PCL Star Polymer, PCL-PS Heteroarm Star Polymer by ATRP, and Core-Carboxylated PS Star Polymer Thereof

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ABSTRACT: Poly(ϵ-caprolactone) (PCL) star polymer with a cross-linked microgel core was synthesized by atom-transfer radical polymerization (ATRP) of divinylbenzene (DVB) using mono-2-bromoisobutyryl PCL ester as a macroinitiator. Then poly(ϵ-caprolactone)-polystyrene (PCL-PS) heteroarm star polymer was produced subsequently by grafting PS from the core of PCL star polymer in which the initiating groups were inherited from PCL star formation using ATRP. Characterization by size exclusion chromatography (SEC) and ^{1}H NMR demonstrated the successful preparation of the target star polymers. Since the PCL was linked with the core through an ester group, the bare microgels bearing carboxylic acid or ester groups were produced by hydrolysis or alcoholysis to degrade the PCL chains of the PCL star polymers, respectively. PS star polymer with a core functionalized with carboxylic acid groups was also prepared by the hydrolysis of PCL-PS heteroarm star polymer. To illustrate the unique characteristics of this novel core-functionalized PS star polymer, it was used to prepare monodispersed lead sulfide (PbS) nanoparticles.

1. Introduction

More and more attention has been attracted to star polymers due to their unique properties.[1,2] The synthesis of star polymers from vinyl monomers using living anionic polymerization,[3,4] cationic polymerization,[5,6] and recently controlled radical polymerization (CRP)[7,8] has been extensively studied. CRP technique has great advantages in preparing well-defined polymers, such as extensively available monomers and mild reaction conditions. Generally, there are two basic methods for preparing star polymers. One is the so-called "core-first" method in which a multifunctional initiator is used to initiate the polymerization of monomer to form a multiarm star polymer.[9,10] The other is the so-called "arm-first" method. A terminally reactive linear polymer initiates the polymerization of a cross-linkable monomer to form a microgel, in which a number of arms are anchored.[4,6,11−15] Grafting a second kind of segment from the core of a star polymer produced by the arm-first method can produce heteroarm star polymers, which have also attracted much attention because of their interesting microphase separation properties in solution and solid state.[16,17] Both anionic polymerization[18−21] and cationic polymerization techniques[22] have been applied to prepare such heteroarm star polymers.

PCL and its star polymers are biodegradable and may therefore have potential applications as biomaterials. Star PCLs were obtained by a termination reaction of the living PCL chains with aluminum alkoxides[23] and by ring-opening polymerization (ROP) of ϵ-caprolactone (CL) using a multifunctional initiator.[24−30] In recent years, attention on synthesis of the heteroarm star polymers with PCL as their arms has been increasing. To build complex polymer architectures, for their potential applications in self-assembly and biomaterials, is the focus of researchers. For example, PCL-PS heteroarm star polymer was prepared by chelation of PS-*b*-PCL copolymer with a bipyridine donor at the block junction to metal ions.[31,32] Poly(ϵ-caprolactone)$_3$-poly(methyl methacrylate)$_3$ (PCL$_3$-PMMA$_3$)[33] and poly(ethylene oxide)-poly(ϵ-caprolactone)-polystyrene (PEO-PCL-PS) heteroarm star polymers[34,35] were produced by a combination of different polymerization techniques.

Recently, we have developed an approach to prepare PEO star polymer by atom-transfer radical polymerization (ATRP) of divinylbenzene (DVB) with a bromoisobutyryl PEO ester as macroinitiator.[36] Since the C−X (X = Br or Cl) groups in the core of the star polymer prepared may undergo an atom-transfer addition reation,[13] PEO-PS heteroarm star polymer was produced by a second ATRP to graft polystyrene (PS).[36] Here we present the successful syntheses of PCL star polymers and PCL-PS heteroarm star polymers by this approach, as shown in Scheme 1. In addition, because the microgel core was linked with PCL by ester groups, the bare polyDVB (PDVB) microgel and PS star polymer with carboxyl-functionalized core were prepared by hydrolysis of PCL arms in PCL star and PCL-PS heteroarm star, respectively. To our knowledge, the syntheses of PCL star polymer and PCL-PS heteroarm star polymers by ATRP approach have not been reported before. Also, core-carboxylated PS star polymer thereof is a novel functionalized polymer, which can be used to prepare monodispersed PbS nanoparticles.

2. Results and Discussion

2.1. PCL Star Polymer by ATRP. Linear bromoisobutyryl PCL macroinitiator (PCL-Br) for ATRP was obtained by the modification of PCL by 2-bromoisobutyryl bromide. The structure of PCL-Br was proven by ^{1}H NMR spectroscopy (Figure 1A). The peak at δ 1.96 ppm is from the protons of $-OCOC(CH_3)_2Br$ at the chain end. The peaks at δ 5.2 and 7.3 ppm are attributed to the protons of the benzyl group situated at the other side of the chain. Other signals are ascribed to the protons of the PCL chain. As shown by SEC traces in Figure 2, a monomodal peak of PCL-*b*-PS diblock

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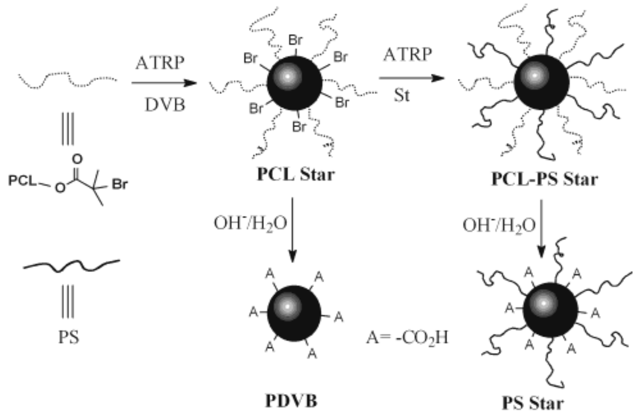
Scheme 1. Schematic of Syntheses of Poly(ϵ-caprolactone) (PCL) Star, Poly(ϵ-caprolactone)-Polystyrene (PCL-PS) Heteroarm Star Polymers by ATRP, and the Hydrolysis of the Two Star Polymers (DVB = Divinylbenzene)



copolymer with low molecular weight distribution was obtained by ATRP chain extension using PCL-Br as the macroinitiator and styrene as a monomer, which further proves the high purity and high initiation efficiency of PCL-Br macroinitiator. DVB has been used widely as a cross-linking reagent for the arm-first approach to the star polymer.[4,12] It is also important in the present work because PDVB is stable against a hydrolysis condition, which was used to degrade the PCL chain. The effects of the molar ratio of DVB to linear PCL, reaction temperature, solvent, and different catalyst system on the star formation were found important for star formation.[12,37] The optimal ATRP condition was applied to the synthesis of PCL star (see Experimental Section).

SEC traces of polymers during the polymerization in Figure 3 illustrate the gradual evolution of PCL star polymer. With time, the molecular weight of star polymer increased correspondingly. After 7 h, almost only one peak was observed in the SEC traces. The kinetic plot of PCL star polymer formation is shown in Figure 4. The plot of ln([M$_0$]/[M$_t$]) against polymerization time seems linear, though it did not cross the zero point. This result also demonstrates that the radical concentration keeps nearly constant during the propagation under the condition used; i.e., the termination is negligible. Illustrated in Figure 1B is the ^{1}H NMR spectrum of PCL star polymers (sample 1 in Table 1). The broad peaks in the region of δ 5.0−7.3 ppm with negligible intensity correspond to the protons of PDVB, which demonstrate the formation of PDVB microgel.[11] The peaks at δ 1.3, 1.8, 2.4, and 4.1 ppm are assigned to the protons of methylenes in PCL arms. The weight fractions of PCL in two PCL star polymers, samples 1 and 2, were evaluated by elemental analysis (EA), and the ratio of CL to DVB could be estimated, as summarized in Table 1. According to the following equation, we can estimate the arm numbers:

$$m = \frac{M_{\mathrm{W,PCLstar}} \cdot \mathrm{PCL\%}}{M_{\mathrm{NMR,PCL}} \cdot \mathrm{PDI}_{SEC}} = \frac{405900 \times 87.4\%}{5400 \times 1.27} = 52$$

where $M_{\mathrm{w,PCLstar}}$ is the absolute molecular weight of sample 2, measured by SEC with a LS detector. PCL% is the weight content of PCL in whole star polymer, determined by EA.

2.2. PCL-PS Heteroarm Star Polymer Formation. Sawamoto et al. have proved that the C−Br on the core of the star polymer is active for atom addition reaction.[13] There is a possibility of coupling between C−Br species since its local concentration can be high during the formation of the above PCL star polymer. However, such termination is negligible, as proven by the kinetic study in the previous section (Figure 4). In addition, very low intensity assigned to the protons of PDVB in the ^{1}H NMR spectrum of PCL star (Figure 1B) has already illustrated very low mobility of PDVB in solution due to limitation of the microgel network. Therefore, the slight termination during the star formation is reasonable since it is not easy for the C−Br of low mobility to couple. Therefore, the number of C−Br on the core should be the same as PCL arm in a star polymer. If second chains are grafted from this star polymer by ATRP, the number of two types of arms should be the same as well.

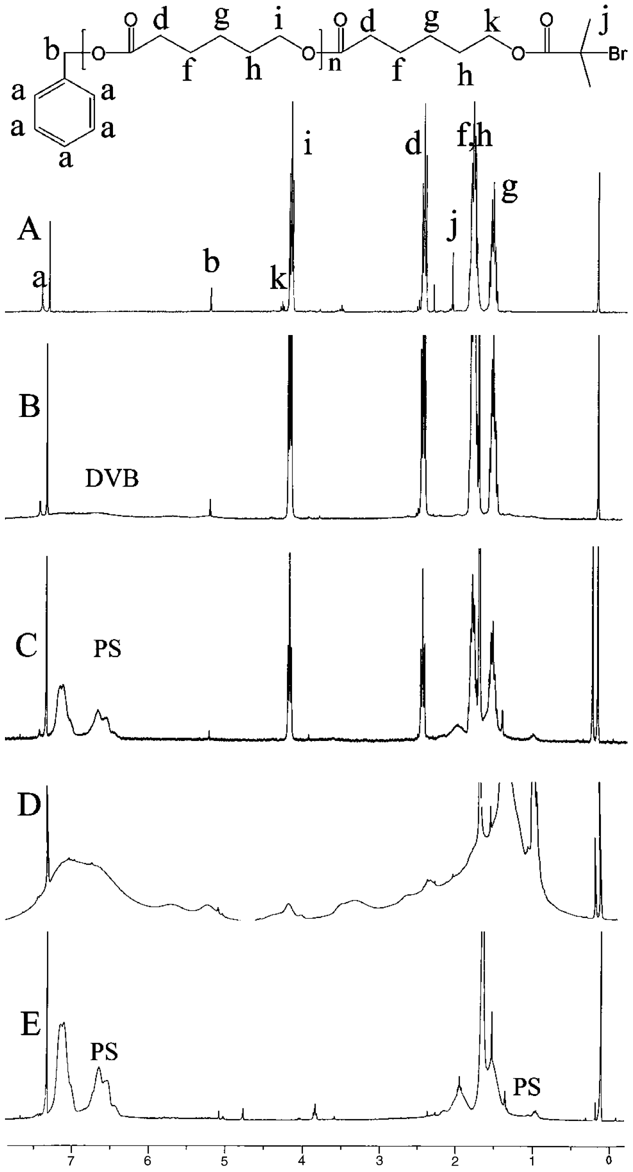


Figure 1. ^{1}H NMR spectra: (A) PCL-Br initiator; (B) PCL star, sample 1 in Table 1; (C) PCL-PS heteroarm star, sample 5; (D) PDVB core obtained from hydrolysis of PCL star; (E) PS star polymer by hydrolysis of PCL-PS heteroarm star polymer, sample 6.

PCL-PS heteroarm star polymer was produced by ATRP of styrene with PCL star, sample 1 or 2, as the macroinitiator. Figure 5 shows the SEC traces of grow-

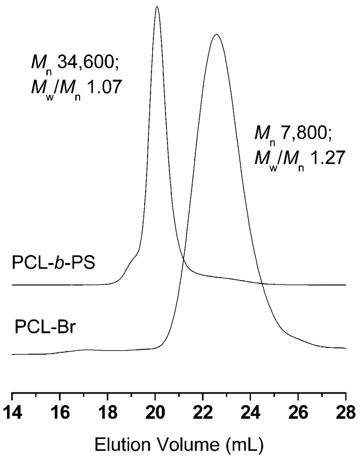


Figure 2. SEC traces of PCL chain extension by ATRP of styrene using PCL-Br as macroinitiator: $[\text{PCL-Br}]_0 = [\text{CuBr}]_0/2 = [\text{PMDETA}]_0/2 = [\text{St}]/650$ at 110 °C in bulk; reaction time = 4.5 h.

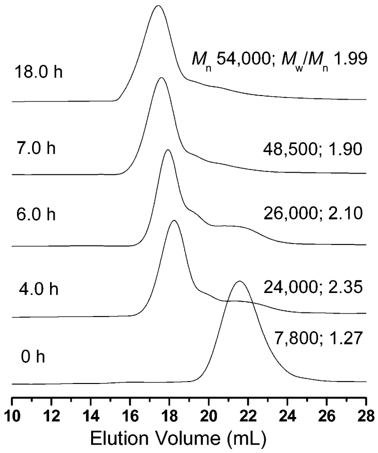


Figure 3. SEC traces of PCL star formation at various times: $[\text{PCL-Br}]_0 = [\text{CuBr}]_0/1.3 = [\text{PMDETA}]_0/1.3 = [\text{DVB}]/26.8$ in anisole (1.000 g of PCL-Br in 4.0 mL of anisole) at 110 °C.

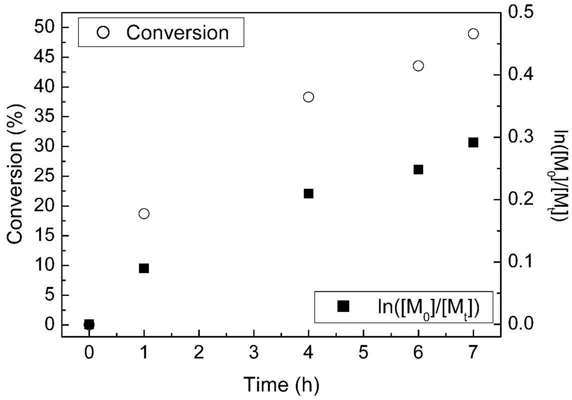


Figure 4. Semilogarithmic kinetic plot of DVB conversion vs reaction time during PCL star polymer formation (under the same conditions as those shown in Figure 3).

Table 1. Characteristics of Poly(ϵ-caprolactone) (PCL) Star Polymers, PCL-Polystyrene (PCL-PS) Heteroarm Star Polymers, and Hydrolyzed PCL-PS Star Polymers

sample	$M_{\text{n SEC}}$[d]	M_w/M_n[d]	M_P[d]	CL%[e]	CL%[f]	St:CL:DVB[g]
1[a]	42 600	2.17	87 300	~100[h]	67.7	0:2.4:1
2[a]	26 000	2.10	60 700	~100[h]	87.4	0:7.9:1
3[b]	69 100	2.74	280 700	20.4	24.2	7:2.4:1
4[b]	78 200	1.9	152 700	48.4	47.4	8.4:7.9:1
5[b]	83 500	1.83	161 400	45.0	44.1	9.8:7.9:1
6[c]	76 900	1.70	122 900	0		9.8:0:1[i]
7[c]	117 100	1.54	178 700	0		8.4:0:1[i]

[a] PCL star. [b] PCL-PS star, sample 3 using 1, others using 2 as an initiator. [c] PS star, 6 from hydrolysis of 5, 7 from 4. [d] Obtained from SEC with PS standard as calibration. [e] Weight fraction of CL unit in PCL star polymers, and PCL-PS heteroarm star polymers determined by ^{1}H NMR. [f] Weight fraction of CL unit in those samples determined by EA, i.e. for PCL star: $\text{CL}_{\text{PCLstar}}\text{wt}\,\% = (C_{\text{DVB}} - C_{\text{PCLstar}})/(C_{\text{DVB}} - C_{\text{CL}}) \times 100\%$; for PCL-PS star: $\text{CL}_{\text{PCL-PS star}}\,\text{wt}\,\% = \text{CL}_{\text{star}}\,\text{wt}\,\%\,(C_{\text{St}} - C_{\text{PCL-PS star}})/(C_{\text{St}} - C_{\text{PCL star}}) \times 100\%$; C stands for the carbon content. [g] Molar ratio of St:CL:DVB, from EA, $(\text{wt}_{\text{St}}\,\%/M_{\text{St}})/(\text{wt}_{\text{CL}}\,\%/M_{\text{CL}})/(\text{wt}_{\text{DVB}}\,\%/M_{\text{DVB}})$, M stands for the molecular weight. [h] Apparent value from ^{1}H NMR spectra. [i] Inherited from the value of corresponding precursors.

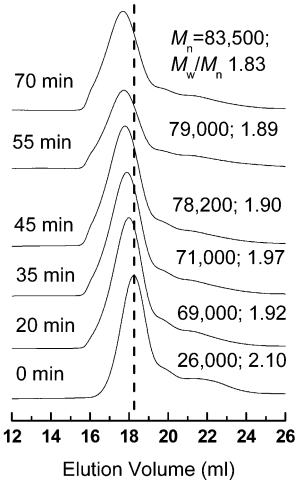


Figure 5. SEC traces of PCL-PS heteroarm star polymer formation at various times: $[-\text{Br in PCL star}]_0/0.087 = [\text{CuCl}]_0 = [\text{PMDETA}]_0 = [\text{St}]/100$ in bulk at 110 °C. The macroinitiator was sample 2.

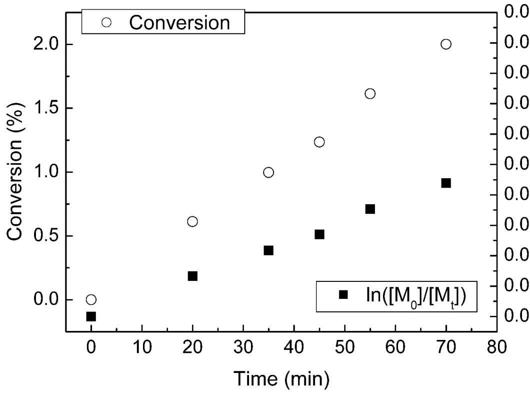


Figure 6. Semilogarithmic kinetic plot of styrene conversion vs reaction time during formation of PCL-PS heteroarm star polymer.

ing polymer by grafting PS from the core of PCL star at various reaction times. The molecular weight increases with relatively low molecular weight distribution. The kinetic study demonstrated that the semilogarithmic plot of styrene conversion vs time seemed to display first-order kinetics with respect to styrene (Figure 6). The styrene conversion did not exceed 3% in the kinetic studies; broad molecular weight distributions appeared above this limit. When styrene conversion was more than 10%, star−star coupling occurred to produce a cross-linked gel. Three typical heteroarm star polymers with different PS content were synthesized, as shown in Table 1. Polymers 4 and 5 were withdrawn from the same reaction flask at different times.

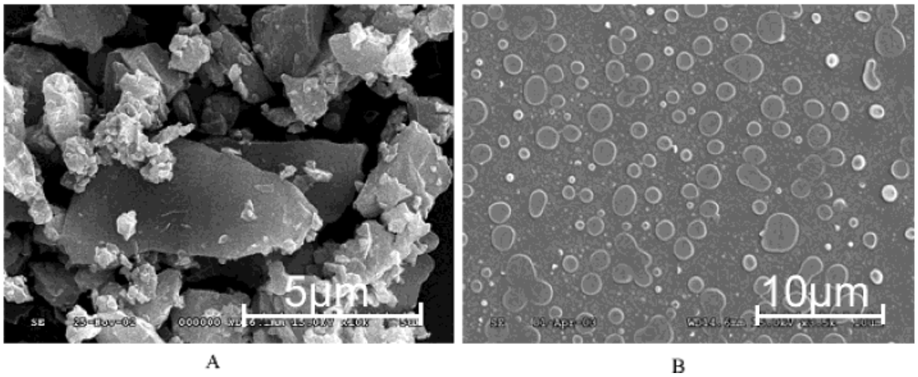


Figure 7. SEM images of PCL star, sample 1 in THF (A); PCL-PS heteroarm star polymer, sample 3, in THF (0.2 mg/mL) (B).

The ^{1}H NMR spectrum (Figure 1C) of the PCL-PS heteroarm star (sample 5 in Table 1) clearly showed that the PS segment (δ 6.3−7.3 ppm) has been introduced into the star. If the small contribution from protons of PDVB in the spectrum was ignored, the molar ratio of CL unit to St unit was estimated to be 1:1.2 by comparing integral areas of corresponding segments in the spectra. By EA, the weight fraction of CL unit decreased from 87.4% (PCL star) to 44.1% (PCL-PS star), which also demonstrated the introduction of PS segment. As shown in Table 1, the molar ratio of St unit to CL unit by EA is 2.9:1, 1.1:1, and 1.2:1 for samples 3, 4, and 5, respectively. Since the number of PCL chains and PS chains is believed to be the same, and the polymerization degree of PCL is known, the polymerization degree of PS chain in three heteroarm stars were thus estimated to be around 138, 50, and 59 for samples 3−5, respectively. The absolute M_w of sample 5 determined by SEC with a light scattering detector is 2 363 000; but this result is doubtful since it is much larger than the one determined by EA, as shown in the following equation. Perhaps aggregates formed in $CHCl_3$ during the measurement of M_w.

$$M_{\mathrm{PCL-PSstar}} = \frac{M_{\mathrm{PCLstar}}}{\mathrm{wt}_{\mathrm{PCLstar-in-heteroarmstar}}\%} = \frac{405\ 900}{50.4\%} = 805\ 400$$

To compare the difference between PCL star and PCL-PS star, the morphology study by scanning electron microscopy (SEM) was performed. Compared in Figure 7 are two SEM images obtained by depositing a drop of dilute tetrahydrofuran (THF) solution of two stars, respectively, onto silica substrates and allowed to dry in the atmosphere. The SEM image of PCL star shows a crystalline morphology as expected since PCL is crystalline at room temperature. However, the PCL-PS star polymer, sample 3, gave a quite different morphology with no obvious crystallinity. Although the formation mechanism is still unclear, introduction of PS should play a great role in the morphological difference between two stars.

2.3. Hair-Cut PDVB Microgels by Hydrolysis and Alcoholysis of PCL Star. Even though many star polymers with PDVB as the microgel core were reported by the arm-first approach in the literatures by different polymerization techniques,[11,12,14] it was hard to know the properties of the core without polymer "hairs" on its surface since all of the arms were linked with the core via a C−C bond. The cross-linked PDVB core here could be obtained easily upon the hydrolysis of ester groups in the junction of the PCL arm and the PDVB core. PCL arms were cut into small molecules under alkaline condition, and one −COOH group from each PCL-Br macroinitiator was left on the core. In Figure 1D, peaks originating from the protons of PCL disappeared completely, which demonstrates that the PCL chains have been removed effectively. Demonstrated in Figure 8B is the SEC trace of the bare PDVB core obtained from hydrolysis of sample 1. It gives a broad polydispersity (M_n = 10 700; M_w/M_n = 5.6), which is much different from the PCL star. On the other hand, an alcoholysis reaction of PCL star was also performed to degrade polyester chains. The reaction was made in ethanol with sulfuric acid as the catalyst. Ethyl esters on the microgel were produced in such a case. Its SEC trace (curve C in Figure 8) is similar to that from alkaline hydrolysis. These findings reveal that the microgel core of star polymers by the arm-first method has a wide size distribution. FTIR spectroscopy (Figure S1 in the Supporting Information) confirmed the presence of protonated carboxylic groups. There are two peaks around 1733 and 1701 cm^{-1}, attributed to ν(C=O) bands for free −COOH groups, or non-hydrogen-bonded and dimeric hydrogen-bonded modes, respectively. The microgel thus produced is functionalized with carboxyl groups on its surface. In principle, the number of the functionalities is the same as the number of arms in the PCL star polymers.

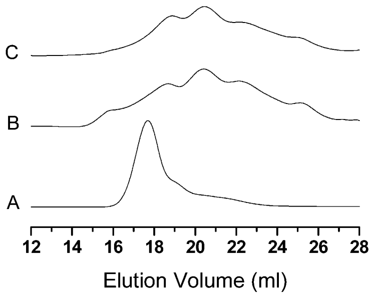


Figure 8. SEC traces of hydrolysis and alcoholysis of PCL star polymers: (A) before hydrolysis; (B) after hydrolysis and then precipitated in methanol; (C) after alcoholysis and then precipitated in methanol.

2.4. PS Star with a Carboxylated Core by Hydrolysis of the Heteroarm Star. Sawamoto's group has prepared the core-functionalized star polymers by applying cross-linking chemicals bearing functionalities during the arm-first way of ATRP.[13,38,39] By sacrificing the PCL arm that was linked with the core of PCL-PS

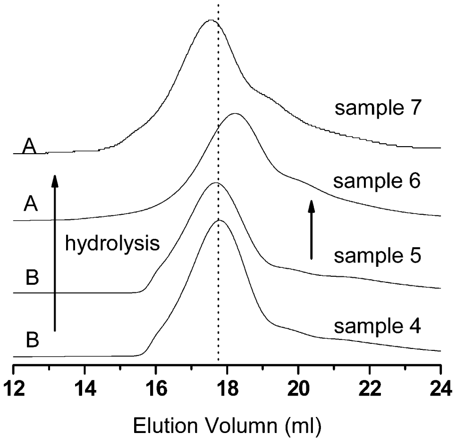


Figure 9. SEC traces of hydrolysis of PCL-PS heteroarm star polymers: (A) after hydrolysis; (B) before hydrolysis and then precipitated in methanol.

star polymers by the ester group, a new approach to give the core-functionalized star polymers was revealed. The number of COOH groups should be the same as the number of PCL arms in the heteroarm star polymers. PCL-PS heteroarm star polymers, samples 4 and 5, were hydrolyzed under alkaline condition to obtain core-carboxylated PS star polymers (samples 7 and 6, respectively). As shown by the ^{1}H NMR spectrum in Figure 1E, the protons of PCL (at δ 4.2, 2.4, 1.8, and 1.5 ppm) disappeared completely, and only PS arms (δ 6.3−7.3 and 1.2−2.0 ppm) remained (sample 6). Thus, hydrolysis was complete. On the other hand, EA of the star polymer and its hydrolytic product, samples 5 and 6, gave results of C 79.42% and H 8.15%, C 88.82% and H 7.67%, respectively. For samples 4 and 7, EA results are of C 78.47% and H 8.14%, C 88.88% and H 7.68%, respectively. The increases of carbon content for both stars demonstrate the removal of the PCL chain. Taking account of the equal theoretical carbon content of 92.31% in both St and DVB, the equal carbon contents in two PS stars with different length of PS arms also confirmed PCL arms were removed completely by hydrolysis. FT-IR spectroscopy confirms the presence of carboxylic groups in the star polymer of sample 6 (1726, 1701 cm^{-1}, Figure S1 in Supporting Information).

Figure 9 shows the SEC traces of heteroarm star polymers before and after hydrolysis. There was a decrease in the relative molecular weight after hydrolysis of sample 5, as expected since the PCL arms were removed. However, the absolute molecular weight (M_w) measured in chloroform is 681, 000, which is larger than the value based on EA results and the absolute M_w of PCL star. In addition, the molecular weight of sample 4 increased unexpectedly after hydrolysis. These results indicate that the PS star polymer might form aggregates in solution due to their amphiphilic nature; and the molecular weights given in solution seem doubtable.

2.5. Application of Core-Functionalized Star Polymers to Preparation of PbS Nanoparticles. PbS nanoparticle is a narrow band gap semiconductor.[40] When its crystal size decreased to a nanometer scale, a large blue shift would occur on its absorption edge.[40,41] Moreover, it may be applied in the field of nonlinear optical materials.[42] Applying amphiphilic copolymers as stabilizers to prepare PbS nanoparticles is an important method.[43,44] Instead, we prepared PbS nanoparticles using the above-mentioned core-carboxylated PS star polymer, which may supply a good nanoenvironment for the formation of PbS nanoparticles. Pb ion was first loaded into the core-carboxylated PS star polymer of sample 6, by refluxing in the presence of Pb acetate. PbS nanoparticle was then obtained by exposure of the star polymer containing Pb ion into a H_2S atmosphere. The hybrid was soluble, and a drop of solution in THF was spread on the grid for TEM analysis. Illustrated in Figure 10 is the TEM image. The spherical nanoparticles separated from each other, having an average diameter 3.0 ± 0.6 nm. The presence of PbS nanoparticle was confirmed by the selected area electron diffraction patterns of the PbS crystals in the PS star polymer, as shown in the inset of Figure 10. Data obtained from the diffraction pattern are shown in Table 2, which is consistent with a cubic structure for PbS nanoparticles. In addition, as shown in Figure 11, energy-dispersive X-ray (EDX) spectra gives a molar ratio of O:S:Pb = 4.19:1:1.20, which is very close to the theoretical value of 4:1:1.

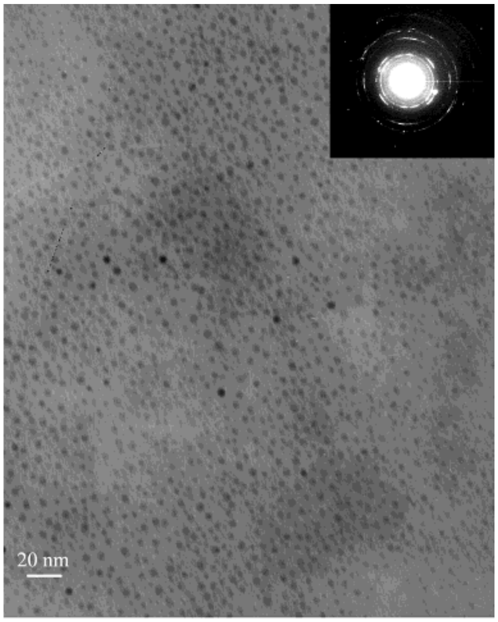


Figure 10. TEM image of PbS nanoparticles in PS star. The inset is the corresponding selected area electron diffraction (SAED) pattern.

Table 2. Selected Area Electron Diffraction (SAED) of PbS Nanocrystals Shown in Figure 10

n_d	Calcd[a] (d/Å)	Card[a] (d/Å)	*hkl*
1	1.781	1.790	311
2	1.506	1.484	400
3	1.297	1.296	421
4	0.902	0.905	533
5	0.786	0.773	553
6	0.653	0.660	663

[a] Calcd and Card stand for the experimental and literature values of *d* spacing, respectively.

3. Experimental Section

3.1. Materials. ϵ-Caprolactone (>99%, Across), DVB (tech. 80%, Aldrich), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA; >99%, Aldrich) were dried over CaH_2 and then distilled under reduced pressure. Stannous 2-ethylhexanoate ($SnOct_2$, approximately 95%, Sigma) was freeze-dried with benzene prior to use. Styrene (>99%, Beijing Chemical Reagent Co.) and anisole (>98%, Beijing Donghuan United Chemical Co.) were washed with 5% aqueous NaOH solution three times and then washed with water until the aqueous phase became neutral. They were dried over anhydrous

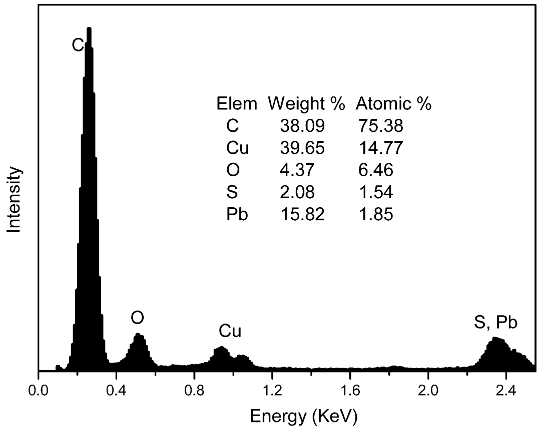


Figure 11. Energy-dispersive X-ray (EDX) spectra of PbS nanoparticles in PS star on the surface of a carbon-coated copper grid.

Na_2SO_4 and CaH_2 and distilled under reduced pressure. CuBr and CuCl were synthesized according to a literature procedure.[45] 2-Bromoisobutyryl bromide (>98%, Aldrich) was used as received. Other reagents were purified according to standard procedures.

3.2. Polymer Characterization. M_n and M_w/M_n of polymers were obtained at 35 °C by SEC equipped with a Waters 515 pump, a Waters 2414 refractive index detector, and a combination of Styragel HT-2, HT-3, and HT-4; the effective molecular weight ranges are 100−10 000, 500−30 000, and 5000−600 000, respectively. Linear polystyrene standards were applied as the calibration. The eluent was THF at a rate of 1.0 mL/min. For M_w measurement of star polymer, a Viscotek TDA 302 SEC equipped with triple detectors (RI, VD, and LS) and GMHHR-L mixed bed columns (pore size, 40−500 Å) was used. The measurement was run in $CHCl_3$ at a rate of 1.0 mL/min at 30 °C. ^1H NMR spectra were recorded on a Bruker DMX300 spectrometer with $CDCl_3$ as solvent at room temperature. FT-IR spectroscopy was performed on a Bruker Equinox 55 FT-IT spectrometer. Elemental analysis was made under helium atmosphere by a FLASH EA1112 instrument. Scanning electron microscopy (SEM) was used to view morphologies formed by PCL star polymers and PCL-PS heteroarm star polymers. To obtain an SEM image a drop of dilute THF solution (0.2 mg/mL) was spread on a silica wafer and left until dryness. It was plated with platinum and viewed by a Hitachi S-4300 electron microscope operated at 15 kV. The images were recorded by a digital camera. TEM images and selected area electron diffraction patterns were obtained using a JEM 2010 instrument operated at 200 kV. To prepare TEM samples, 5 μL of THF solution of star polymer/PbS hybrid was dropped onto a carbon-coated copper grid and were dried in air.

3.3. Syntheses of PCL and PCL-Br. The syntheses of PCL and its modification with 2-bromoisobutyryl bromide to produce PCL-Br macroinitiator followed the procedures in the literature.[25]

3.3.1. Synthesis of PCL. A Schlenk flask with a magnetic stir bar was flamed under reduced pressure for a half-hour prior to use to remove any residual water in its inner wall. ϵ-Caprolactone (22.1 mL, 0.400 mol) and benzyl alcohol (0.52 mL, 0.01 mol) were added into the flask by syringe under N_2 atmosphere. After the temperature of the oil bath was thermostated at 110 °C, $SnOct_2$ (7.2 μL, 2.50×10^{-3} mmol) was introduced by syringe. The solution was stirred at 110 °C for 20 h, cooled to around 60 °C, diluted with 30 mL of anhydrous THF, and then dropped into 800 mL of cool methanol. The white precipitate was stirred for 2 h and then collected by a suction filter. The white powder was dried under reduced pressure at 30 °C overnight. Yield: 95%. SEC: M_n, 7700; M_w/M_n, 1.27.

3.3.2. Synthesis of PCL-Br Macroinitiator. PCL-OH (16.00 g, 2.960 mmol) and triethylamine (1.60 mL, 11.5 mmol) were dissolved in anhydrous THF (150 mL) in a three-neck flask, and the solution was cooled to 0 °C in an ice-water bath. Then 2-bromoisobutyryl bromide (1.43 mL, 11.5 mmol) in anhydrous THF (10 mL) was added dropwise via funnel over 1 h. The mixture was stirred for 24 h at room temperature. After filtering the yellow precipitate, the THF was removed by rotary evaporator. The crude product was dissolved in 100 mL of methylene chloride, and then the organic phase was washed successively with 100 mL water, 1 M HCl, and 1 M NaOH aqueous solution and finally dried over $MgSO_4$. The concentrated solution was poured into 500 mL of methanol. The white powder was collected by suction filtration and then dried in a vacuum. Yield: 83%. SEC: M_n, 7800; M_w/M_n, 1.27.

3.4. Polymerization Procedures of Star Polymers. In a general procedure, a Schlenk flask was charged with CuBr (36.7 mg, 0.255 mmol), PCL-Br macroinitiator (1.000 g, 0.191 mmol, $M_n = 5400$ by ^1H NMR, $M_w/M_n = 1.27$), DVB (0.91 mL, 5.1 mmol), and anisole (4.0 mL). The flask was degassed by three freeze−pump−thaw cycles. PMDETA (53.0 μL, 0.254 mmol) was deoxygenated by bubbling N_2 for a half-hour before injection into the reaction system. The flask was then immersed into an oil bath thermostated at 110 °C. At predetermined time of 1, 4, 6, 7, and 18 h, about 0.5 mL of solution was withdrawn to measure conversion and injected into SEC (SEC results are shown in Figure 3; conversion results are shown in Figure 4). The crude product was dissolved in THF, passed through a column of basic alumina, and precipitated in methanol.

Heteroarm star polymers were synthesized using PCL star polymers as macroinitiators. The operation procedures were similar to that of star polymers. Assuming there was no loss for Br functionality, the molar content of −Br was calculated by

$$n_{Br} = \frac{W_P \times \text{PCLwt\%}}{M_{PCL}} \tag{1}$$

where W_P is the mass of the PCL star polymer and M_{PCL} is the molecular weight of PCL-Br (5400) determined by ^1H NMR. The weight fraction of PCL in PCL star was determined by EA. Conditions: CuCl (30.0 mg, 0.30 mmol), PMDETA (66.0 μL, 0.30 mmol), PCL star (sample 2, 0.300 g, 0.026 mmol of Br), and styrene (12.0 mL, 0.104 mol); the temperature is 110 °C.

Aliquots of the solution were withdrawn at 20, 35, 45, 55, and 70 min to measure conversion and injected into SEC (SEC results are shown in Figure 5; conversion results are shown in Figure 6). Monomer conversion was obtained by gravimetry. To avoid polymer loss during the period of precipitation, methanol was added into sample vials slowly, with vigorous shaking for 20 min. The vial was then left overnight and the liquid phase was slightly drawn out by syringe. Finally, the samples were dried at 50 °C under reduced pressure for 48 h.

3.5. Hydrolysis and Alcoholysis of Star Polymers. For the hydrolysis of PCL star polymer, a star polymer (200 mg, sample 5 in Table 1) was dissolved in a mixture of 30 mL of THF and 20 mL of methanol. KOH (1.35 g) was added into the solution. The solution color changed from colorless to pink. After refluxing for 48 h, the solution was neutralized with dilute HCl aqueous solution. The solution color became straw yellow from pink when pH is less than 7. Solvent was removed by rotary evaporator and residue was washed with THF. After being precipitated from methanol, solid sample was dissolved in THF and SEC analysis was made. Yield: 22%. SEC: M_n, 10 700; M_w/M_n, 5.6.

For the alcoholysis of PCL star polymers, star polymers (0.200 g, sample 1 in Table 1), THF (20 mL), and ethanol (24 mL) were mixed to form a homogeneous system in a 50 mL flask. Into the solution 16 drops of concentrated sulfuric acid were added, and the mixture was refluxed for 6 days. After neutralized with 1.0 M aqueous sodium hydroxide, solvents were removed by rotary evaporator. The crude product was extracted by THF and then precipitated in methanol. Yield: 17%. SEC: M_n, 10 700; M_w/M_n, 5.6.

For the hydrolysis of PCL-PS heteroarm star polymer, the star polymer (0.080 g) was dissolved in 5 mL of THF and the solution was mixed with 0.100 g of KOH in 2 mL of ethanol. The mixture was refluxed for 2 days. The neutralization and purifying procedures were the same as the hydrolysis of PCL star. SEC: M_n, 76 900; M_w/M_n, 1.7.

3.6. Preparation of Core-Carboxylated PS Star Lead(II) Salt Inomers and Formation of PbS Nanoparticles. Core-functionalized PS star polymer (0.010 g sample 6 in Table 1) was dissolved in 5 mL of toluene, and then methanol solution containing 0.25 M lead acetate (0.008 mL) was added into polymer solution, which was then refluxed for 4 h for metal ion exchange. The final yellow powder was obtained by precipitation in methanol twice and dried at reduced pressure overnight. Yield: 56%.

PbS nanoparticle was prepared by treating the ionomers with H_2S (~10 mL) in solid state for 1 h. Once the hydrogen sulfide was introduced, the yellow powder turned brown within several minutes. The resulting PbS hybrids could be dissolved in THF to give a stable yellow solution. A drop of 1.0 mg/mL hybrid THF solution was spread on a carbon-coated copper grid for TEM analysis. Results of TEM and selected area electron diffraction (SAED) are shown in Figure 10. The calculated SAED data are shown in Table 2. TEM-based energy-dispersive X-ray results are shown in Figure 11.

4. Conclusions

A new approach to prepare PCL star polymer and PCL-PS heteroarm star polymer through ATRP was presented. PCL star with a microgel core was first prepared by ATRP of DVB with PCL-Br macroinitiator. Then heteroarm star polymer was obtained by ATRP of St with the PCL star polymer as an initiator. SEM images revealed that PCL-PS heteroarm star polymer could form spherical and thin pancakelike morphologies on silica substrate, which was different from the crystalline morphology of PCL star polymer. The bare PDVB core of the star was produced by hydrolysis and alcoholysis of PCL star polymers. SEC traces revealed that the bare core has a broad molecular weight distribution. PS star polymer with a carboxylic functionalized core was prepared by hydrolysis of the PCL-PS star polymer. As one example of potential applications for this novel star, monodispersed cubic shaped PbS nanoparticles were prepared. It may become a new type of polymer for fabricating inorganic nanoparticles. This novel amphiphilic star polymer also apparently aggregates in solution, and the results will be published in a forthcoming paper.

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Supporting Information Available: Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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