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Synthesis and Characterization of a novel star shaped Rod-Coil Block Copolymer

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Summary

A novel star shaped rod-coil block copolymer, tri-armed star poly (ε-caprolactone)-b-poly {2,5-bis[(4-methoxyphenyl) oxycabony] styrene} [S-(PCL-b-PMPCS)$_3$], was successfully synthesized via atom transfer radical polymerization in chlorobenzene solution using macro-initiator and CuBr/Sparteine complex as catalyst. The results showed that the number average molecular weigh M_n was increased versus monomer conversion, and that the polydispersities M_w/M_n was quite narrow (<1.35), which were the character of controlled polymerization. The structure of the star shaped blcok copolymers was experimentally confirmed by ^{1}H NMR. The liquid crystalline behavior of them was studied using DSC and POM. The star shaped block copolymer with low molar percentage of PMPCS block could show T_m of PCL. And only those copolymers with long rigid segment PMPCS could form liquid crystalline phase which was quite stable with a high clearing point.

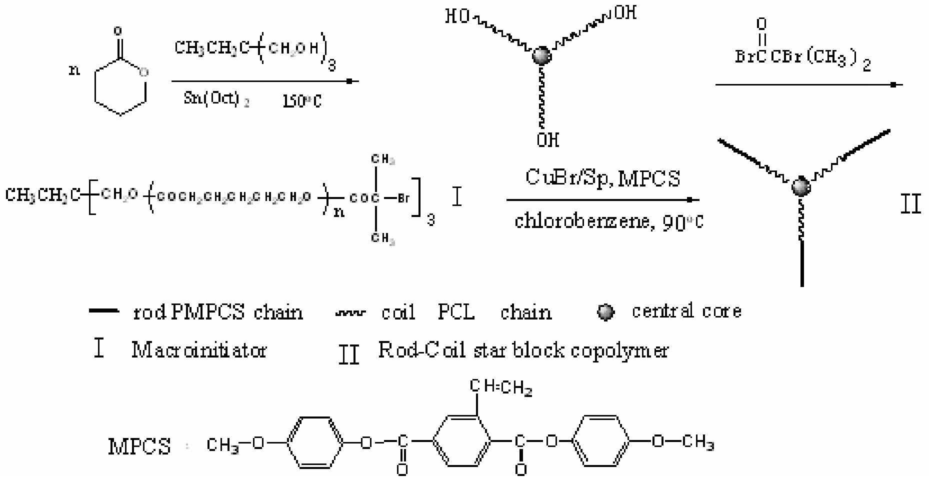
Introduction

Block copolymers are a fascinating class of soft material that can self-assemble into a nanoscale ordered structures. Rod-coil block copolymers which consist of a rigid rod block and a flexible coil block, have attracted much research interest because of both the science and potential applications behind this novel class of self-assembling polymers. To date, a number of experimental studies of synthetic rod-coil macromolecules have been reported with regard to their phase behavior, self-assembly and microstructures [1-8]. Of these studies, poly(ε-caprolactone) (PCL) was usually used as flexible coil block and related information was reported [9-14]. Furthermore, the copolymer with PMPCS, poly{2,5-bis [4-methoxyphenyl] oxycarbonyl} styrene}, as rod segment has been a subject of great deal of interest. As we reported earlier, PMPCS was a new mesogen jacketed liquid crystal polymer in which the mesogenic units were attached laterally to the main chain via a direct connection or via short spacers. The high population of the rigid, bulky side-groups formed a jacket along the polymer chain and therefore forced the main chain to take extended or rod-like conformation. Early studies on lytropic behavior, banded texture and solution properties have proved the rod-like nature of MJLCPs [15-16]. Beforetime we have also demonstrated that MPCS monomers could be used to confer living character to radical polymerization [17]. Using mesogen-jacketed liquid crystalline polymers (MJLCPs) as the rod block, a series of rod-coil block copolymers have been synthesized, and their solution self-assembly behavior has been investigated [18-20]. Morphology and rheological behavior of rod-coil poly(styrene)-block-poly(2,5-bis(4-butylbenzoyl) oxystyrene) (PS-PBBOS) has also been reported [21].

Star-shaped block copolymers have different properties and functions from those of linear block copolymers because of their spherical shapes and more condense structure. Them present a promising system for studying highly branched polymeric architectures. There are many methods employed for star-shaped block copolymer synthesis: core-first method; arm-first method; and linking of linear living polymers with a divinyl compound. Present advances in the area of controlled radical polymerization by nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation transfer (RAFT) have contributed to the synthesis of novel macromolecular architectures such as stars, dendrimers, and hyperbranched polymers [22-27].

However, the studies of the synthesis of star shape rod-coil block copolymers were very few, thus we synthesized a novel star shaped block copolymer S-(PCL-b-PMPCS)$_3$, which consists of a rigid rod block (PMPCS) and a flexible coil block (PCL). We expect that the unique molecular design could potentially lead to different morphologies than those observed to date in rod-coil systems, and also hope the synthesis of S-(PCL-b-PMPCS)$_3$ by combining the anionic polymerization and ATRP would make some contribution to this field, while it is difficult to obtain rod-coil block copolymer with long rigid chain via normal polymerization. Of course, the viscosity, rheology and self-assembly behavior of S-(PCL-b-PMPCS)$_3$ might be much different compared with the linear ones, which were still underway and related information would be reported in the future.

The synthetic route of S-(PCL-b-PMPCS)$_3$ is shown in scheme 1.



Scheme1. Synthetic route of star shaped rod-coil block copolymer S-(PCL-b-PMPCS)$_3$.

Experimental

Materials

ε-Caprolactone (CL. from Aldrich) was vacuum distilled over calcium hydride. $Sn(Oct)_2$ (Aldrich) was used as received. Trimethylolpropane (A.R.) was recrystallized from dried acetone and then dried for 12h under reduced pressure. 2-Bromoisobutyryl bromide was procured from Acros. Chlorobenzene (Acros.99%) was purified prior to use. CuBr was prepared from $CuBr_2$ and purified by stirring in acetic acid, washing with methanol and then drying in vacuum. Sparteine (Sp. from Aldrich) was distilled under reduced pressure over calcium hydride and stored under nitrogen atmosphere at 4℃ in the dark. Tetrahydrofuran (A.R.) was distilled over CaH_2. Other solvents and reagents were used without further purification, except as noted.

Measurements

The M_n and molecular weight distribution (M_w/M_n) were measured on a WATER 2414 gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5, μ-styrayel columns with THF as an eluent (1.0mL/min) at 35℃. Calibration was made with standard polystyrene (PSt). The ^1H NMR spectrum was taken at 25℃ on a INOVA-300 NMR spectrometer with chloroform-d as a solvent and with tetramethylsilane (TMS) as an internal reference. Thermograms were obtained using a Perkin Elmer DSC-7 instrument. Polarized optical microscope (POM) observation was performed on a Leitz Laborlux 12POL microscope with a Leitz 350 hot stage.

Synthesis of star-shaped macro-initiator S-(PCL-Br)$_3$

The tri-armed star shaped PCL (S-$(PCL)_3$) was obtained from CL initiated by trimethylolpropane with $Sn(Oct)_2$ as catalyst. Then the star shaped bromoisobutyryl PCL macro-initiator S-$(PCL\text{-}Br)_3$ for ATRP was obtained via the modification of S-$(PCL)_3$ by 2-bromoisobutyryl bromide according to the method described by Chang et al[28]. The structure of them was proven by ^1H NMR spectroscopy and illustrated as later.

Synthesis of MPCS monomer

The monomer 2,5-bis[(4-methoxyphenyl) oxycarbonyl] styrene] (MPCS), was synthesized by the reaction of 2-vinylterephathalic acid according to the method described by Zhang et al[29], ^1H NMR($CDCl_3$): $\delta = 3.83$, 6H for $-OCH_3$, 5.1-5.90, 2H for $=CH_2$, 6.60-6.95, 1H for $-CH=$ and 7.00-8.30, 11H for the phenylene rings.

Polymerization

A dry glass tube was charged with MPCS, S-$(PCL\text{-}Br)_3$, CuBr, Sp and chlorobenzene solution, where the molar ratio of MPCS, S-$(PCL\text{-}Br)_3$, CuBr, Sp was n:1:1:2. Then the system was degassed three times and the tube was sealed under vacuum. In succession the tube was placed in an oil bath at the desired temperature maintained by a thermostal. After an expected time, the tube was placed in an ice bath to stop the reaction. The reaction mixture was diluted with THF and added dropwise into ether, after filtration and washing two times with ether, followed by drying at 30℃ under vacuum for 24 h, star shaped rod-coil block copolymer S-$(PCL\text{-}b\text{-}PMPCS)_3$ was obtained. The conversion of the monomer was determined gravimetrically.

Results and Discussion

The star shaped bromoisobutyryl PCL macro-initiator S-(PCL-Br)$_3$ for ATRP was obtained via the modification of S-(PCL)$_3$ by 2-bromoisobutyryl bromide. The chemical structure of the star shaped macro-initiator S-(PCL-Br)$_3$ with the $M_{n},_{GPC}$ value of 2.18×10^4 g/mol and an M_w/M_n value of 1.16 was characterized by ^{1}H NMR spectroscopy as shown in Figure 1. The signals at 4.05, 2.30, 1.64, 1.31 and 0.92 ppm represent methylene groups (peak e), methylene groups (peak b), methylene groups (peak c), methylene groups (peak d) and methyl groups (peak a), respectively. Moreover, the absorptions at 1.92 ppm (peak g), 4.17 ppm (peak i) and the disappearance of 3.64 ppm (methylene group of terminal –CH_2-OH which consist in S-PCL end) proved the presence of the end group, -CH_2-$OCOCBr(CH_3)_2$. The $M_{n,NMR}$ value of star shaped macro-initiator S-(PCL-Br)$_3$ was estimated from the ratio of the methylene protons (b) and methyl protons (a). The $M_{n,NMR}$ value (1.95×10^4) was close to the $M_{n},_{GPC}$ (2.18×10^4). These facts verified that the well-defined star shaped macro-initiator S-(PCL-Br)$_3$ with terminal bromine was obtained.

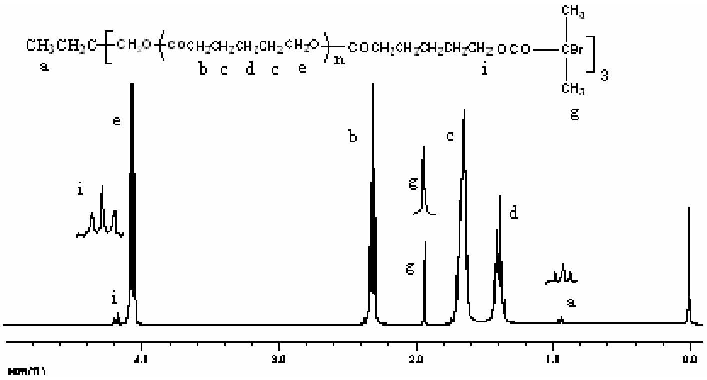


Fig.1. ^{1}H NMR spectra of the star shaped macro-initiator (S-PCL-Br)$_3$ in $CDCl_3$.

It was reported in our previous paper that the MPCS monomers could be used to confer living character to radical polymerization [21]. So all the polymerization was carried out in chlorobenzene as solvent. Figure 2 shows the GPC spectrum of star macro-initiator S-(PCL-Br)$_3$ and its star shaped block copolymers, an increase in molecular weight was found from 2.85×10^4 g/mol (M_w/M_n=1.23) to 6.30×10^4 g/mol (M_w/M_n=1.24). Both curves had single symmetric peaks, and the weight distribution was very narrow. After the chain extension reaction, the GPC curves of the copolymers obviously shifted to a higher molecular weight. The results showed that the polymerization underwent well by this way, which were listed in Table 1.

Figure 3 gave an example of the ^{1}H NMR spectra of the star shaped block copolymer. The signals at 4.05 (peak a), 2.30 (peak d), 1.64 (peak b) and 1.30 (peak c) ppm were ascribed to the repeated CL unit. Characteristic resonance of the benzene ring signals (peak h, peak i) and –OCH_3 protons signal (peak l) in MPCS units were both present in the ^{1}H NMR spectrum of the copolymer. These data illustrated the presence of PCL and PMPCS blocks in the star copolymer chain. The composition of the star shaped block copolymers was determined by the integral ratio of the signals at 2.30 ppm (peak d, methylene of CL units) and 3.30-3.90 ppm (peak l, -OCH_3 proton of MPCS units) according to Eq (1).

$$\text{mol (\%) rod unit} = (I_l/6)/[(I_l/6)+(I_d/2)] \times 100\% \qquad (1)$$

The molar percentages of rod units (PMPCS) in tri-armed star shaped block copolymer ranged from 19.1% to 57.1%, which were listed in Table 1.

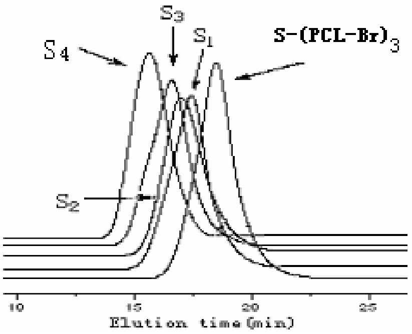


Fig.2. GPC curves of $S\text{-}(PCL\text{-}Br)_3$ and it’s related star shaped block copolymer.

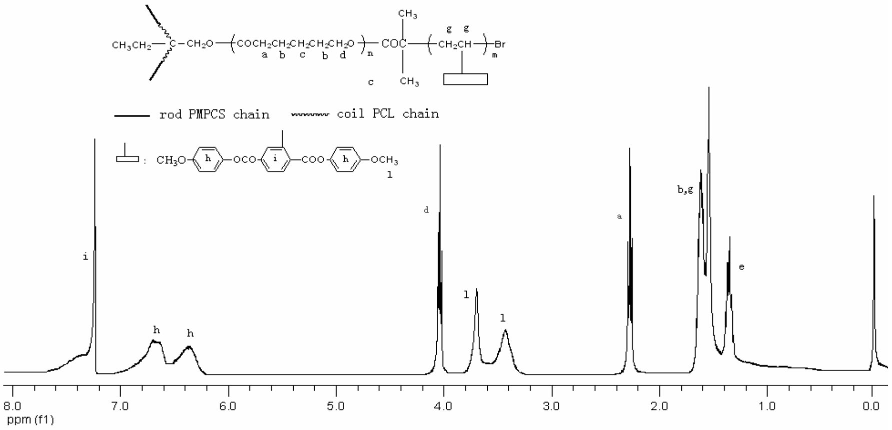


Fig. 3. ^1H NMR spectra of the star shaped block copolymer $S\text{-}(PCL\text{-}b\text{-}PMPCS)_3$ ($M_n=4.71\times 10^4$, $M_w/M_n=1.27$) in $CDCl_3$.

All these facts verified that MPCS underwent ATRP well. Based on the conversion of MPCS and molar ratio of MPCS {$[MPCS]_o$} to tri-armed star shaped S-PCL-Br {$[S\text{-}PCL\text{-}Br]_o$}, the $M_{n,th}$ of the star shaped block copolymer $S\text{-}(PCL\text{-}b\text{-}PMPCS)_3$ could be calculated according to Eq. (2).

$$M_{n,th} = \text{Conv.} \times \{ [MPCS]_o/[S\text{-}(PCL\text{-}Br)_3]_o \} \times 404 + M_{n,NMR}(S\text{-}(PCL\text{-}Br)_3) \qquad (2)$$

Where $M_{n,NMR}$ $(S\text{-}(PCL\text{-}Br)_3)$ was the M_n of macro-initiator $S\text{-}(PCL\text{-}Br)_3$ on the basis of ^1H NMR date, 404 was the molar weight of MPCS.

It can be observed from Table 1 that the $M_{n,th}$ of S-(PCL-*b*-PMPCS)$_3$ was different from the results obtained from GPC. This might be due to the difference in solvent property between star shaped block copolymer and standard polystyrene, another reason is that the molecular-weight-dependence of the hydrodynamic volume should be different between linear polymers and star polymers.

Table 1. GPC、DSC、NMR result and liquid crystallinity of [S-(PCL-*b*-PMPCS)$_3$].

Polym. No	Yield (%)[1]	$M_{n,GPC}$ ($\times10^{-4}$)	$M_{n,th}$[2] ($\times10^{-4}$)	M_w/M_n	Theoretical[3] mol% rod unit	mol %[4] rod unit	T_m[5] (^oC)	LC[6]
S_1	80.5	2.85	3.52	1.23	18.5	19.1	61.6	No
S_2	73.2	3.90	5.21	1.20	32.1	32.5	61.1	No
S_3	83.6	4.71	6.35	1.27	38.9	38.2	60.2	Yes
S_4	91.7	6.30	8.55	1.24	48.9	48.7	/	Yes
S_5	86.3	7.25	9.81	1.34	53.2	51.2	/	Yes
S_6	93.1	8.30	11.25	1.31	57.4	57.1	/	Yes

1.Yield was calculated according to Yield(%) = (W_p - W_i)/W_m ×100%, where W_p, W_i and W_m were the weight of the star shaped block copolymer, macro-initiator and MPCS, respectively.
2.$M_{n,th}$ was calculated according to Eq. (2).
3.Calculated according to $M_{n,th}$ of star block copolymers and $M_{n,NMR}$ of S-(PCL)$_3$.
4.The molar % was calculated according to Eq. (1).
5.T_m was measured at the first heating scan.
6.Phase behavior was observed by POM.

The thermal properties of the star shaped block copolymers were studied by differential scanning calorimetric (DSC). For all samples, the following procedure was used: samples were heated from 10℃ to 160℃ recorded the transition temperature. Then cooled down to 10℃, and then reheated to 160℃, all at a rate of 10℃/min. The recorded temperatures were calibrated using indium as standard. The information of the neat linear PMPCS (M_n=1.32×10^4 g/mol, M_w/M_n = 1.18), star shaped block copolymer and the prepolymer were shown in Figure 4. From it we can see that the T_g of linear PMPCS was 134^{o}C during the first heating scan, while no glass transition was observed in the star shaped block copolymer. This may be due to the good compatibility between the PCL and the PMPCS block. Figure 4. also shows that the melting point temperatures (T_m) of the prepolymer S-(PCL)$_3$(M_n=2.18×10^4 g/mol, M_w / M_n = 1.16) and the macro-initiator S-(PCL–Br)$_3$ are 63.8℃ and 62.7℃, respectively. Only the star shaped block copolymer with low molar percentage of PMPCS could the T_m be observed at the first heating scan, but not at the second heating scan. As we can find from the figure 4, T_m of these star shaped rod coil block

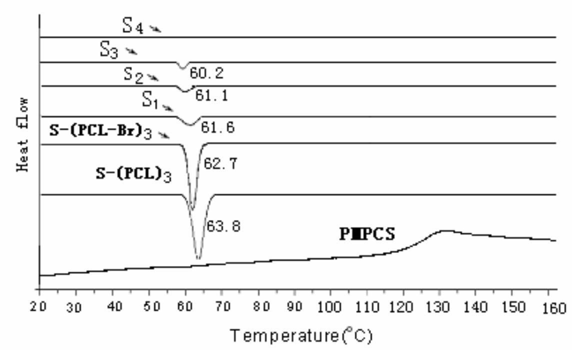


Fig.4. DSC traces recorded during the first heating scan of neat linear PMPCS, S-(PCL-b-PMPCS)$_3$ and the prepolymer.

copolymers is lower than that of the prepolymer S-$(PCL)_3$ and the macro-initiator S-$(PCL\text{-}Br)_3$. And the T_m become low with the increase of molar percentage of rod unit (PMPCS) in S-$(PCL\text{-}b\text{-}PMPCS)_3$. The reason probably can be found in the fact that the PCL block separated in the copolymer system with nanoscale, further study of which will be reported in the future.

Wan et al have synthesized diblock copolymers PS-block-PMPCS using 2, 2, 6, 6-tetramethy-piperidinyl-oxy(TEMPO)–mediated free radical polymerization [30]. They have found two copolymers, in which the M_n of the rigid block equals 5400 and 10800 g/mol, respectively, are thermotropic liquid crystals. We also reported early[17] that only the linear PMPCS with $M_{n,GPC}$ beyond 10200 g/mol could form liquid crystalline phases, and the liquid crystalline behavior was dependent on the molecular weights of polymer, These phenomena of MJLCP are much different from that of conventional side chain and main chain liquid-crystalline polymers. It was interesting to consider what the effect of branching on the liquid crystalline state and morphology of rod-coil block copolymer. So we studied the liquid crystalline state of the tri-armed star shaped rod-coil block copolymer using DSC and POM. The results were show in Table 1. And Figure 5 shows a representative photomicrograph of the texture of S_3 taken at 200°C. We found that only when the $M_{n,NMR}$ of each rigid arm in S-$(PCL\text{-}b\text{-}PMPCS)_3$ beyond 1.46×10^4 g/mol $[(4.40\times10^4)/3]$ could the liquid crystalline phase be observed when heated above 140℃, and birefringence develops with no detectable clearing temperature. The birefringence did not disappear until reached the decomposition temperature, indicating a good stability of the liquid crystal phase of the polymers.

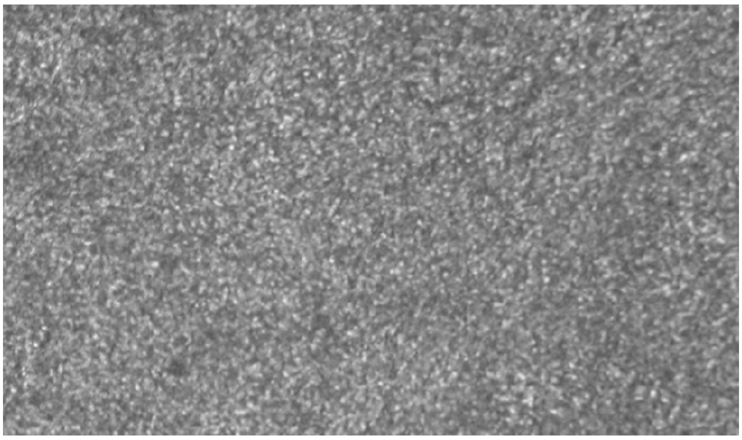


Fig.5. Representative polarized optical micrograph (400x magnification) of the texture of S-$(PCL\text{-}b\text{-}PMPCS)_3$-$S_3$ with a $M_{n,GPC}$ value of 6.35×10^4g/mol at 200℃.

Tu et al have proved that those novel rod-coil diblock copolymers comprising a polystyrene block and a MJLCPs block have unique supermolecular structure and self-assembly behavior [31]. It will be interesting to investigate the self-assembly behaviors and the dilute-solution properties of the tri-armed star shaped rod-coil block copolymer. We believe that the self-assembly behavior of S-$(PCL\text{-}b\text{-}PMPCS)_3$ and its liquid crystallinity will be affected by the rigid rod segment (PMPCS) length. The related information will be reported in the future.

Conclusion

Synthesis of tri-armed star shaped block copolymer [S-(PCL-b-PMPCS)$_3$] with different molecular weight and low polydispersity was successfully achieved via ATRP in chlorobenzene solution using macro-initiator and CuBr/Sp complex as catalyst. The liquid-crystalline behavior of S-(PCL-b-PMPCS)$_3$ was studied using DSC and POM. And the star shaped block copolymers with low molar percentage of PMPCS could show T_m. Furthermore, only the M_n of the each arm's rigid block beyond 1.46×10^4 g/mol[$(4.40\times10^4)/3$] could the star shaped block copolymer form a liquid crystalline phase, which was stable with a high clearing point.

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