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Synthesis of Star-Shaped Poly(ϵ -caprolactone)-*b*-Poly(styrene) Block Copolymer by Combining Ring-Opening Polymerization and Atom Transfer Radical Polymerization

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*Newly designed star-shaped block copolymers made of poly(ϵ -caprolactone) (PCL) and polystyrene (PS) were synthesized by combining ring-opening polymerization (ROP) of ϵ -caprolactone (CL) and atom transfer radical polymerization (ATRP) of styrene (St). The switch from the first to the second mechanism was obtained by selective transformation of “living” radical sites. First, tri- and tetrafunctional initiators were used as an initiator for the “living” ring opening polymerization (ROP) of ϵ -caprolactone producing a hydroxyl terminated three or four arm star-shaped polymer. Next, the OH end groups of PCL star branches were derivatized into 2-bromoisobutyrate groups which gave rise to the corresponding tri- and tetrabromoester ended-PCL stars; the latter served as macroinitiators for the ATRP of styrene at 110°C in the presence of CuBr/2,2-bipyridine (Bipy) catalyst system affording star-shaped block copolymers PCL_n-*b*-PS_n ($n = 3$ or 4). The samples obtained were characterized by ¹H-NMR spectroscopy and GPC (gel permeation chromatograph). These copolymers exhibited the expected structure. The crystallization of star-shaped block copolymers was studied by DSC (differential scanning calorimetry). The results show that when the content of the PS block increased, the T_m of the star-shaped block copolymer decreased.*

Keywords star-shaped block copolymer, ϵ -caprolactone, styrene, ROP, ATRP

Introduction

More and more attention has been attracted to star-shaped polymers due to their unique properties and important applications (1, 2). Generally, star-shaped polymers can be prepared by two different routes: the “arm-first” (3, 4) strategy and the “core-first”

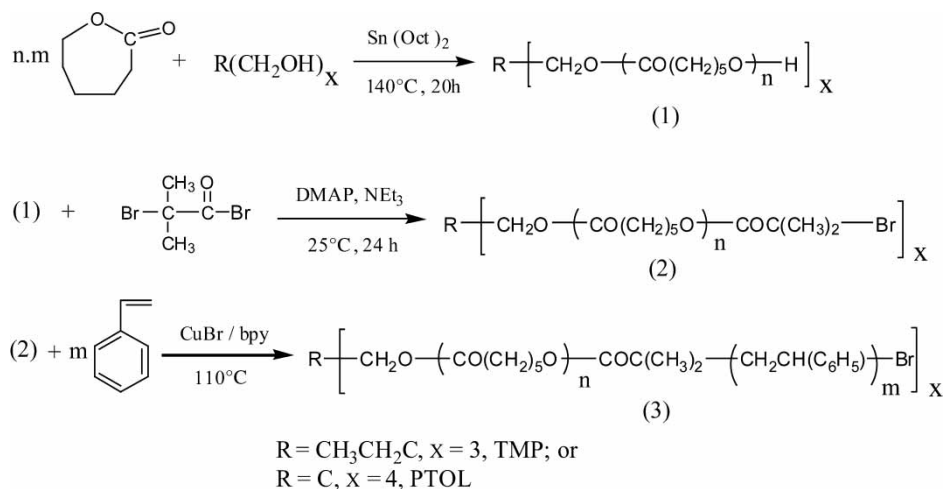
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(5, 6) method. In the arm-first approach, the linear arms of the star-shaped polymer are synthesized first followed by binding of the arms to form the core. The binding of the arms is achieved by using either a difunctional monomer or a multifunctional terminating agent. The core-first method is based on a multifunctional core used as initiator to initiate the polymerization of monomer to form a multiarm star-shaped polymer (7, 8). Between the two methods, the core-first approach with multifunctional initiator has received greater attention, since it is easy to control the structure of a star polymer. All the living anionic polymerization (9, 10), cationic polymerization (5, 11), controlled radical polymerization (CRP) (12, 13) and ring-opening polymerization (ROP) (14–20) have been applied to prepare such star-shaped polymers, and the ROP technique has great advantages in preparing well-defined polymers.

PCL and its star-shaped polymers are biodegradable. Therefore, it may have potential applications as biomaterials. In recent years, attention on synthesis of star-shaped PCL and star-shaped block copolymers with PCL as their arms has been increasing. For example, Lele et al. (21) reported the synthesis of star-shaped poly(ϵ -caprolactone)-b-poly(N-(2-hydroxypropyl)methacrylamide) by combination of ring-opening and chain transfer polymerization. Dong et al. (22) reported the synthesis of Poly(ϵ -caprolactone)-b-poly(DL-lactic acid-alt-glycolic acid) using a multifunctional initiator and stannous octoate catalyst. Also, Du et al. (23) reported the synthesis of the PCL star polymer, PCL-PS heteroarm star polymer by ATRP. Hedrick et al. (24) have also contributed to this field with their dendrimer-like block copolymer which was obtained upon combining ring-opening polymerization of ϵ -caprolactone for the inner part and ATRP of methyl methacrylate for the external branches.

However, it appears to us that the studies on the preparation of star-shaped block copolymer PCL_n-b-PS_n are rare. In this paper, we wish to report a convenient approach to prepare a star-shaped block copolymer PCL_n-b-PS_n by the combination of ring-open polymerization (ROP) of ϵ -caprolactone and atom transfer radical polymerization (ATRP) of styrene. We describe the synthesis of two classes of branched architectures, all based on PCL and PS subchains. As described below, these structures comprised of three-armed star-block copolymers PCL₃-b-PS₃ and four-armed star-block copolymers PCL₄-b-PS₄. The synthesis is outlined in Scheme 1.



Scheme 1. Synthesis of star-shaped PCL_n-b-PS_n block copolymer.

Experimental

Materials

SnOct₂ (Aldrich) and DMAP (4-dimethylaminopyridine) (A.R.) were used as received. ϵ -Caprolactone (CL) (Aldrich) was distilled from CaH₂ *in vacuo* under N₂. Trimethylolpropane (TMP) (A.R., Analytic Reagent) was recrystallized from dried acetone and then dried for 12 h under reduced pressure. Pentaerythritol (PTOL) (A.R.) was sublimated under reduced pressure. Bipy was recrystallized from petroleum ether. 2-Bromoisobutyryl bromide was procured from Acros. Styrene (St) was purchased from Aldrich (99%), stirred with CaH₂ overnight, and distilled prior to use. CuBr was prepared from CuBr₂ and purified by stirring in acetic acid, washing with methanol and then drying in vacuum. Dichloromethane (DCM) was washed with oil of vitriol and then distilled from CaH₂. Tetrahydrofuran (A.R., Beijing Chemical Co.) was distilled over CaH₂. Petroleum ether, and reagents were used without further purification, except as noted.

Methods

The ¹H-NMR spectra were recorded at 25°C on a INOVA-400 NMR spectrometer with chloroform-*d* as a solvent and with tetramethylsilane (TMS) as an internal standard. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured on a water 1515 gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5. μ -styragel columns with THF as an eluent (1.0 ml/min) at 35°C. The differential scanning calorimetry (DSC) analysis was carried out using a TA instruments Q10 differential scanning calorimeter equipped with a RCS accessory under nitrogen atmosphere (10 ml/min) at 10°C/min.

Synthesis of Star-Shaped PCL

About 10 ml of CL, a certain amount of SnOct₂ ((CL)/(SnOct₂) = 500), various amounts of TMP or PTOL, and a dry stirring bar were quickly put into the warm tube. The tube was then connected to a Schlenkline, vacuum was applied to the tube for 10 min, then, the tube was filled with nitrogen. This was repeated three times. Finally, the tube was closed under vacuum and immersed in an oil bath preheated to 140°C. Polymerization was allowed to proceed for 20 h under stirring. The polymerization tube was cooled to room temperature. The crude product was dissolved in DCM and reprecipitated in *n*-hexane. Star-shaped PCL was isolated by filtration and dried in vacuum until a constant weight (21, 22), the monomer conversion was then determined gravimetrically.

Preparation of Star-Shaped PCL Macroinitiator

A certain amount of PCL was placed into a 250 ml round-bottom flask with 100 ml of DCM and 0.5 g (0.005 mol) triethylamine and 0.915 g (0.0075 mol) DMAP. A 3.45 g (0.015 mol) solution of 2-bromoisobutyryl bromide and 20 ml DCM was added to a 50 ml pressure equalizing addition funnel fit to the flask under N₂, the reactor was cooled to 0°C in an ice/water bath, and the acid halide solution was added dropwise. The reaction was stirred overnight and allowed to warm to room temperature. The reaction mixture was filtered in order to remove the amine salt and added dropwise into *n*-hexane, after filtration and washing two times with *n*-hexane, followed by drying at 50°C under vacuum for 24 h, then the macroinitiator was obtained.

Synthesis of Star-Shaped Block Copolymer

A dry glass tube was charged with CuBr, St, Bpy, and PCL-Br. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum, the tube was placed in an oil bath at the 110°C maintained by a thermostat. After an expected time, the tube was placed in an ice bath to stop the reaction. The reaction mixture was dissolved with THF and added dropwise into petroleum ether. After filtration and it was washed two times with petroleum ether, followed by being dried at 50°C under vacuum for 24 h, a star-shaped block copolymer was obtained. The conversion of the monomer was determined gravimetrically.

Results and Discussion

Synthesis of Star-Shaped PCL

The first step in the synthesis of a star-shaped block copolymer was synthesizing star-shaped PCL, which were obtained by ring-opening polymerization of ϵ -caprolactone (CL) using a multifunctional initiator and SnOct₂ as catalyst (14-20). We combine the two methods which have been reported by Lele et al. (21) and Dong et al. (22), found more suitable conditions for polymerizing CL, that is, (CL)/(SnOct₂) = 500; polymerization temperature controls at 140°C and polymerization time is 20 h. Figure 1 shows the representative ¹H-NMR spectrum of well defined three-armed star-shaped PCL with a $M_{n, GPC}$ value of 2.18×10^4 g/mol and a M_w/M_n value of 1.30. The signals at 0.92 ppm represents methyl groups (peak a), the signals at 4.05, 2.30, 1.64, 0.92 ppm, and 1.31 ppm represent $-\text{CH}_2-\text{O}-\text{CO}-$ groups (peak e), $-\text{CH}_2-\text{O}-$ groups (peak b), methylene groups (peak c), and methylene groups (peak d), respectively. Moreover, the absorptions at 3.64 (peak f) proved the presence of the terminal hydroxyl group. The $M_{n, NMR}$ value of three-armed star-shaped PCL was estimated from the ratio of the methylene protons (b) and terminal one (f). The $M_{n, NMR}$ value (1.95×10^4) was close to $M_{n, GPC}$ (2.18×10^4) (Table 1). It is a proof that the well-defined star-shaped PCL with terminal hydroxyl was provided.

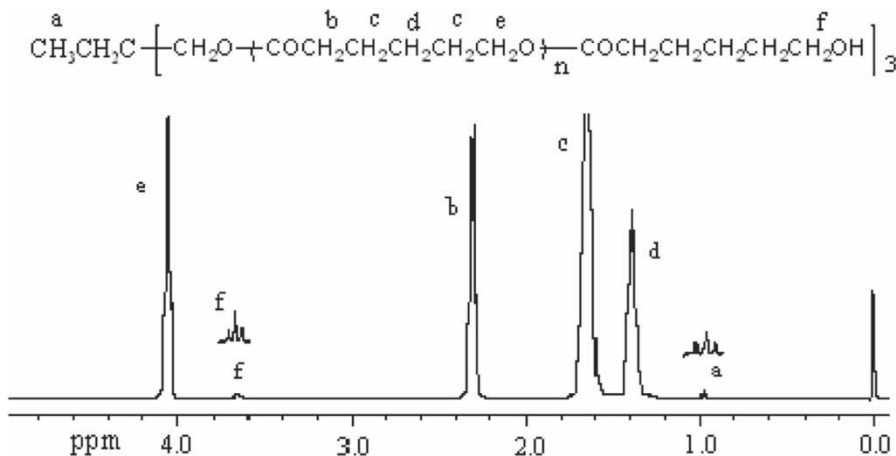


Figure 1. ¹H-NMR spectroscopy of three-armed star-shaped PCL [PCL(TMP)-2, Table 1].

Table 1
GPC, NMR data of three-armed star-shaped block copolymers

Sample	$M_{n,th}^a (\times 10^{-4})$	$M_{n,GPC}^b (\times 10^{-4})$	$M_{n,NMR}^c (\times 10^{-4})$	M_w/M_n
PCL(TMP)-1	1.51	2.18	1.95	1.30
PCL ₃ - <i>b</i> -PS ₃ -1	3.53	3.74	3.44	1.30
PCL ₃ - <i>b</i> -PS ₃ -2	4.30	4.44	4.26	1.20
PCL ₃ - <i>b</i> -PS ₃ -3	4.97	5.11	—	1.26
PCL(TMP)-2	3.00	3.04	2.56	1.30
PCL ₃ - <i>b</i> -PS ₃ -4	4.40	4.46	4.70	1.24
PCL ₃ - <i>b</i> -PS ₃ -5	5.01	5.28	6.15	1.25
PCL ₃ - <i>b</i> -PS ₃ -6	5.67	6.06	—	1.30

^a $M_{n,th}$ was calculated according to Equation (1).

^b $M_{n,GPC}$ measured on water-2414 GPC instrument.

^c $M_{n,NMR}$ was calculated based on proton NMR data.

Preparation of Star-Shaped PCL Macroinitiator

The second step in the synthesis of star-shaped block copolymer consists of the preparation of the star-shaped macroinitiator. This was achieved through chemical modification of the OH end groups carried by the branches of these star-shaped PCL into 2-bromoisobutyrate functions that can initiate controlled ATRP of styrene. For the quantitative derivatization of their OH functions, star-shaped PCL were thoroughly deprotonated using a solution of triethylamine. Then the obtained alkoxides reacted with an excess of 2-bromoisobutyryl bromide at room temperature. Isolation of the star-shaped macroinitiator was accomplished by successive precipitations in diethyl ether. The complete substitution of the hydroxyl groups was evidenced by NMR. Figure 2 is the ¹H-NMR spectrum (CDCl₃; 400M) of the three-armed star-shaped macroinitiator. Compared with Figure 1, it has been found that the typical signals of the hydroxyl

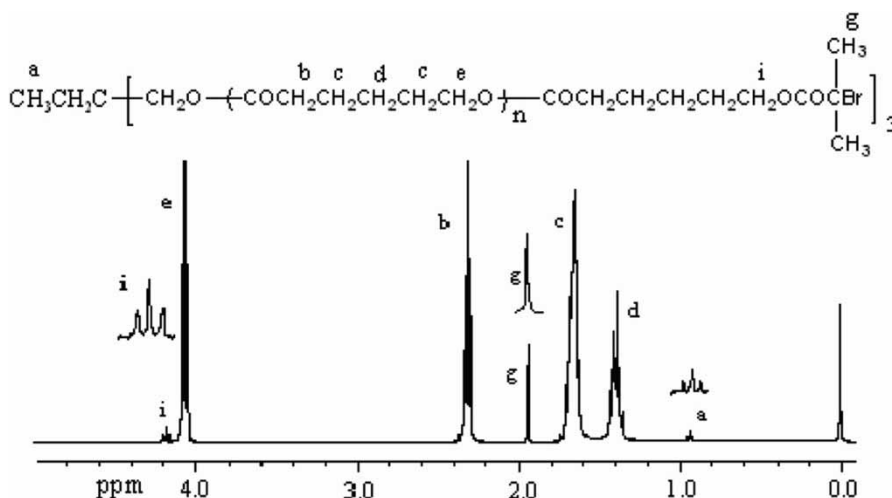


Figure 2. ¹H-NMR spectrum of three-armed star-shaped macroinitiator corresponding to PCL(TMP)-2.

terminal completely disappeared (3.64 δ , 6H, (terminal $-\text{CH}_2-\text{OH}$ of PCL arms (f))) and the typical signals of the methyl end and the $-\text{CH}_2\text{COO}-$ methylene terminal appeared. (1.94 δ , 18H, (terminal $-\text{CH}_3$ of PCL-Br arms (g))) (4.17 δ , 6H (terminal $-\text{CH}_2-\text{O}-\text{CO}-$ of PCL-Br end (i))). It indicates the star-shaped PCL completely turned into a corresponding macroinitiator.

Synthesis of Star-Shaped PCL_n-PS_n Block Copolymer

The final step in the synthesis of the star-shaped PCL-PS block copolymer was the growth of PS blocks from 2-bromoisobutyrate ended star-shaped PCL. This could be achieved upon polymerizing styrene by ATRP. The conditions consisted of polymerizing styrene at 110°C in the presence of CuBr/Bpy as a catalyst system, and stopping the chain growth at rather low monomer conversion. Since styrene is a good solvent for PCL, the polymerization could be performed under bulk conditions. St, macroinitiator, CuBr, Bpy molar ratio was 100n:n:n:2n or 200n:n:n:2n (n = 3 or 4); each time we reacted several test tubes under the same conditions. After an expected time, we took out a tube, and placed it in an ice bath to stop the reaction. After a series of disposal processes previously mentioned, a star-shaped block copolymer was obtained. The conversion of the monomer was determined gravimetrically and M_n^{GPC} was subsequently gained. The results can be seen in Tables 1 and 2. The molecular weight distributions ($M_w/M_n = 1.15-1.30$) were rather narrow in every case, and the molecular weights measured by GPC ($M_{n,\text{GPC}}$) were a little higher than the calculated values: $M_{n,\text{th}}$ according to Equation (1).

$$M_{n,\text{th}} = \text{Conversion} \times (M_{\text{St}}/M_{\text{I}}) \times 104 + A \quad (1)$$

where M_{St} and M_{I} are the initial moles of St and the macroinitiator, respectively; 104 and A are the molecular weight of St and macroinitiator, respectively.

Figure 3 indicates the molecular weights of the obtained star-shaped block copolymers linearly increased with an increase in the monomer conversion. Moreover, the molecular weight distributions ($M_w/M_n = 1.15-1.30$) were rather narrow in every case.

Table 2
GPC, NMR date of four-armed star-shaped block copolymers

Sample	$M_{n,\text{th}}^a (\times 10^{-4})$	$M_{n,\text{GPC}}^b (\times 10^{-4})$	$M_{n,\text{NMR}}^c (\times 10^{-4})$	M_w/M_n
PCL(PTOL)-1	2.01	2.36	1.92	1.28
PCL ₄ -b-PS ₄ -1	3.21	3.63	3.09	1.27
PCL ₄ -b-PS ₄ -2	4.09	4.73	4.21	1.16
PCL ₄ -b-PS ₄ -3	5.52	5.94	5.83	1.26
PCL(PTOL)-2	3.24	3.65	3.13	1.30
PCL ₄ -b-PS ₄ -4	4.04	4.46	—	1.15
PCL ₄ -b-PS ₄ -5	4.86	5.22	5.88	1.24
PCL ₄ -b-PS ₄ -6	5.69	6.01	—	1.30

^a $M_{n,\text{th}}$ was calculated according to Equation (1).

^b $M_{n,\text{GPC}}$ measured on water-2414 GPC instrument.

^c $M_{n,\text{NMR}}$ was calculated based on proton NMR date.

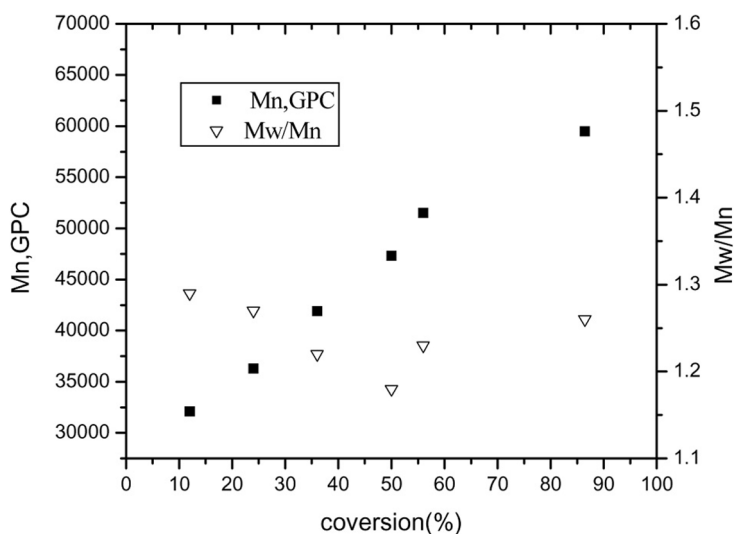


Figure 3. Dependence of star-shaped PCL₄-*b*-PS₄ block copolymer the average number molecular weight and polydispersity on the conversion of monomer at 110°C. Conditions: St/PCL-Br/CuBr/Bpy = 400 : 1 : 4 : 8.

Figures 4 and 5 show the typical GPC curves of the star-shaped block copolymers as compared with those of original star-shaped PCL. This indicates that in each block copolymer the peak is shifted toward a higher molecular weight region compared with that of its original star-shaped PCL with little change in molecular weight distribution. These preliminary results show that the block copolymerization of the star-shaped PCL and St monomer via ATRP methods was successful under the experimental conditions used (shown in Scheme 1).

Figure 6 shows a typical ¹H-NMR spectrum of the three-armed star-shaped PCL₃-*b*-PS₃ block copolymer. It clearly shows that besides the typical signals of the main chain of PS at 6.45–7.07 ppm (δ H (f)) and 1.86 ppm (δ H (g)) and the typical signals of the main

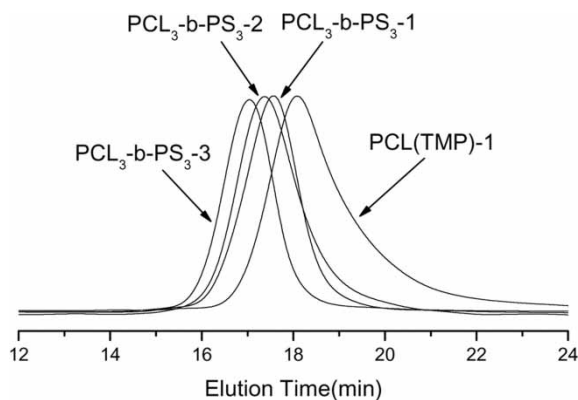


Figure 4. GPC curves of the star-shaped PCL(TMP)-1 and the star-shaped PCL₃-*b*-PS₃ block copolymer.

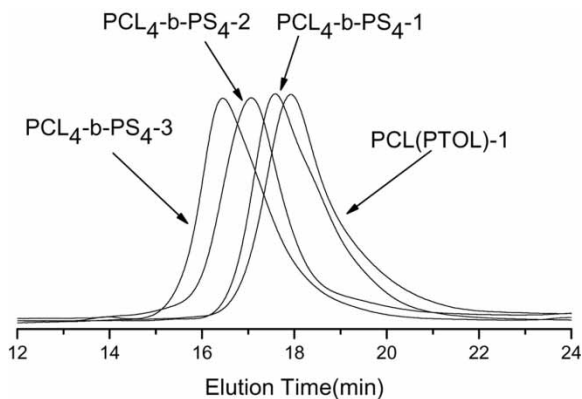


Figure 5. GPC curves of the star-shaped PCL(PTOL)-1 and the star-shaped PCL₄-b-PS₄ block copolymer.

chain of the PCL at 4.07 (δ H (e)), 2.32 (δ H (b)), 1.65 (δ H (c)), and 1.39 ppm (δ H (d)), there are also some other additional signals of the end groups of the obtained block copolymer, that is, the signals assigned to the proton (h) on the vinyl group (δ H (h) = 3.52), which is the end groups of the PS chain, and the proton (a) on the methyl group of TMP initiator (δ H (a) = 0.86). Otherwise, compared with Figure 2, it is seen that the terminal $-\text{C}(\text{CH}_3)_2-$ methyl proton (g) signals of the macroinitiator at 1.96 ppm drifted to 1.29 ppm (d) at the star-shaped block copolymer, and the new signal at 3.52 ppm (h) for the produced end groups of PS block was observed. This demonstrates that the macroinitiator had completely copolymerized with St via ATRP to form a star-shaped block copolymer within the detection limits of NMR.

The most reliable method to determine the actual molar mass of such copolymers is by ¹H-NMR. Based on the integral values of the peaks at $\delta = 6.45\text{--}7.07$ (I_f) and at $\delta = 2.30$ ppm (I_b), the $M_{n,\text{NMR}}$ can be calculated according to Equation (2), where n

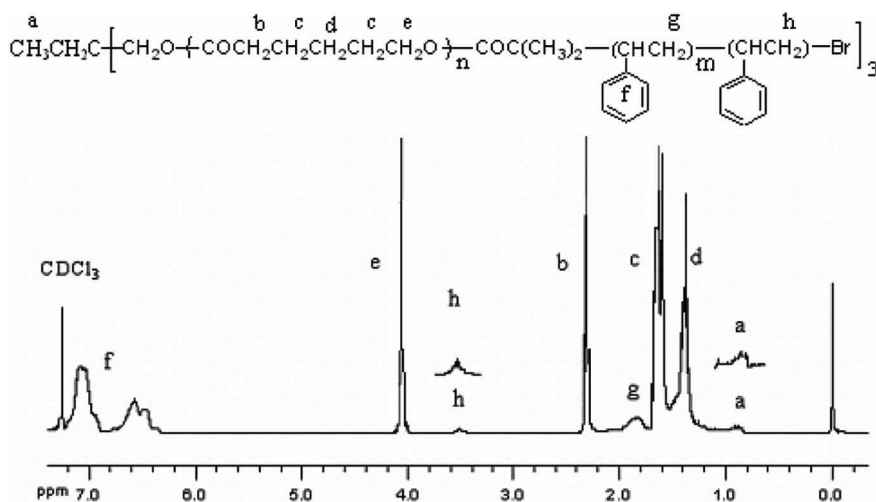


Figure 6. ¹H NMR spectrum of the three-armed star-shaped block copolymer: PCL₃-b-PS₃-1.

defines the degree of polymerization of macroinitiator and the value 104 is the molar masses of St, A defines the $M_{n,NMR}$ of the macroinitiator.

$$M_{n,NMR} = (2n \times I_f/5 \times I_b) \times 104 + A \quad (2)$$

The results were listed in Tables 1 and 2. They show the M_n values drawn from NMR and GPC are rather close confirming that the synthesized copolymer exhibits the expected structure.

Thermal analysis was performed with a TA instruments Q10 differential scanning calorimeter equipped with a RCS accessory under nitrogen atmosphere. For all samples, the following procedure was used: samples were heated from 20°C to 100°C, the transition temperature was recorded, then the samples were cooled down to 0°C, and reheated to 100°C, all at a rate of 10°C/min. The recorded temperatures were calibrated using indium as a standard. From Figures 7 and 8, it can be seen that the T_m of the star-shaped copolymer at the first heating process was lower than the prepolymer, and the peaks of T_m could not be observed on the second heating scan. This is reasonable because of the copolymers containing the PS segment and the influence of the thermal history. Furthermore, when the content of the PS block segments increased, the T_m of the PCL block segments decreased and so did the melting enthalpy of the crystalline PCL block segments. This is because PCL is crystalline, but the PS block is amorphous and the T_g of the PS block is higher than the T_m of the PCL block, which influences the crystallinity of PCL.

The detailed PCL crystalline behavior in the confined environment of PS and the self-assembly behaviors of these obtained star-shaped block copolymer will be reported on in the near future.

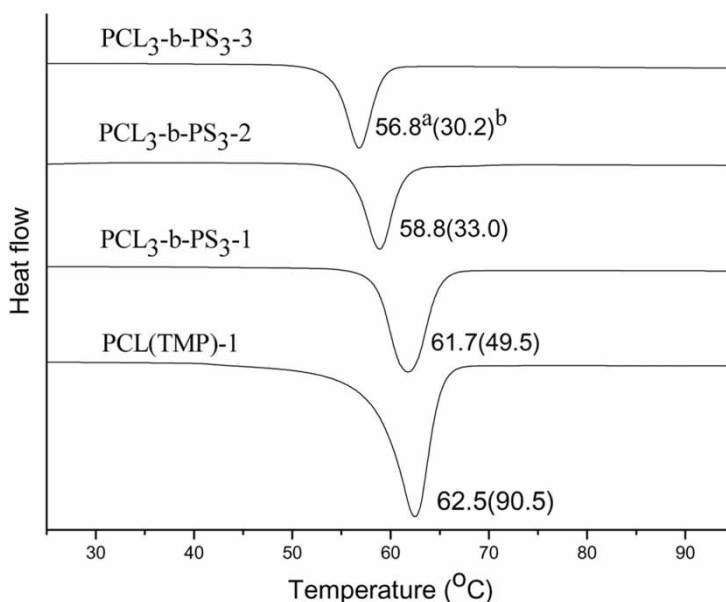


Figure 7. DSC traces recorded during the first heating scan of three-armed star-shaped PCL and its block copolymer at a heating rate of 10°C/min. (a) denotes the melting point (T_m) of PCL block segments(°C). (b) denotes melting enthalpy of crystalline PCL block segments (J/g).

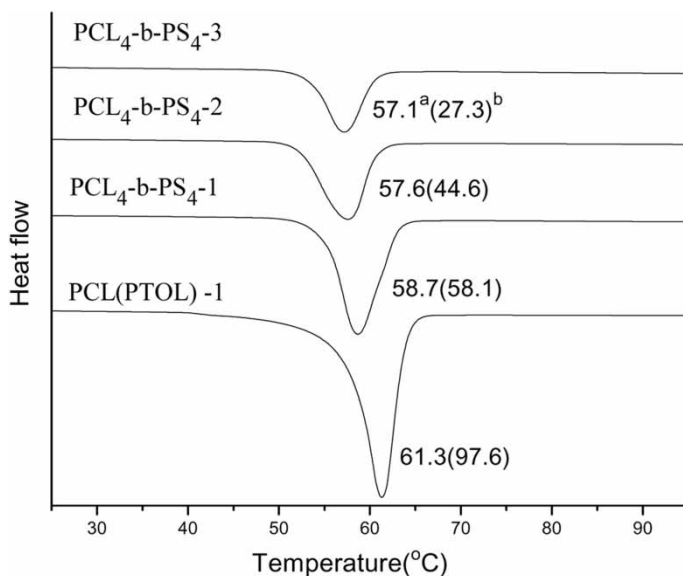


Figure 8. DSC traces recorded during the first heating scan of four-armed star-shaped PCL and its block copolymer at a heating rate of 10°C/min. (a) denotes the melting point (T_m) of PCL block segments (°C). (b) denotes melting enthalpy of crystalline PCL block segments (J/g).

Conclusions

Synthesis of star-shaped PCL_n-b-PS_n ($n = 3$ or 4) block copolymer with different molecular weight and low polydispersity were successfully achieved by ATRP in bulk using macroinitiator and CuBr/Bpy complex as catalyst. The ‘living’ ATRP of star-shaped block copolymer is verified by the following evidence, first-order kinetics, a linear molecular weight conversion profile and narrow molecular weight contribution ($M_w/M_n \leq 1.30$), and the structure which deduced from NMR spectrum of copolymer is the same as we designed previously. We also studied the crystallization of the star-shaped block copolymers using DSC. With the content of the PS block increased, the T_m of the star-shaped copolymer decreased.

Acknowledgements

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