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# Synthesis, Characterization, and Fluorescence of Pyrene-Containing Eight-Arm Star-Shaped Dendrimer-Like Copolymer with Pentaerythritol Core

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**ABSTRACT:** Novel and well-defined pyrene-containing eight-arm star-shaped dendrimer-like copolymers were successfully achieved by combination of esterification, atom transfer radical polymerization (ATRP), divergent reaction, ring-opening polymerization (ROP), and coupling reaction on the basis of pentaerythritol. The reaction of pentaerythritol with 2-bromopropionyl bromide permitted ATRP of styrene (St) to form four-arm star-shaped polymer (PSt-Br)<sub>4</sub>. The molecular weights of these polymers could be adjusted by the variation of monomer conversion. Eight-hydroxyl star-shaped polymer (PSt-(OH)<sub>2</sub>)<sub>4</sub> was produced by the divergent reaction of (PSt-Br)<sub>4</sub> with diethanolamine. (PSt-(OH)<sub>2</sub>)<sub>4</sub> was used as the initiator for ROP of  $\epsilon$ -caprolactone (CL) to produce eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>. The molecular weights of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> increased linearly with the increase of monomer. After the coupling reaction of hydroxyl-terminated (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with 1-pyrenebutyric acid, pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> was obtained. The eight-arm star-shaped dendrimer-like copolymers presented unique thermal properties and crystalline morphologies, which were different from those of linear poly( $\epsilon$ -caprolactone) (PCL). Fluorescence analysis indicated that (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> presented slightly stronger fluorescence intensity than 1-pyrenebutyric acid when the pyrene concentration of them was the same. The obtained pyrene-containing eight-arm star-shaped dendrimer-like copolymer has potential applications in biological fluorescent probe, photodynamic therapy, and optoelectronic devices. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 2788–2798, 2008

**Keywords:** atom transfer radical polymerization (ATRP); dendrimers; fluorescence; ring-opening polymerization; star-shaped dendrimer-like copolymer

## INTRODUCTION

Considerable interest exists in design and synthesis of special polymers with various and well-defined architectures, such as star polymers, star-block polymers, comb-like polymers, hyper-

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branched polymers, and dendrimers, because of their unique structures and properties that are different from those of linear polymers.<sup>1–10</sup> Dendrimers are monodisperse molecules with well-defined and perfectly branched structure, and many terminal groups are located on the surface of molecule, which provides unique properties such as high-surface reactivity.<sup>11–14</sup> They present many applications arranging from drug delivery to nanoreactor, because of their unique microenvironment of the nanoscale molecular architecture.<sup>15–20</sup> Percec et al. reported the synthesis of star-dendrimer polymers by living radical polymerization.<sup>21–23</sup> Hedrick and coworkers reported the synthesis of dendrimer-like star polylactone using hexahydroxy-functional compound initiator.<sup>24–26</sup> Gnanou and coworkers reported 4, 6, or 8 arms dendrimer-like polystyrene (PSt) with calixarene-based cores by atom transfer radical polymerization (ATRP) and chain-end modification.<sup>27</sup> Pan and coworkers have employed dendrimer-star polymer and block copolymer by addition-fragmentation chain transfer (RAFT) polymerization.<sup>28</sup> Chen and coworkers synthesized the star-dendrimer copolymer through a combination of ATRP and click reaction.<sup>29</sup> Duran and coworkers prepared the dendrimer-like copolymer with eight-arm star polystyrene core and a 16-arm poly(*tert*-butyl acrylate) or poly(acrylic acid) corona.<sup>30</sup>

Meanwhile, poly( $\epsilon$ -caprolactone) (PCL) has been extensively used for drug delivery system, biodegradable sutures, implantable screws, and temporary scaffold for tissue, because of its biodegradability, biocompatibility, and permeability.<sup>31–37</sup> However, PCL suffers from the difficulty of controlled degradation based on its high crystallinity. Therefore, it is necessary to modify its architecture and property of PCL.<sup>38,39</sup>

Pyrene compounds and pyrene-containing polymers are attracting interest because of their excellent fluorescence and long-lived excited state, and therefore have been used as the fluorescent probe, labeling chromophore, fluorescence-detecting materials, optoelectronic devices, and drug delivery vesicles.<sup>40–43</sup> The pyrene molecules could be linked onto the surface of the star-shaped dendrimer-like copolymer by covalent bond. The pyrene-containing star-shaped dendrimer-like copolymer presented unique spherical structure and had advantage over small molecules (pyrene compounds) or linear polymer in avoiding molecular aggregation.<sup>44–46</sup> Therefore, the pyrene-containing star-shaped

dendrimer-like copolymer is expected to present different thermal and fluorescent properties from those of pyrene compounds or linear polymer.

The work presented here demonstrated the preparation of novel well-defined pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> based on pentaerythritol core. The reaction of pentaerythritol with 2-bromopropionyl bromide permitted ATRP of styrene (St) to form four-arm star-shaped polymer (PSt-Br)<sub>4</sub>. Eight-hydroxyl star-shaped polymer (PSt-(OH)<sub>2</sub>)<sub>4</sub> was produced by the divergent reaction of (PSt-Br)<sub>4</sub> with diethanolamine. (PSt-(OH)<sub>2</sub>)<sub>4</sub> was used as the initiator for the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) to produce eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>. After the coupling reaction of hydroxyl-terminated (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with 1-pyrenebutyric acid, pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> was obtained (see Schemes 1 and 2). Then the thermal properties, crystalline morphologies, and fluorescence of the star-shaped dendrimer-like copolymer were investigated.

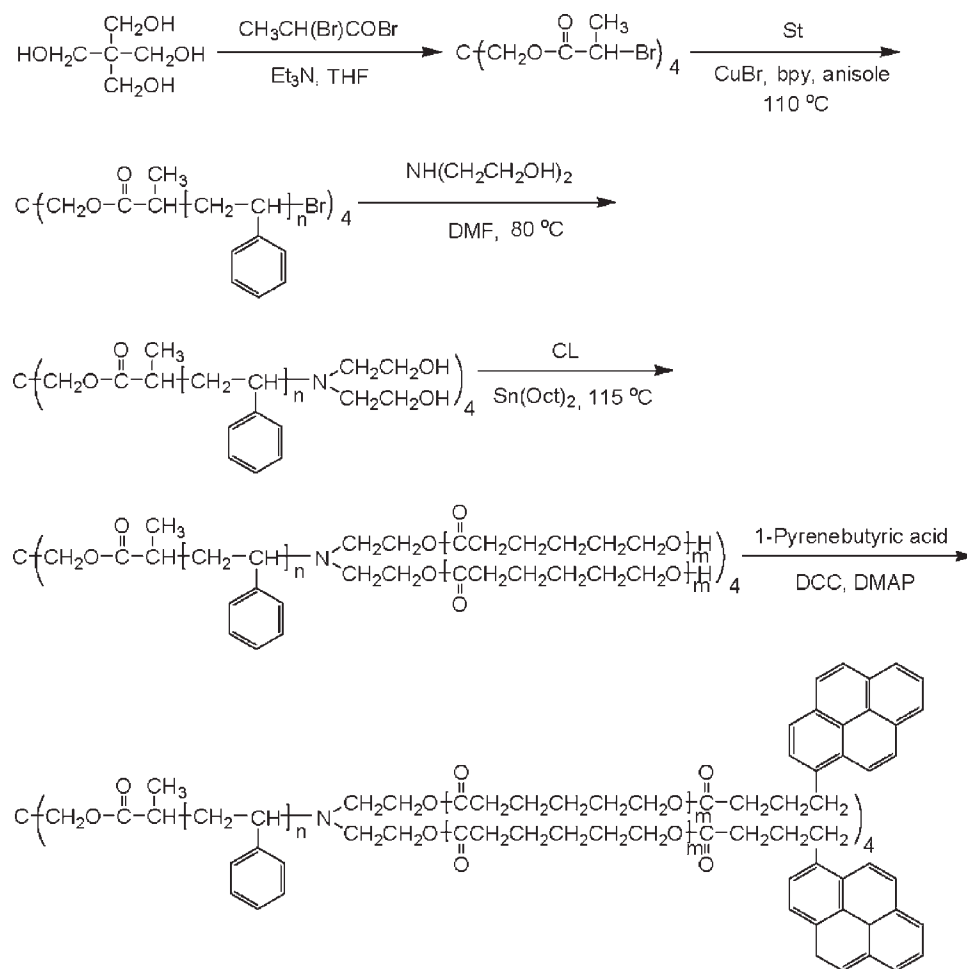
## EXPERIMENTAL

### Materials

Pentaerythritol (Acros Organic, USA) was dried at 60 °C *in vacuo* for 24 h before use. CL (Acros Organic, USA) was purified with CaH<sub>2</sub> by vacuum distillation. Tin 2-ethylhexanoate (Sn(Oct)<sub>2</sub>) and 2-bromopropionyl bromide (Aldrich, USA) was distilled under reduced pressure before use. CuBr was purified by stirring in acetic acid and washing with ethanol and then dried in vacuum. 2,2'-Bipyridine (bpy, Aldrich, USA) was purified by recrystallization from hexane. Styrene (St; Acros Organic, USA) was distilled from CaH<sub>2</sub>. Diethanolamine (Aldrich, USA), 1-pyrenebutyric acid (Alfa Aesar, USA), dicyclohexylcarbodiimide (DCC; Alfa Aesar, USA), and 4-dimethylaminopyridine (DMAP; Fluka, USA) were used as received. Chloroform, tetrahydrofuran (THF), triethylamine, hexane, *N,N*-dimethylformamide (DMF), anisole were dried over CaH<sub>2</sub> and distilled before use.

### Characterization

<sup>1</sup>H NMR spectra were obtained from JOEL JNM-ECA300 NMR spectrometer with CDCl<sub>3</sub> as



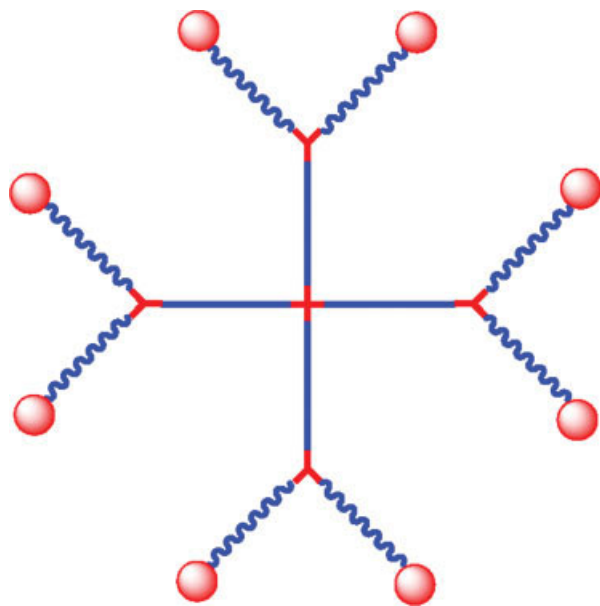
**Scheme 1.** Synthesis of pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> with pentaerythritol core.

a solvent. The chemical shifts were relative to tetramethylsilane at  $\delta = 0$  ppm for protons. The molecular weight and molecular weight distribution were measured on a Viscotek TDA 302 gel permeation chromatography equipped with two columns (GMHHR-H, M Mixed Bed). THF was used as an eluent at a flow rate of 1 mL/min at 30 °C. Differential scanning calorimetric analysis (DSC) was carried on a DSC 2910 thermal analysis system with a heating rate of 10 °C/min from -20 to 100 °C under nitrogen atmosphere. The AFM images of the polymer films were recorded on a SPM-9500J3 atomic force microscope (Shimadzu, Japan). The films on transparent mica substrate were obtained from spin-coating of the solution of polymer in chloroform (8.9 mg/mL), and the thickness was about 100 nm. The fluorescence emission measurements were carried out using a fluorescence

spectrometer (Perkin-Elmer, LS55). The solution of 1-pyrenebutyric acid and pyrene-containing copolymer in chloroform (pyrene concentration:  $10^{-5}$  mol/L) was poured into quartz cuvette. The emission spectra were recorded with an excitation wavelength at 244 nm.

#### Synthesis of Pentaerythritol Tetrakis (2-bromopropionate) (PENTA-Br)

The tetrakis initiator of PENTA-Br was synthesized according to the literature with modification.<sup>47,48</sup> Pentaerythritol (2.72 g, 20 mmol) was dispersed in anhydrous THF (100 mL) in a 250-mL round-bottom flask. To this suspension was added triethylamine (12 g, 120 mmol) under nitrogen at room temperature. A solution of 2-bromopropionyl bromide (25.9 g, 120 mmol) and anhydrous THF (20 mL) was added dropwise to



**Scheme 2.** The structure of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the above suspension within 30 min at 0 °C with vigorous stirring. The reaction mixture was stirred overnight at room temperature before it was washed with diethyl ether, 0.5 M NaCO<sub>3</sub> aqueous solution, and deionized water, and then the combined organic layer was dried overnight with MgSO<sub>4</sub>. After evaporation of solvent, the yellow solid was purified by recrystallization with petroleum ether and ethanol. The resulting product of white powder was obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 4.38 (s, CCH<sub>2</sub>O), 4.25 (q, CHBr), 1.82 (d, C(Br)CH<sub>3</sub>).

#### Synthesis of Four-Arm Star-Shaped Polymer (PSt-Br)<sub>4</sub>

A typical polymerization procedure was as follows: A dry Schlenk flask with magnetic stirrer was charged with PENTA-Br (141 mg, 209 μmol), CuBr (120 mg, 0.84 mmol), bpy (278 mg, 1.78 mmol), anisole (3 mL), and St (5.2 g, 50 mmol). The flask was degassed with three freeze-evacuate-thaw cycles. Then the polymerization was performed at 110 °C for 3 h. The crude product was dissolved in THF and passed through a basic alumina column to remove the copper catalysts. The polymer was obtained by precipitation into methanol and dried under vacuum at 40 °C.

$M_{n,NMR} = 11,920$ ,  $M_{n,GPC} = 10,570$ ,  $M_w/M_n = 1.18$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 6.28–7.33 (m, aromatic protons in PSt), 4.48 (m, terminal CH

in PSt), 4.08–4.28 (m, CCH<sub>2</sub>OOCCH), 1.06–2.46 (m, OOCCHCH<sub>3</sub> and CH<sub>2</sub>CH in PSt).

#### Synthesis of Eight-Hydroxyl Star-Shaped Polymer (PSt-(OH)<sub>2</sub>)<sub>4</sub>

A typical synthetic procedure for the divergent reaction of PENTA-PSt-Br with diethanolamine was as follows: (PSt-Br)<sub>4</sub> (1.9 g,  $M_{n,NMR} = 11,920$ , 159 μmol) was dissolved in dry DMF, and then diethanolamine (1 g, 9.54 mmol) was added. The reaction was carried out at 80 °C for 24 h. The resulting polymer was obtained by precipitation into methanol and dried under vacuum at 40 °C.

$M_{n,NMR} = 12,000$ ,  $M_{n,GPC} = 10,630$ ,  $M_w/M_n = 1.19$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 6.28–7.33 (m, aromatic protons in PSt), 4.06–4.26 (m, CCH<sub>2</sub>OOCCH), 3.54 (m, NCH<sub>2</sub>CH<sub>2</sub>OH), 2.56 (m, NCH<sub>2</sub>CH<sub>2</sub>OH), 1.06–2.46 (m, OOCCHCH<sub>3</sub> and CH<sub>2</sub>CH in PSt).

#### Synthesis of Eight-Arm Star-Shaped Dendrimer-Like Copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>

The eight-arm star-shaped dendrimer-like copolymer, (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>, was synthesized by ROP of CL with (PSt-(OH)<sub>2</sub>)<sub>4</sub> as macroinitiator. A typical polymerization procedure was as follows: (PSt-(OH)<sub>2</sub>)<sub>4</sub> (0.3 g,  $M_{n,NMR} = 12,000$ , 25 μmol) was dissolved in 3 mL of freshly prepared anhydrous toluene in a fire-dried polymerization tube. CL (457 mg, 4 mmol), a catalytic amount Sn(Oct)<sub>2</sub> (1.62 mg, 4 μmol), and a dried magnetic stirring bar were added into the polymerization tube. The tube was then connected to a Schlenkline, where exhausting–refilling processes were repeated three times. The tube was immersed into an oil bath at 115 °C under nitrogen atmosphere with vigorous stirring for 24 h. After cooled to room temperature, the resulting polymer was dissolved in chloroform and precipitated twice with methanol to afford the purified star-shaped dendrimer-like copolymer. The purified copolymer was dried in a vacuum oven at 40 °C until constant weight.

$M_{n,NMR} = 28,400$ ,  $M_{n,GPC} = 26,900$ ,  $M_w/M_n = 1.20$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 6.28–7.33 (m, aromatic protons in PSt), 4.01–4.29 (m, CCH<sub>2</sub>OOCCH, NCH<sub>2</sub>CH<sub>2</sub>OOC, and COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O in PCL), 3.64 (t, terminal CH<sub>2</sub> in PCL), 2.59 (m, NCH<sub>2</sub>CH<sub>2</sub>OH), 2.30 (m, COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.64 (m, COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).



**Table 1.** Results for ATRP of St with PENTA-Br Initiator

Sample	Time (h)	$M_{n,th}^a$	$M_{n,NMR}^b$	$M_{n,GPC}^c$	$M_w/M_n^c$	Conversion (%) <sup>d</sup>
1	1	5,670	5,380	4,910	1.26	20.0
2	2	8,800	8,640	7,680	1.21	32.5
3	3	12,250	11,920	10,570	1.18	46.3
4	4	14,920	14,250	12,590	1.23	57.0
5	5	17,140	16,020	14,100	1.16	65.9

<sup>a</sup>  $M_{n,th} = M_{monomer} \times ([monomer]/[C-Br]) \times 4 \times \text{Conversion\%} + M_{initiator}$ ,  $[monomer]/[C-Br] = 60$ .

<sup>b</sup>  $M_{n,NMR}$  was determined by  $^1H$  NMR spectroscopy of four-arm star-shaped PSt.

<sup>c</sup>  $M_{n,GPC}$  and  $M_w/M_n$  were determined by GPC analysis with polystyrene standards. THF was used as eluent.

<sup>d</sup> Conversion was measured with gravimetric method.

$CH_2CH_2O$ ), 1.38 (m,  $COCH_2CH_2CH_2CH_2CH_2O$ ), 1.06–2.46 (m,  $OOCHCH_3$  and  $CH_2CH$  in PSt).

### Synthesis of Pyrene-Containing Eight-Arm Star-Shaped Dendrimer-Like Copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>

A typical synthetic procedure was as follows: To a stirred solution of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (0.3 g,  $M_{n,NMR} = 28,400$ , 10.6  $\mu\text{mol}$ ) and 1-pyrenebutyric acid (24.5 mg, 84.8  $\mu\text{mol}$ ) in dry chloroform (6 mL) was added DCC (35 mg, 0.17 mmol) and DMAP (5.1 mg, 42  $\mu\text{mol}$ ). The reaction mixture was stirred at room temperature. The reaction byproduct dicyclohexylcarbodiurea was removed by filtration. (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> was isolated by repeated precipitation from chloroform into hexane.

$^1H$  NMR ( $CDCl_3$ ,  $\delta$ , ppm): 7.87–8.32 (m, pyrenyl protons), 6.28–7.33 (m, aromatic protons in PSt), 4.01–4.33 (m,  $CCH_2OOCCH$ ,  $NCH_2CH_2OOC$ , and  $COCH_2CH_2CH_2CH_2CH_2O$  in PCL), 3.39 (t, pyrene- $CH_2CH_2CH_2$ ), 2.43–2.60 (m,  $NCH_2CH_2OH$  and pyrene- $CH_2CH_2CH_2$ ), 2.30 (m,  $COCH_2CH_2CH_2CH_2CH_2O$ ), 2.16 (t, pyrene- $CH_2CH_2CH_2$ ), 1.64 (m,  $COCH_2CH_2CH_2CH_2CH_2O$ ), 1.38 (m,  $COCH_2CH_2CH_2CH_2CH_2O$ ), 1.06–2.46 (m,  $OOCHCH_3$  and  $CH_2CH$  in PSt).

## RESULTS AND DISCUSSION

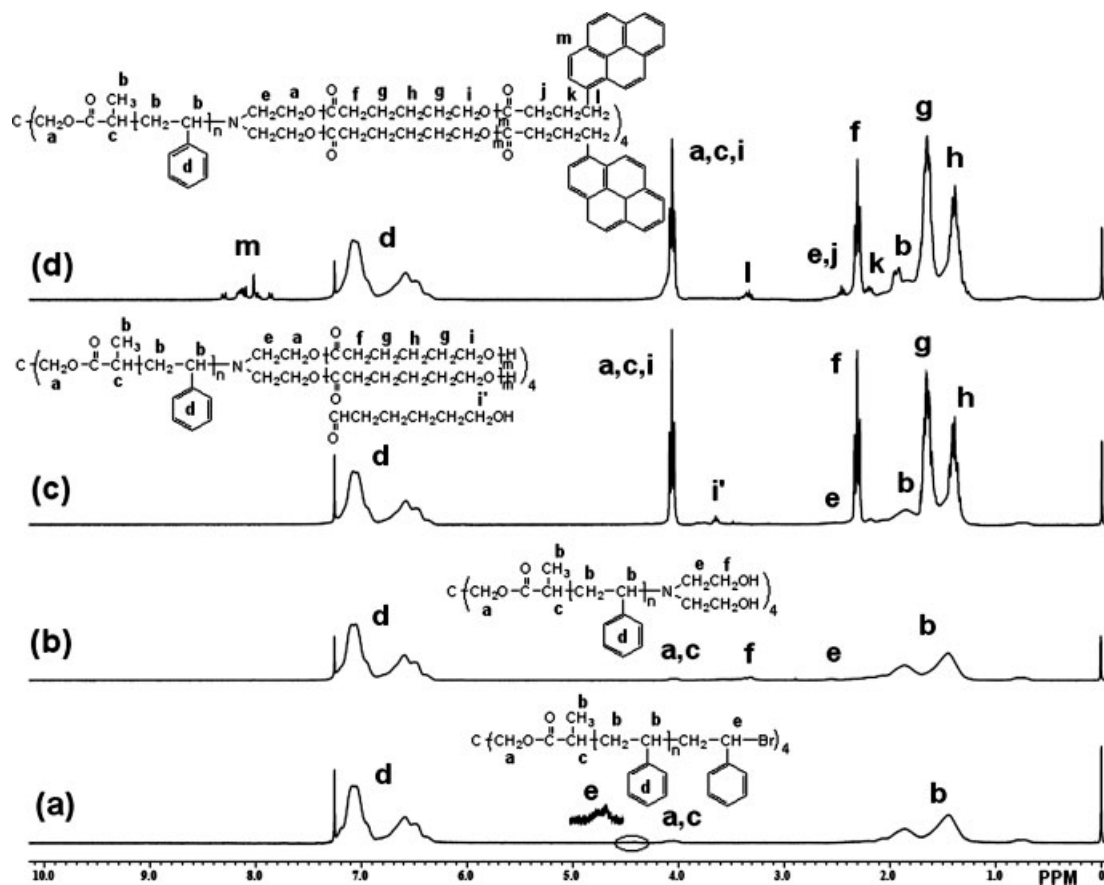
### Preparation of Four-Arm Star-Shaped Polymer (PSt-Br)<sub>4</sub>

The PENTA-Br initiator was obtained by the esterification of pentaerythritol with 2-bromopropionyl bromide.  $^1H$  NMR spectrum was used to prove the successful synthesis of the tetrafunctional initiator. Then four-arm star-shaped polymer (PSt-Br)<sub>4</sub> could be synthesized by the

ATRP of St with PENTA-Br as initiator at 110 °C in anisole with  $[St]:[C-Br]:[CuBr]:[bpy] = 60:1:1:2$ . The results are listed in Table 1. The molecular weight of four-arm star-shaped polymer (PSt-Br)<sub>4</sub> was increased with the evolution of polymerization. For confirmation of the polymer structure, the  $^1H$  NMR spectra were measured and a typical spectrum is shown in Figure 1(a). All the proton signals of the star-shaped polymer could be detected. The average degree of polymerization of PSt arm was obtained from the integration of the proton signals at 6.28–7.33 ppm (aromatic protons in PSt) and 4.48 ppm (methine proton next to the terminal bromine group in PSt). The kinetic plot of star-shaped PSt formation is shown in Figure 2. The conversion of St reached 65.9% at 5 h in anisole. The plot of  $\ln([M_0]/[M])$  against polymerization time seemed linear, and crossed the zero point. This result could demonstrate that the first-order kinetics could be maintained until relative high conversion, suggesting the concentration of active species remained constant throughout the course of polymerization of St. It could be seen in Figure 3 that  $M_{n,NMR}$  values were close to  $M_{n,th}$ , which increased linearly with conversion, indicating the molecular weight of the star-shaped PSt could be manipulated by the control of monomer conversion. Moreover, the molecular weight distributions of the copolymers were narrow ( $M_w/M_n = 1.16$ –1.26). Obviously, the PENTA-Br could be used as an efficient initiator for living polymerization of St to form four-arm star-shaped polymer (PSt-Br)<sub>4</sub>.

### Preparation of Eight-Arm Star-Dendrimer Copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>

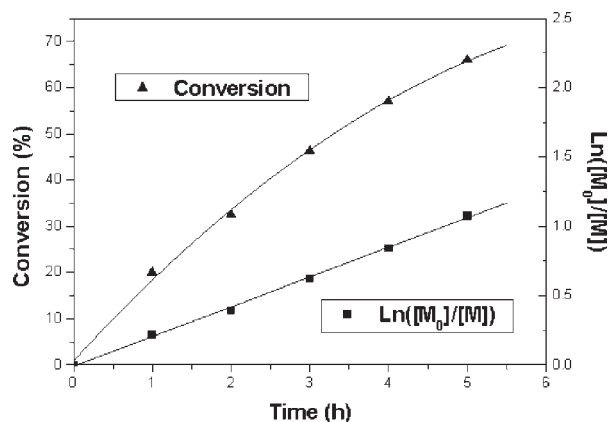
To prepare the eight-arm star-dendrimer copolymer, the divergent reaction for transformation of



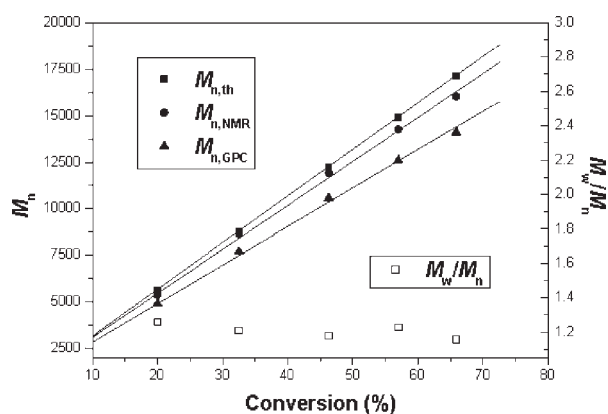
**Figure 1.**  $^1\text{H}$  NMR spectra of (a)  $(\text{PSt-Br})_4$ , (b)  $(\text{PSt-(OH)}_2)_4$ , (c)  $(\text{PSt-}b\text{-(PCL)}_2)_4$ , and (d)  $(\text{PSt-}b\text{-(PCL-pyrene)}_2)_4$ .

four bromine groups into eight hydroxyl groups is necessary. As a result, diethanolamine was used to react with  $(\text{PSt-Br})_4$  to produce eight-hydroxyl star-shaped polymer  $(\text{PSt-(OH)}_2)_4$  by the nucleophilic substitution reaction.<sup>49,50</sup> An

excess amount of diethanolamine was used in this reaction to ensure complete transformation of one terminal bromine group into two hydroxyl groups. According to  $^1\text{H}$  NMR [Fig. 1(b)], the peak assigned to methine proton at 4.48 ppm in



**Figure 2.** Kinetic plot for ATRP of St with PENTA-Br initiator.  $[\text{St}]:[\text{C-Br}]:[\text{CuBr}]:[\text{bpy}] = 60:1:1:2$  in anisole at  $110^\circ\text{C}$ .



**Figure 3.** Evolution of  $M_n$  and  $M_w/M_n$  of  $(\text{PSt-Br})_4$  with conversion for ATRP of St. See Table 1 for reaction conditions.

**Table 2.** Results for Polymerization of Eight-Hydroxyl Star-Shaped Polymer (PSt-(OH)<sub>2</sub>)<sub>4</sub> Initiator with Various Amounts of CL by ROP<sup>a</sup>

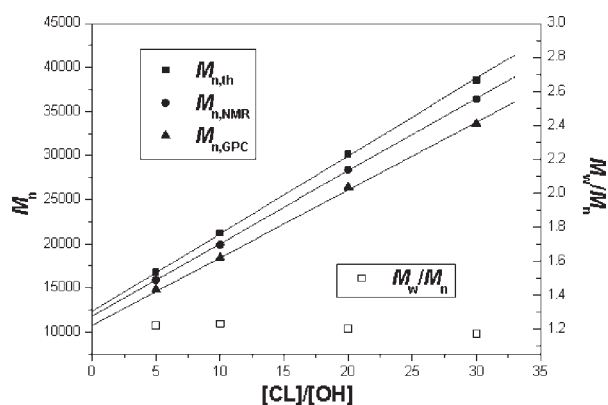
Sample	[CL]/[OH] <sup>b</sup>	$M_{n,th}$ <sup>c</sup>	$M_{n,NMR}$ <sup>d</sup>	$M_{n,GPC}$ <sup>e</sup>	$M_w/M_n$ <sup>e</sup>	Conversion (%)
6	5	16,800	15,900	14,800	1.22	98.4
7	10	21,200	19,900	18,400	1.23	97.3
8	20	30,200	28,400	26,400	1.20	98.1
9	30	38,600	36,400	33,600	1.17	96.1

<sup>a</sup> Reaction conditions: [CL]/[Sn(Oct)<sub>2</sub>] = 1000, polymerization time = 24 h, polymerization temperature = 115 °C.<sup>b</sup> The product obtained from the reaction of Sample 3 with diethanolamine was used as the initiator for the ROP of CL.<sup>c</sup>  $M_{n,th} = [CL]/[OH] \times 4 \times M_{CL} \times \text{Conversion\%} + M_{initiator}$ ,  $M_{n,th}$  denotes the average number molecular weight of eight-arm star-dendrimer copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>.<sup>d</sup>  $M_{n,NMR}$  was determined by <sup>1</sup>H NMR spectroscopy of eight-arm star-dendrimer copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>.<sup>e</sup>  $M_{n,GPC}$  and  $M_w/M_n$  were determined by GPC analysis with polystyrene standards. THF was used as eluent.

Figure 1(a) disappeared completely, and the new peaks at 3.54 and 2.59 ppm were observed, which belong to the two methylene protons, respectively, next to the hydroxyl and the amino groups. This indicated that terminal bromine groups were transformed completely. The terminal hydroxyl groups of (PSt-(OH)<sub>2</sub>)<sub>4</sub> were used as the initiators to initiate ROP of CL to synthesize the eight-arm star-dendrimer copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> at 115 °C. A typical <sup>1</sup>H NMR spectrum of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with assignment is presented in Figure 1(c). The major resonance peaks were attributed to PSt and PCL, and the methylene proton signal (*i'*,  $\delta = 3.64$  ppm) indicated that PCL was terminated by hydroxyl end groups. Therefore, the eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with hydroxyl groups was successfully synthesized from the polymerization of PCL with (PSt-(OH)<sub>2</sub>)<sub>4</sub> macroinitiator. To obtain copolymers with different molecular weight, various amounts of CL ([CL]/[OH] = 5, 10, 20, 30) were used. The average number molecular weights determined by <sup>1</sup>H NMR spectroscopy were calculated from the integration ratio between the methylene protons in the repeat units (*i*) and the methylene protons in the terminal unit (*i'*). The results of polymerization on CL are shown in Table 2. It can be seen from Table 2 and Figure 4 that the number-average molecular weight of the resulting eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> linearly increased with the molar ratio of monomer to initiator and the molecular weight distributions were narrow ( $M_w/M_n = 1.17$ – $1.23$ ), which indicated that the terminal hydroxyl groups in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> were used as effective propagation centers.

### Preparation of Pyrene-Containing Eight-Arm Star-Shaped Dendrimer-Like Copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>

The coupling reaction of hydroxyl-terminated (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with 1-pyrenebutyric acid was carried out at room temperature in the presence of DCC and DMAP. Comparing with <sup>1</sup>H NMR of the parent copolymer (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> in Figure 1(c), new signals assigned to pyrenyl protons and methylene protons in 1-pyrenebutyric acid could be observed in Figure 1(d), while the signal at 3.64 ppm (terminal methylene protons of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>) wholly disappeared, revealing that all the terminal hydroxyl groups have reacted with 1-pyrenebutyric acid completely. The average number molecular weight of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> measured by <sup>1</sup>H NMR can be calculated from the relative integral values of the pyrenyl protons (*m*) to the methylene protons (*i*) of PCL blocks. The results are listed in Table 3.

**Figure 4.** Dependence of  $M_n$  on the molar ratio of [CL]/[OH] with (PSt-(OH)<sub>2</sub>)<sub>4</sub> initiator and Sn(Oct)<sub>2</sub> catalyst at 115 °C.



**Table 3.** Synthesis of Eight-Arm Star-Shaped Dendrimer-Like Copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> by Coupling Reaction<sup>a</sup>

Sample	Copolymer Precursor	$M_{n,NMR}^b$	$M_{n,GPC}^c$	$M_w/M_n^c$	Yield (%)
10	Sample 6	18,000	16,600	1.26	96.8
11	Sample 8	30,600	27,300	1.23	98.1

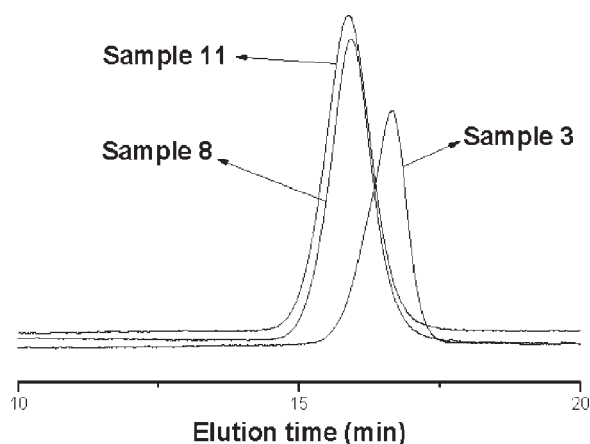
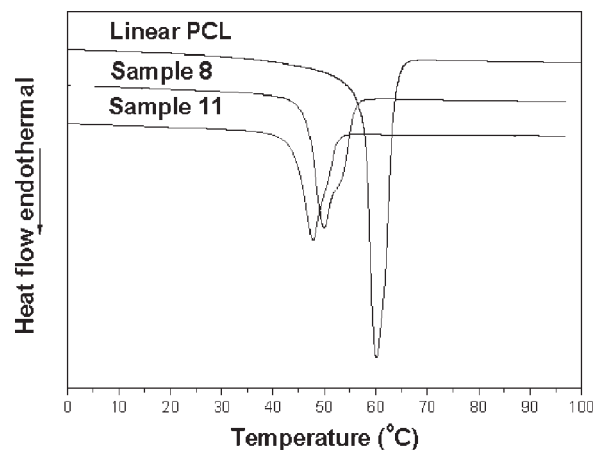
<sup>a</sup> Feed molar ratio of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>/1-pyrenebutyric acid/DCC/DMAP = 1/8/16/4, solvent: chloroform.<sup>b</sup>  $M_{n,NMR}$  was determined by <sup>1</sup>H NMR data.<sup>c</sup>  $M_{n,GPC}$  and  $M_w/M_n$  were determined by GPC analysis with polystyrene standards. THF was used as eluent.

The GPC traces of (PSt-Br)<sub>4</sub> (Sample 3), (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8), and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11) are shown in Figure 5. These traces were monomodal, suggesting that these purified polymers were pure star-shaped or star-shaped dendrimer-like copolymers.

### Thermal Properties and Crystalline Morphologies of Star-Shaped Dendrimer-Like Copolymer

The thermal properties of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> were investigated by DSC. As shown in Figure 6 and Table 4, the melting temperature ( $T_m$ ) and the degree of crystallinity ( $X_c$ ) of PCL segments in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> were lower than those of linear PCL and increased with the increase in the length of the PCL chains, which should be attributed mainly to the crystalline imperfection of the short chain length of PCL segments in the star-shaped dendrimer-like copolymers. Moreover, the dendritic structure of these polymers should make contribution to the imperfection. In the star-shaped dendrimer-like copolymer, chain movements of PCL segments were hin-

dered and their crystallizability was weakened. Moreover, the crystallizability of PCL segments was seriously hindered by amorphous PSt segments in the star-shaped dendrimer-like polymer. To (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>, the crystallizability of PCL segments was further weakened. For example, the  $T_m$  and  $X_c$  of PCL segments in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8) were 49.9 °C and 23.9%, respectively, whereas the  $T_m$  and  $X_c$  of PCL segments that existed in (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11) decreased to 47.8 °C and 17.0%, respectively. It is obvious that the crystallizability of PCL segments was hindered by pyrene groups. Furthermore, the chain conformation of star-shaped dendrimer-like copolymer resulted in less intermolecular interaction, which led to the decrease of the enthalpy of fusion. As a result, the crystallizability of PCL segments was restrained. As shown in Figure 6, there were no perfect single melting signal in DSC curves of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8) and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11), which should be attributed to the imperfection of the crystallinities of copolymers.

**Figure 5.** GPC traces of (PSt-Br)<sub>4</sub> (Sample 3), (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8), and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11).**Figure 6.** DSC curves of linear PCL, (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8), and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11).

**Table 4.** Thermal Properties of Eight-Arm Star-Shaped Dendrimer-Like Copolymers by DSC

Sample <sup>a</sup>	$T_m$ (°C) <sup>b</sup>	$\Delta H$ (J/g) <sup>c</sup>	$X_c$ (%) <sup>d</sup>
Linear PCL	60.2	71.4	52.5
6	40.1	5.6	4.1
7	45.3	17.4	12.8
8	49.9	32.5	23.9
9	53.6	40.3	29.6
11	47.8	23.2	17.0

<sup>a</sup> Samples are the same as in Table 1. The molecular weight of linear PCL ( $M_{n, GPC}$ ) is 18,100.

<sup>b</sup>  $T_m$  denotes the melting temperature of linear PCL and PCL segments in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub>.

<sup>c</sup> Heat of melting of crystalline linear PCL and PCL segments in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>.

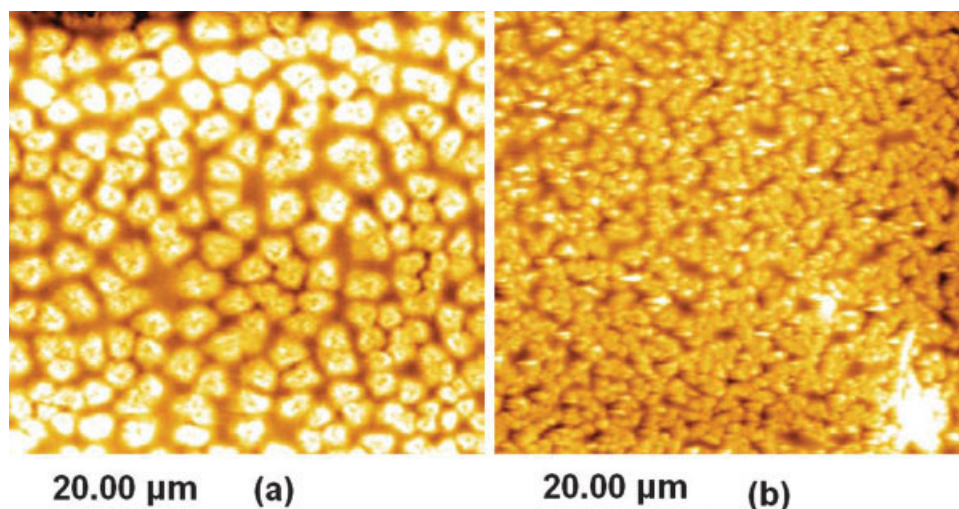
<sup>d</sup> The degree of crystallinity of linear PCL and PCL segments in (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>. Calculated from the heat of melting using the melting of 136.1 J/g of 100% crystalline PCL.

AFM images were used to observe the different crystalline morphologies of copolymers with different structure and composition. The AFM height images of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> are shown in Figure 7. In our previous report, the linear PCL presented large spherulites, which indicated that linear PCL possessed good crystallizability.<sup>51</sup> However, according to the image of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> [Fig. 7(a)], the spherulites were much smaller than those of linear PCL, which could be ascribed to the star-shaped dendrimer-like structure and PSt segments inducing the decrease of the crystallizability of copolymer. In star-shaped den-

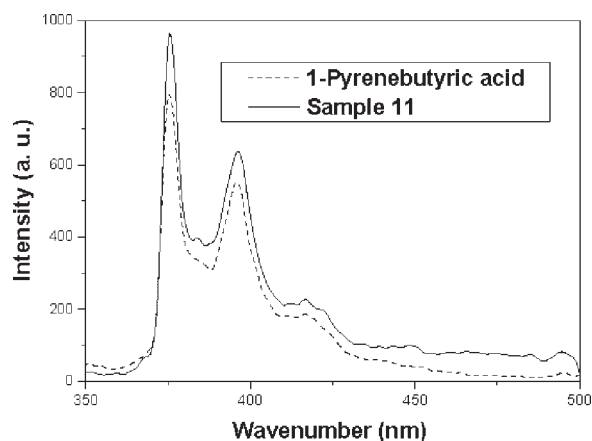
drimer-like copolymer, the movement ability of the chains of PCL segments decreased and the nucleation ability increased, therefore, the formation of large spherulites was impossible and only many small spherulites could be formed. The morphology of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> is shown in Figure 7(b), and the spherulites were tiny, which could be attributed to the presence of pyrene groups in copolymer leading to further weakening of the crystallizability.

#### Fluorescence Analysis of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>

The obtained eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> were further characterized by fluorescence spectroscopy. 1-Pyrenebutyric acid was used as a counterpart. The pyrene concentration was 10<sup>-5</sup> mol/L in chloroform. The maximum-excitation wavenumber of pyrene was 244 nm according to the measurement of UV-vis spectroscopy. Figure 8 shows the fluorescence spectra of 1-pyrenebutyric acid and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>. The maximum-emission wavenumber was 376 nm. According to Figure 8, the pyrene fluorescence intensity of 1-pyrenebutyric acid was somewhat weaker than that of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>. Namely, (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> presented slightly stronger fluorescence intensity than 1-pyrenebutyric acid small molecule when the pyrene concentration of them were the same. This should be attributed to the formation of ester bond in (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> after the cou-



**Figure 7.** AFM height images of (a) (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> (Sample 8) and (b) (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11).



**Figure 8.** Fluorescence spectra of 1-pyrenebutyric acid and (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> (Sample 11) in chloroform (pyrene concentration: 10<sup>-5</sup> mol/L).

pling reaction of (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with 1-pyrenebutyric acid, which could enhance the fluorescence intensity of (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub>. To some extent, this will be beneficial for detection of the luminescent moiety and enable (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> for fluorescence materials, biological probe, and photodynamic therapy applications.

## CONCLUSIONS

Novel and well-defined pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> were successfully synthesized. Bromine-terminated four-arm star-shaped polymers (PSt-Br)<sub>4</sub> with narrow molecular weight distributions were synthesized by ATRP of St initiated by PENTA-Br. Subsequently, eight-hydroxyl star-shaped polymer (PSt-(OH)<sub>2</sub>)<sub>4</sub> was produced by the divergent reaction of (PSt-Br)<sub>4</sub> with diethanolamine. Then eight-arm star-shaped dendrimer-like copolymers (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with expected molecular weights and narrow molecular weight distributions were synthesized by living ROP of CL in the presence of (PSt-(OH)<sub>2</sub>)<sub>4</sub> macroinitiator and Sn(Oct)<sub>2</sub> catalyst at 115 °C. Pyrene-containing eight-arm star-shaped dendrimer-like copolymer (PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> was prepared from the coupling reaction of hydroxyl-terminated (PSt-*b*-(PCL)<sub>2</sub>)<sub>4</sub> with 1-pyrenebutyric acid. The eight-arm star-shaped dendrimer-like copolymers presented unique thermal properties and crystalline morphologies, which were different from those of linear PCL. Fluorescence analysis indicated that

(PSt-*b*-(PCL-pyrene)<sub>2</sub>)<sub>4</sub> presented slightly stronger fluorescence intensity than 1-pyrenebutyric acid when the pyrene concentration of them were the same. The pyrene-containing eight-arm star-shaped dendrimer-like copolymer has potential applications in biological fluorescent probe, photodynamic therapy, and optoelectronic devices.

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