice more. The precipitate was collected and dried in vacuum to afford Br-HO-PEG-OH-Br macroinitiator **2**. The yield of **2** (4.0 g) is 87%. ^1H NMR (CDCl_3): see Fig. 2. ^{13}C NMR (CDCl_3): $\delta = 169.8$, 169.0, (C=O) 70.2–71.8, 68.8, 64.2 ($\text{OCH}_2\text{CH}_2\text{O}$), 39.8, 38.3 ($\text{CH}_2\text{-CHBr}$), 64.4, 62.5, 32.5, 28.4, 25.6, 25.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$).

2.4. Preparation of PS-OH-PEG-OH-PS

A typical synthetic procedure was as follows. A glass tube was charged with macroinitiator **2** (4.6 g, 1 mmol), CuBr (0.3 g, 2 mmol), 2,2'-bipyridine (bpy, 0.94 g, 6 mmol), styrene (25.0 mL). Under Ar atmosphere, the reaction mixture was

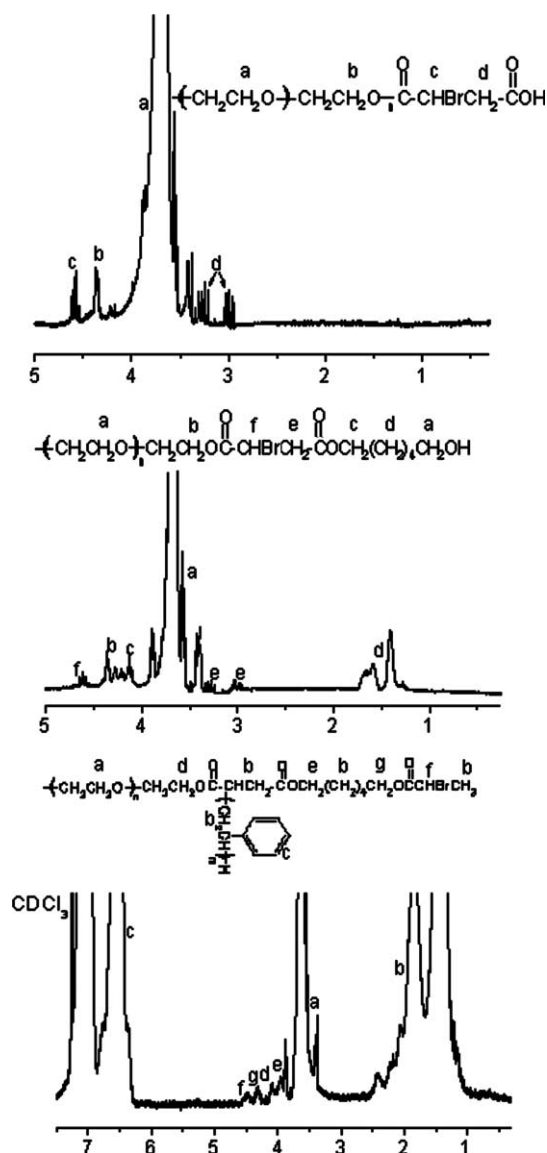


Fig. 2. ^1H NMR spectra of macroinitiators: Br-COOH-PEG-COOH-Br, Br-HO-PEG-OH-Br and PS-Br-PEG-Br-PS.

thermostated at 110 °C. After a prescribed time, tributyltin hydride (1.6 mL, 6 mmol) in benzene (20 mL) was added and the reaction mixture was further stirred for 4 h. Following passing the polymer solution through a column with neutral alumina, the copolymer was purified by precipitation (THF/MeOH, THF/1:3 saturated aqueous NH₄Cl/MeOH, and THF/MeOH). The precipitate was dried to afford compound **3**, PS–OH–PEG–OH–PS **1**. Conversion: 39% (based on ¹H NMR data). ¹H NMR (CDCl₃): δ=6.30–7.25 (m, ArH), 4.09 (m, CH₂O(C=O), 4H), 3.95 (m, CH₂O(C=O), 4H), 3.40–3.89 (OCH₂CH₂O), 1.10–2.50 (m, CH₂CH and CH₂CH₂CH₂CH₂). ¹³C NMR (CDCl₃): δ=175.8, 172.1 (C=O), 145.0–147.1, 125.8–129 (ArC) 70.1–71.9, 68.9, 64.3 (OCH₂CH₂O), 40.0–43.0, 36.0(CH₂CH), 64.0, 62.6, 32.3, 29.6, 25.8(CH₂CH₂CH₂CH₂CH₂CH₂OH).

2.5. Synthesis of PS–Br–PEG–Br–PS macroinitiator.

In a typical protocol, to a solution of PS–OH–PEG–OH–PS **1** (11.9 g, 0.85 mmol), NEt₃ (0.31 g, 3.0 mmol) in THF (20 mL) cooled at 0 °C, 2-bromopropionyl bromide (0.65 g, 3.0 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 CH₃OH, the precipitate was dried to provide macroinitiator **4**, PS–Br–PEG–Br–PS **1** (11.0 g). Yield: 91%. ¹H NMR (CDCl₃): see Fig. 2. ¹³C NMR (CDCl₃): δ=175.6, 172.0, 170.2 (C=O), 145.0–147.1, 125.8–129 (ArC) 70.1–71.9, 68.9, 64.3 (OCH₂CH₂O), 40.0–43.0, 36.0(CH₂CH), 65.8, 64.0, 30.5, 26.1(O(CH₂)₆O) 40.2, 21.6 (CHBrCH₃).

2.6. Preparation of H-shaped copolymer, (PS–PtBA)–PEG–(PtBA–PS)

In a typical polymerization procedure, a glass tube was charged with macroinitiator PS–Br–PEG–Br–PS **1** (1.43 g, 0.1 mmol), CuBr (15 mg, 0.1 mmol), 2,2'-bipyridine (bpy, 47 mg, 0.3 mmol), *t*BA (3 mL) and acetone (1 mL). After being degassed by three freeze–vacuum–thaw cycles, the tube was sealed under vacuum. The reaction mixture was thermostated at 60 °C for a prescribed time, then rapidly cooled by ice water and diluted with THF. After passing the polymer solution through a column with neutral alumina and precipitating in CH₃OH, the precipitate was dried to afford H-shaped copolymers **5**, (PS–PtBA)–PEG–(PtBA–PS) **1**. Conversion: 28% (based on gravimetric method). ¹H NMR: 6.30–7.25 (m, ArH), 3.40–3.89 (OCH₂CH₂O), 1.10–2.50 (CHCH₂ and OC(CH₃)₃).

2.7. Preparation of dendrimer-like copolymer, (PEG–(PS–PtBA))₃

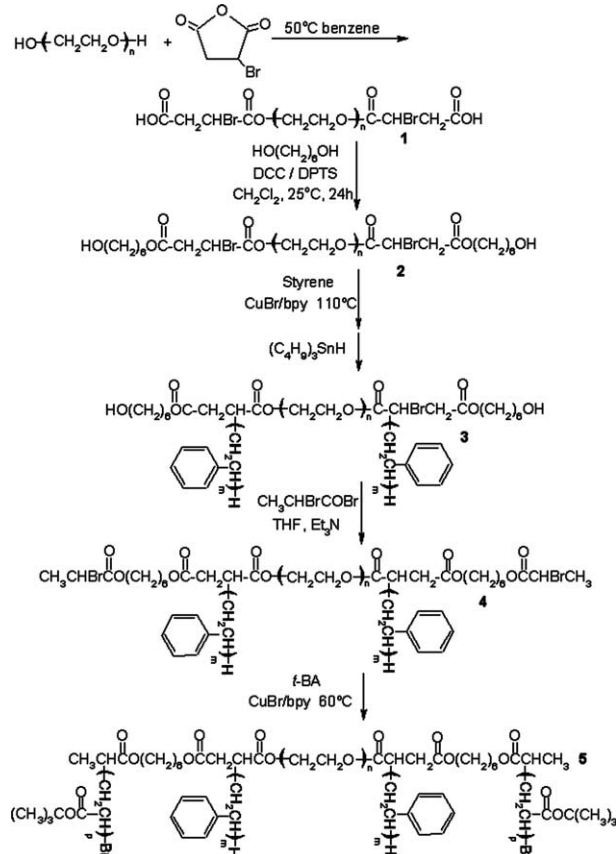
The procedure was the same as that of the synthesis of H-shaped copolymers **5**, (PS–PtBA)–PEG–(PtBA–PS), except that triarmed PEG was used in place of linear PEG.

2.8. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker DMX-300 nuclear magnetic resonance (NMR) instrument with CDCl₃ 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 micro-styragel columns (10³, 10⁴, and 10⁵ Å) and a Waters refractive index detector.

3. Results and discussion

In our synthetic route (Scheme 1) toward the target ABC ternary H-shaped copolymers, the first step is esterification of PEG with 2-bromosuccinic anhydride (BSA). For successfully achieving well-defined segregated H-shaped molecular architecture, no bromine loss and complete esterification of PEG are necessary. Under some reaction conditions, such as 55 °C in CHCl₃ and pyridine, some bromines are eliminated to form –OOC–CH=CH–COO– group, which will result a peak at 6.87 ppm in the spectrum of ¹H NMR. Thus, we conduct this reaction in benzene without pyridine. In accordance of literature [22], after esterification with BSA, polymer ends have been converted from hydroxyl into



Scheme 1. Synthesis route of ABC ternary copolymer with segregated H-shaped architecture.

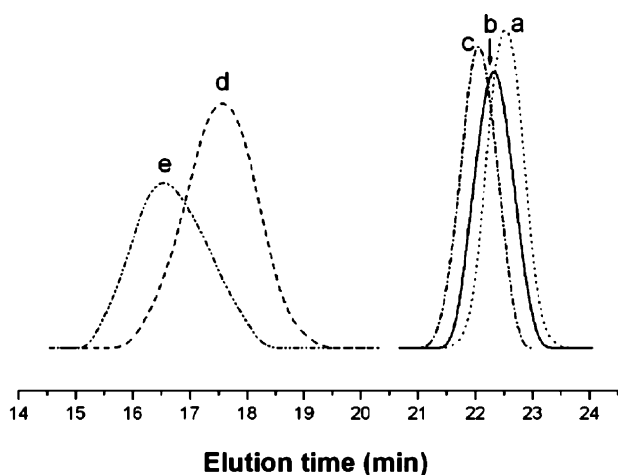


Fig. 3. GPC traces of PEG (a), Br–COOH–PEG–COOH–Br (b), Br–HO–PEG–OH–Br (c), PS–OH–PEG–OH–PS 2 (d), and segregated H-shaped copolymer (PS–PrBA)–PEG–(PrBA–PS) 2 (e).

–CH₂CH₂O(C=O)CHBrCH₂COOH group. ¹H NMR spectrum confirms the product **1**, Br–COOH–PEG–COOH–Br: peak at 4.60 ppm is assigned to a methine proton connected to bromine; peak at 4.36 ppm corresponds to the methylene protons connected to ester oxygen of bromosuccinate groups; peak at 3.24 ppm is assigned to one of methylene protons in bromosuccinate group and peak at 3.00 ppm correspond to the other one. The integration ratio of these peaks is approximated to 1.0:2.0:1.0:1.0, which tell us that the hydroxyl group of PEG reacted with BSA completely; no peak at 6.87 ppm appears indicating no debromination in this reaction. Besides, all the peaks of ¹³C NMR spectrum are well attributed. After successfully obtaining compound **1**, the esterification with 1,6-hexanediol was conducted and activated by DCC/DPTS to achieve macroinitiator **2** under a very mild reaction condition. Comparing ¹H NMR spectra of compound **1** and macroinitiator **2** (Fig. 2), a new signal at 4.11 ppm appears which is ascribed to the methylene protons adjacent to new-formed ester oxygen, as well as signals from 1.35 ppm to 1.75 ppm due to the middle methylene protons of hexamethylene group. The integration ratio of signals at 4.60 ppm (–CHBr–), 4.11, 3.87 ppm (–OCH₂CH₂OCO–) and 1.35–1.75 ppm is around 1.0:2.0:2.1:8.2. The GPC trace of product **2** (Fig. 3) is

symmetrical, single and no side-peaks, which shows slightly higher M_n than that of **1**. In ¹³C NMR spectra, the peak at 173.4 ppm of compound **1**, which was assigned to the carbon atom of –COOH, shifts to 169.8 ppm in the spectrum of **2** after esterification. Meantime, the spectrum of **2** also affords a signal at 62.5 ppm attributed to –CH₂OH, which is absent in the spectrum of **1**. All of these evidence confirmed that macroinitiator **2** was successfully achieved and no side-reaction occurred.

The next synthetic step was to perform atom transfer radical polymerization of styrene from macroinitiator **2** and dehalogenation of the terminal bromide. Styrene was polymerized in bulk at 110 °C with the molar ratio in feed: CuBr/bpy/macroinitiator **2** = 1/3/1. After a prescribed time, to quench the active halide ends of PS chains, according to the method reported [37,38], tributyltin hydride was added into the polymerization reaction mixture. The mixture was further stirred for 4 h and the resulting copolymer was purified by passing a column of neutral alumina and precipitation. The product copolymers were stirred at 110 °C with styrene and CuBr/bpy for approximately 3 days, and no new growth of M_n determined by GPC shows that all the terminal bromine was replaced by hydrogen. In comparison of ¹H NMR spectrum of **2**, the spectrum of **3**, PS–OH–PEG–OH–PS, shows disappearance of peaks at 4.60, 3.24 and 3.00 ppm, and no peaks around 4.50 ppm (4.20–4.80 ppm). The molecular weights and polydispersities of resulting copolymers were determined by ¹H NMR and GPC, as listed in Table 1.

Towards well-defined architecture, the hydroxyl groups of **3** reacted with 2-bromopropionyl bromide to form new ATRP initiating sites. The resulting macroinitiator **4** is confirmed by ¹H NMR and ¹³C NMR spectra. ¹H NMR data (Fig. 2) show that a new peak at 4.36 ppm appears due to CH–Br group compared with that of **3**. The peak at 62.5 ppm in ¹³C NMR spectrum of **3** completely vanished in the spectrum of macroinitiator **4**, indicating that all of –CH₂OH groups of **3** have been esterified. Subsequently, the polymerization of the third monomer, *t*-butyl acrylate, was also conducted under ATRP condition in acetone solution: CuBr/bpy/macroinitiator **4** = 1/3/1 (molar ratio). The resulting copolymers were characterized by ¹H NMR and GPC (Table 1). All

Table 1
Molecular weight characteristics of ABC ternary copolymers with segregated H-shaped, dendrimer-like architectures and their precursors

Polymer	GPC ^a		¹ H NMR ^b			
	M_n (g mol ⁻¹)	M_w/M_n	M_n (g mol ⁻¹)	PEG (wt%)	PS (wt%)	PrBA (wt%)
Br–HO–PEG–OH–Br	5100	1.02	4600			
PS–OH–PEG–OH–PS 1	9900	1.28	14,100	41.2	58.8	
(PS–PrBA)–PEG–(PrBA–PS) 1	15,000	1.31	21,600	26.7	38.0	35.3
PS–OH–PEG–OH–PS 2	38,700	1.26	40,400	10.4	89.6	
(PS–PrBA)–PEG–(PrBA–PS) 2	78,800	1.34	99,000	5.3	46.0	48.7
(PEG–OH) ₃	2800	1.05	2400			
(PEG–OH–PS) ₃	12,400	1.19	14,800	22.6	78.4	
(PEG–(PrBA–PS)) ₃	17,500	1.29	22,800	16.0	54.7	29.3

^a Based on polystyrene calibration.

^b The relative fractions of the PEG, PS and PrBA blocks are determined on the basis of the ratio of the area of the signal 3.40–3.89 ppm, the signal 6.30–7.25 ppm and the signal 1.05–2.50 ppm in ¹H NMR spectrum.

polymers obtained have relatively low molecular weight distributions ($M_w/M_n \leq 1.35$). Fig. 3 shows representative GPC traces of a product copolymer, (PS-*Pt*BA)-PEG-(*Pt*BA-PS) 2, and its precursors. These traces show all single and nearly symmetrical peaks, which further confirm the well-defined segregated H-shaped architecture of resulting copolymers. But a very slight tail towards low molecular weight of GPC trace of target copolymer, (PS-*Pt*BA)-PEG-(*Pt*BA-PS) is noticed, which is possibly caused by unreacted macroinitiator 4, PS-Br-PEG-Br-PS. According to the method afforded by literature [8,34], the initiator efficiencies of macroinitiators can be calculated on the basis of initial molar concentrations of monomer and macroinitiator, gravimetric conversion and $M_{n, H NMR}$. The initiator efficiencies calculated are 91% for PS-Br-PEG-Br-PS 1 and 90% for PS-Br-PEG-Br-PS 2, and both are acceptable.

As an extension of present synthetic route, we also successfully synthesized a kind of ABC ternary copolymer with dendrimer-like architecture (Fig. 1(b)), (PEG-(PS-*Pt*BA))₃. The synthetic procedure was the same as that of the synthesis of segregated H-shaped copolymers, (PS-*Pt*BA)-PEG-(*Pt*BA-PS), except that triarmed PEG was used in place of linear PEG. The resulting ABC copolymer with dendrimer-like architecture was also confirmed by ¹H NMR and GPC. The molecular weight characterization results of dendrimer-like copolymer, (PEG-(PS-*Pt*BA))₃, and its precursors, (PEG-OH)₃ and (PEG-OH-PS)₃ are listed in Table 1.

4. Conclusion

In summary, a novel ABC ternary heteroarm H-shaped copolymer was designed and synthesized, which comprises hydrophilic PEG as the middle block, hydrophobic blocks PS and *Pt*BA. The well-defined structure and narrow molecular weight distributions of resulting copolymers were confirmed by NMR and GPC. Moreover, via the same synthesis route, a kind of ABC ternary copolymer with dendrimer-like architecture has also been achieved.

Acknowledgements

We thank the National Nature Science Foundation of China (No. 20474059) and Specialized Research Fund for the Doctoral Program of Higher Education (No. 20040358017) for financial support.

References

- [1] Arai K, Kotaka T, Kitano Y, Yoshimura K. *Macromolecules* 1980;13:455–7.

- [2] Matsushita Y, Choshi H, Fujimoto T, Nagasawa M. *Macromolecules* 1980;13:1053–8.
- [3] Shibayama M, Hasegawa H, Hashimoto T, Kawai H. *Macromolecules* 1982;15:274–80.
- [4] Stupp SI, LeBonheur V, Walker K, Li LS, Huggins K, Keser A, et al. *Science* 1997;276:384–9.
- [5] Goldacker T, Abetz V, Stadler R, Erukhimovich IY, Leibler L. *Nature* 1999;398:137–9.
- [6] Tsarevsky NV, Sarbu T, Göbelt B, Matyjaszewski K. *Macromolecules* 2002;35:6142–8.
- [7] Zhang H, Sun X, Wang X, Zhou Q. *Macromol Rapid Commun* 2005;26:407–11.
- [8] Xu K, Wang Y, Bai R, Lu W, Pan CY. *Polymer* 2005;46:7572–7.
- [9] Bates FS, Fredrickson GH. *Phys Today* 1999;52:32–7.
- [10] Krappe U, Stadler R, Voigt-Martin I. *Macromolecules* 1995;28:4558–61.
- [11] Brinkmann S, Stadler R, Thomas EL. *Macromolecules* 1998;31:6566–72.
- [12] Shefelbine TA, Vigild ME, Matsen MW, Hajduk DA, Hillmyer MA, Cussler EL, et al. *J Am Chem Soc* 1999;121:8457–65.
- [13] Fukunaga K, Hashimoto T, Elbs H, Krausch G. *Macromolecules* 2002;35:4406–13.
- [14] Fujimoto T, Zhang H, Kazama T, Isono Y, Hasegawa H, Hashimoto T. *Polymer* 1992;33:2208–13.
- [15] Quirk RO, Yoo T, Lee BJ. *Macromol Sci, Pure Appl Chem* 1994;A31:911.
- [16] Hückstädt H, Göpfert A, Abetz V. *Macromol Chem Phys* 2000;201:296–307.
- [17] Iatrou H, Hadjichristidis N. *Macromolecules* 1992;25:4649–51.
- [18] Sioula S, Tselikas Y, Hadjichristidis N. *Macromolecules* 1997;30:1518–20.
- [19] Lambert O, Dumas P, Hurtrez G, Riess G. *Macromol Rapid Commun* 1997;18:343.
- [20] Lambert O, Reutenauer S, Hurtrez G, Riess G, Dumas P. *Polym Bull (Berlin)* 1998;40:143–9.
- [21] Lu Z, Chen S, Huang J. *Macromol Rapid Commun* 1999;20:394–400.
- [22] Feng XS, Pan CY. *Macromolecules* 2002;35:2084–9.
- [23] Hadjichristidis N. *J Polym Sci, Part A: Polym Chem* 1999;37:857–71.
- [24] Gerard R. *Prog Polym Sci* 2003;28:1107.
- [25] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. *Chem Rev* 2001;101:3747.
- [26] Matyjaszewski K. *Chem Eur J* 1999;5:3095–102.
- [27] Stephanie A, Daniel T, Yves G. *Macromolecules* 2000;33:5418–26.
- [28] Boerner HB, Beers K, Matyjaszewski K. *Macromolecules* 2001;34:4375–83.
- [29] Li YG, Shi PJ, Pan CY. *Macromolecules* 2004;37:5190–5.
- [30] Peleshanko S, Jeong J, Shevchenko VV, Genson KL, Pikus Y, Ornatska M, et al. *Macromolecular* 2004;37:7497–506.
- [31] Matmour R, Lepoittevin B, Joncheray TJ, El-khouri RJ, Taton D, Duran RS, et al. *Macromolecules* 2005;38:5459–67.
- [32] Yu X, Shi T, Zhang G, An L. *Polymer* 2006;47:1538–46.
- [33] Hawker CJ, Bosman AW, Harth E. *Chem Rev* 2001;101:3661–88.
- [34] Matyjaszewski K, Xia J. *Chem Rev* 2001;101:2921–90.
- [35] Masami K, Tsuyoshi A, Mitsuo S. *Chem Rev* 2001;101:3689–745.
- [36] Stephanie A, Daniel T, Yves G. *Macromolecules* 2000;33:5418–26.
- [37] Coessens V, Matyjaszewski K. *Macromol Rapid Commun* 1999;20:66–70.
- [38] Adam PS, Cassandra LF. *J Polym Sci, Part A: Polym Chem* 2002;40:4250–5.