

Synthesis and Self-assembly of a Triarm Star-shaped Rod-Rod Block Copolymer^{*}

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Abstract We designed and synthesized a triarm star-shaped rod-rod block copolymer (BCP), (poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene}-block-poly(γ -benzyl-L-glutamate))₃, (PMPCS-*b*-PBLG)₃. The triarm core with three PMPCS-N₃ segments was prepared by copper-mediated atom transfer radical polymerization of 2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene initiated by a trifunctional initiator and a subsequent azide reaction. And the PBLG block with alkyne functionality was synthesized through ring-opening polymerization of γ -benzyl-L-glutamate *N*-carboxyanhydride initiated by propargylamine. Finally, Huisgen's 1,3-dipolar cycloaddition was employed to combine the triarm (PMPCS-N₃)₃ and PBLG segments. The chemical structure of the BCP was confirmed by ¹H-NMR spectroscopy, Fourier-transform infrared spectroscopy, and gel permeation chromatographic analysis. Results from differential scanning calorimetry, polarized light microscopy, one-dimensional and two-dimensional wide-angle X-ray diffraction, and transmission electron microscopy techniques demonstrate that the triarm star-shaped rod-rod BCP self-assembles into a hexagon-in-lamella morphology, with the PMPCS block in the columnar nematic phase and the PBLG block in the hexagonal columnar arrangement packed in bilayers due to the rigid nature of the two blocks and the covalent connections in the star-shaped BCP.

Keywords: Star polymer; Liquid crystalline polymer; Block copolymer; Self-assembly.

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INTRODUCTION

Star-shaped block copolymers (BCPs) are branched polymers consisting of at least one chemical junction point that connects three or more linear BCP “arms”. Compared with linear counterparts of the same composition, star-shaped BCPs exhibit dramatic differences in morphologies and properties, which facilitate their applications in colloid stabilizers^[1], drug delivery carriers^[2], and thermoplastic elastomers^[3, 4]. Star-like copolymers based on poly(amidoamine) dendrimers and poly(ethylene glycol) (PEG) “arms” could be used as polymer templates to stabilize gold and cadmium sulfide nanoparticles^[1]. A star amphiphilic BCP based on poly(ϵ -caprolactone) and PEG was synthesized and studied as a potential drug delivery carrier^[2]. Hydrophobic dyes and drugs could be encapsulated in the micelles, and a high loading of a hydrophobic anticancer drug was achieved. Matyjaszewski and co-workers studied the thermoplastic elastomer behavior of star-like poly(*n*-butyl acrylate)-*b*-poly(methyl

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methacrylate) (PBA-*b*-PMMA), and found significant improvement in the ultimate tensile strength and the elastic modulus compared to those of the linear ABA-type counterparts with similar compositions^[4].

Star-shaped BCPs can be synthesized by two major strategies, the arm-first and the core-first^[5]. In the arm-first approach, the preformed polymer chains are bound together through a multifunctional linking agent. The advantage of this method is that the chemical structure of each arm can be characterized clearly, while the disadvantage is that the number of arms cannot be easily controlled due to the strong steric effect. The core-first strategy involves the synthesis of a multifunctional initiator from which the arms are grown. The star polymers synthesized by this method have defined number of arms. However, the chemical structures of each arm may not be identical. Click reaction like Huisgen's 1,3-dipolar cycloaddition, which has quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups, is suitable for the synthesis of polymers with various architectures^[6–9]. The application of click chemistry combines the advantages of the arm-first and core-first strategies in synthesizing star-shaped BCPs. By using a click reaction, the core segment can be prepared by the core-first method with the arm segment prepared at the same time, and the two blocks with well-defined chemical structures can be bound together at last, forming a well-defined star-shaped BCP. Studies on the synthesis of miktoarm star-shaped BCPs with click chemistry have been reported^[7, 10].

According to the flexibilities of the two blocks, star-shaped BCPs can be divided into coil-coil, rod-coil, and rod-rod ones. The self-assembling behaviors of coil-coil and rod-coil star-shaped BCPs have been investigated during the past few decades. Francis and co-workers synthesized amphiphilic star BCPs based on poly(ethylene oxide) and polystyrene, and the polymers were active at the air-water interface^[11]. The microphase-separated morphologies of star-like BCPs based on PBA and polyacrylonitrile (PAN)^[3] or PMMA^[4] were studied, and a morphology with hexagonally arranged PAN or PMMA cylinders in PBA matrix was observed. In addition, many studies on miktoarm star BCPs have been reported^[12–17]. However, to the best of our knowledge, star-shaped rod-rod BCPs have not been synthesized and studied so far. Studies on linear rod-coil^[18–21] and rod-rod^[22–24] BCPs show that the introduction of rod blocks greatly influences the self-assembling structures and properties of BCPs. Therefore, star-shaped rod-rod BCPs may have different phase behaviors compared to their rod-coil and coil-coil counterparts.

Mesogen-jacketed liquid crystalline polymers (MJLCPs)^[25–27], in which bulky, laterally attached pendants are densely packed around the backbone and force the backbone to adopt an extended-chain conformation, have many advantages as rigid-rod blocks. The rod length of an MJLCP can be tuned by the degree of polymerization, while the rod diameter can be altered by varying the chemical structure of the side chain^[27–30]. MJLCPs have already been used as rod blocks in synthesizing well-defined linear^[31–34] and star-shaped^[5, 35, 36] rod-coil BCPs. Gopalan *et al.* reported the first triarm star rod-coil BCPs based on MJLCPs and found that the star BCPs had lower viscosities compared to the linear ones^[37]. Poly(γ -benzyl-L-glutamate) (PBLG) forms an α -helix or a β -sheet conformation with a relatively large persistence length, and a great deal of research has been reported about its use as a rod block^[38–45]. Recently, we synthesized a series of linear rod-rod BCPs based on an MJLCP, poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene} (PMPCS), and PBLG, and we also investigated their phase behaviors and obtained hierarchical self-assembling structures on the nanometer length scale^[46].

In this study, we designed and synthesized a triarm star-shaped rod-rod BCP, (PMPCS-*b*-PBLG)₃, and we also studied its self-assembling behavior. The BCP was synthesized by combining copper-mediated atom transfer radical polymerization (ATRP) of 2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene (MPCS) initiated by a trifunctional initiator and a subsequent azide reaction, ring-opening polymerization (ROP) of γ -benzyl-L-glutamate *N*-carboxyanhydride (Bz-L-GluNCA), and a subsequent click chemistry to connect the two blocks. The resultant triarm star-shaped rod-rod BCP self-assembles into a hexagon-in-lamella morphology with the three arms packed in two opposite directions. Because the size and packing of rod-like polymers can be more easily predicted, the self-assembly of star-shaped rod-rod BCPs may be more readily tuned compared with rod-coil ones. And the two rod blocks in this work are obtained by controlled polymerization methods, making the size of the star-shaped BCP controllable compared with similar polymers with some other rod blocks such as conjugate polymers.

EXPERIMENTAL

Materials

1,3,5-Trihydroxybenzene (Aldrich, 98%), propargylamine (Aldrich, 98%), 2-bromo-2-methylpropionyl bromide (Acros, 98%), *N,N,N',N'',N'''*-pentamethyl diethylenetriamine (PMDETA) (TCI, 98%) and trifluoroacetic acid (TFA) (Acros, 99%) were used as received. *N,N*-Dimethylformamide (DMF), triethylamine (TEA), and tetrahydrofuran (THF), all A.R. grade from Beijing Chemical Reagents Co., were used after being distilled. Chlorobenzene was washed with H₂SO₄, NaHCO₃, and distilled water, dried with anhydrous calcium chloride, and finally distilled. CuBr (Beijing Chemical Reagents Co., A.R.) was purified by washing with acetic acid, followed by washing with methanol, and then dried for use. All other commercially available chemicals were used as received.

Synthesis of 1,3,5-(2'-Bromo-2'-methylpropionato) Benzene

This compound was synthesized following an already published procedure^[5]. 1,3,5-Trihydroxybenzene (0.88 g, 7.0 mmol), TEA (0.60 mL, 42 mmol) and CH₂Cl₂ (30 mL) were placed in a flask. The reaction mixture was cooled in an ice/water bath and stirred at 0 °C. 2-Bromo-2-methylpropionyl bromide (5.2 mL, 42 mmol) was added slowly, and then the solution was stirred for another 4 h. After completion of the reaction, triethylammonium bromide was removed by filtration, and the solution was washed with deionized water three times and then dried with anhydrous MgSO₄. The product was recovered as a white powder that was recrystallized three times from petroleum ether. Yield: 2.2 g (73%). ¹H-NMR (CDCl₃, 400 MHz, δ): 6.97 (s, 3H, aromatic H), 2.06 (s, 18H, —CH₃). Anal. Calcd for C₁₈H₂₁Br₃O₆: C 37.73, H 3.69. Found: C 37.74, H 3.78.

Synthesis of α -Azido Triarm Star-shaped PMPCS

The monomer of PMPCS, MPCS, was prepared as described in the literature^[47]. In a typical experiment for polymerization, MPCS (0.30 g, 0.75 mmol), 1,3,5-(2'-bromo-2'-methylpropionato) benzene (2.9 mg, 5.0 μ mol), CuBr (2.2 mg, 15 μ mol), sparteine (5.0 mg, 30 μ mol), and chlorobenzene (2.0 mL) were charged into a polymerization tube under ambient atmosphere. After stirring and degassing by three freeze-pump-thaw cycles, the tube was sealed under vacuum. Subsequently, the tube was immersed into an oil bath thermostated at 90 °C for 8 h, and then quenched in ice/water to ambient temperature. The solution was passed through a neutral alumina column in order to remove copper salt. The triarm (PMPCS-Br)₃ was precipitated in a large volume of methanol and dried in a vacuum overnight.

In order to obtain the N₃-endcapped triarm PMPCS, (PMPCS-N₃)₃, the triarm (PMPCS-Br)₃ (0.38 g, 13 μ mol) and NaN₃ (0.43 g, 6.6 mmol) were dissolved in DMF (10 mL) and stirred at ambient temperature for 2 days. The solution was filtered, dissolved in CH₂Cl₂, washed with deionized water three times, and then dried by anhydrous MgSO₄. The final polymer product was precipitated in a large volume of methanol and dried under vacuum overnight.

Synthesis of α -Alkyne PBLG

Bz-L-GluNCA was prepared according to a procedure in literature^[48]. In a typical experiment, Bz-L-GluNCA (0.60 g, 2.3 mmol), propargylamine (0.63 mg, 11 μ mol), and 3.0 mL of anhydrous DMF were introduced into a dry Schlenk flask. After degassing by three freeze-pump-thaw cycles, the solution was stirred at ambient temperature for 3 days under Ar atmosphere. The polymer was precipitated in diethyl ether and dried under vacuum.

Synthesis of Triarm Star-shaped PMPCS-*b*-PBLG Block Copolymer by Huisgen's 1,3-Dipolar Cycloaddition

Typically, triarm (PMPCS-N₃)₃ (0.15 g, 5.0 μ mol, 1.0 equiv.), α -alkyne PBLG (0.24 g, 18 μ mol, 3.6 equiv.), CuBr (4.3 mg, 30 μ mol, 6.0 equiv.), and PMDETA (5.2 mg, 30 μ mol, 6.0 equiv.) were introduced into a Schlenk flask in 3.0 mL of anhydrous DMF. After degassing by three freeze-pump-thaw cycles, the Schlenk flask was immersed into an oil bath thermostated at 35 °C for 24 h under Ar atmosphere. The reaction mixture was then passed through a neutral alumina column in order to remove copper salt and precipitated in excess of diethyl ether. The product was filtered and washed with a mixed solvent of methanol and acetone to remove the excess PBLG.

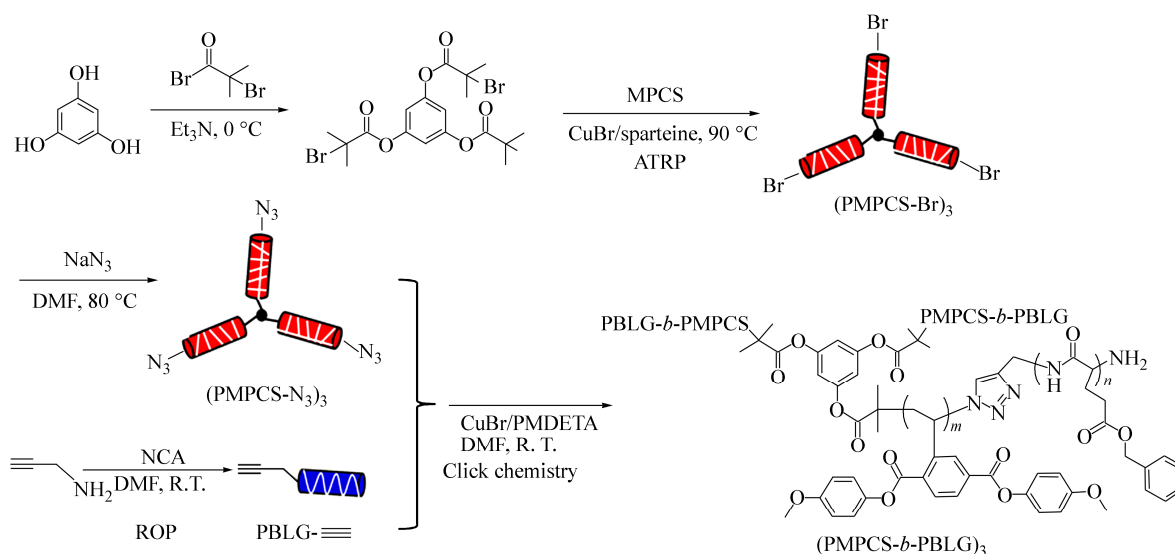
Characterization

The molecular weights (MWs) of the polymers were determined with the combination of gel permeation chromatography (GPC) and $^1\text{H-NMR}$. GPC experiments were conducted on a Waters 2410 instrument equipped with a Waters 2410 RI detector, with THF or DMF in presence of LiBr (1.0 mg/mL) as eluent (1.0 mL/min). The calibration curve was obtained with linear polystyrenes as standards. $^1\text{H-NMR}$ spectra were obtained with a Bruker 400 MHz spectrometer. Fourier-transform infrared spectroscopy (FTIR) was carried out using a Thermo Scientific Nicolet iN10-MX spectrophotometer between 4000 and 1000 cm^{-1} at a spectral resolution of 4 cm^{-1} , and the number of scans was 16. Differential scanning calorimetry (DSC) examination was carried out on a TA Q100 DSC calorimeter in a nitrogen atmosphere. Polarized light microscopy (PLM) observation was performed on a Nikon DS-Ri1 microscope with an Instec HCS302 hot stage. One-dimensional (1D) wide-angle X-ray diffraction (WAXD) experiments were carried out on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source ($\text{Cu K}\alpha$) and an X'celerator detector. Two-dimensional (2D) WAXD patterns were obtained using a Bruker D8 Discover diffractometer with a GADDS as a 2D detector calibrated with silicon powder and silver behenate. The oriented films by mechanical shearing were mounted on the sample stage with the point-focused X-ray incident beam either parallel (X direction) or perpendicular (Y or Z direction) to the shear direction (X direction). Transmission electron microscopy (TEM) was used to investigate the microphase separation of samples on a Hitachi H-9000NAR electron microscope. The solution-cast sample films were stained with RuO_4 vapor for 3 min to enhance contrast.

RESULTS AND DISCUSSION

Synthesis and Characterization of Triarm Star-shaped PMPCS-*b*-PBLG Block Copolymer

The synthesis of the star-shaped rod-rod BCP, $(\text{PMPCS-}b\text{-PBLG})_3$, is shown in Scheme 1. The triarm initiator, 1,3,5-(2'-bromo-2'-methylpropionato) benzene was synthesized by 1,3,5-trihydroxybenzene and 2-bromo-2-methylpropionyl bromide, and it was used to initiate the ATRP of MPCS in chlorobenzene, using CuBr complexed by sparteine as the catalyst, following the procedures previously reported^[5, 35]. The number-averaged MW (M_n) and polydispersity index (PDI) of the triarm PMPCS determined by GPC (using THF as the eluent) are 3.00×10^4 g/mol and 1.10, respectively, and the low PDI value indicates that the star-shaped polymer is well-defined. Because the star-shaped polymer has different hydrodynamic properties compared with linear polystyrenes used as standards in GPC measurements, the M_n value obtained will greatly deviate from the



Scheme 1 Synthetic route of star-shaped rod-rod block copolymer

absolute MW. Therefore, we applied $^1\text{H-NMR}$ to determine the MW of the polymer. Figure S1 in Supporting Information shows the $^1\text{H-NMR}$ spectrum of $(\text{PMPCS-Br})_3$. The resonance peak at $\delta = 1.25$ can be attributed to the methyl protons of the initiator core. The resonance peaks at $\delta = 1.40\text{--}2.10$, $3.35\text{--}3.90$, and $6.20\text{--}8.00$ result from the methylene protons, $-\text{OCH}_3$ protons, and aromatic protons in the PMPCS unit, respectively. And the resonance peak at $\delta = 4.75\text{--}4.79$ can be assigned to the methylene protons in the monomer unit adjacent to bromine. They confirm the well-defined structure of the triarm star-shaped PMPCS with terminal bromines. The M_n value is calculated to be 5.51×10^4 g/mol on the basis of the integral values of the resonance peaks at $\delta = 3.35\text{--}3.90$ and $\delta = 1.25$, which can be attributed to the side-chain $-\text{OCH}_3$ of PMPCS arms and the methyl protons in the initiator, respectively.

Next, the bromide end groups were quantitatively converted into azido groups using NaN_3 in DMF at ambient temperature to give the star-shaped polymer $(\text{PMPCS-N}_3)_3$. The conversion was monitored by $^1\text{H-NMR}$ (shown by Fig. 1A and Fig. S1 in Supporting Information), with the disappearance of the characteristic multiplet

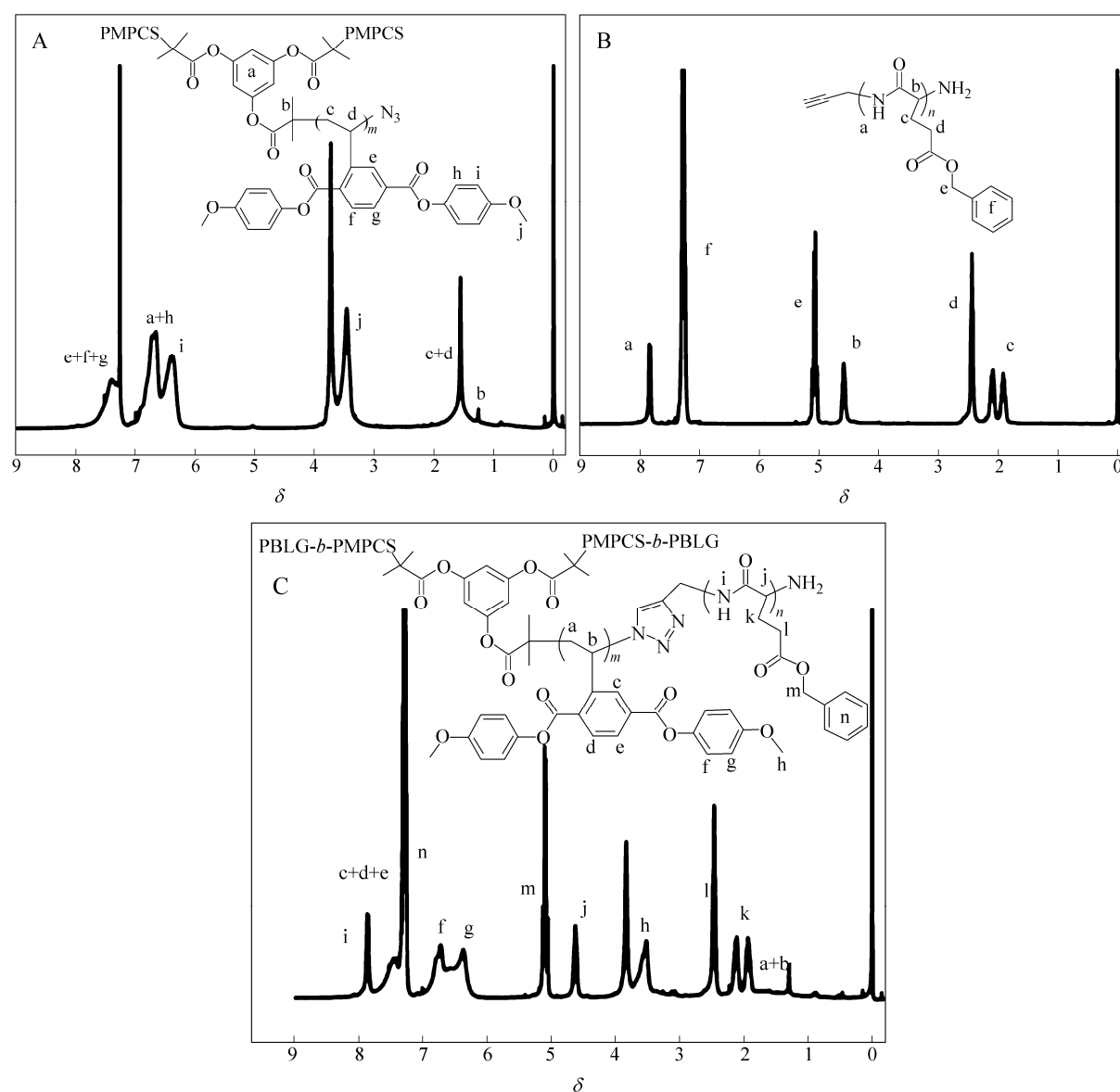


Fig. 1 400 MHz $^1\text{H-NMR}$ spectra of $(\text{PMPCS}_{45}\text{-N}_3)_3$ (A), alkyne-PBLG $_{72}$ (B) and $(\text{PMPCS}_{45}\text{-b-PBLG}_{72})_3$ (C) in CDCl_3 with 15% of TFA

signal of CH-Br protons ($\delta = 4.75\text{--}4.79$). According to the literatures^[7], the resonance of the newly formed CH-N_3 may appear at about $\delta = 3.61$. However, the resonance of $-\text{OCH}_3$ protons of PMPCS is also in this region, which may overlap with the resonance peak of CH-N_3 . Nevertheless, the disappearance of the signal of CH-Br protons proves that the bromide end groups are completely converted to azido functionalities. The FTIR spectrum of $(\text{PMPCS-N}_3)_3$, shown in Fig. S2 of Supporting Information, also evidences an azido stretching band at 2098 cm^{-1} compared to that of $(\text{PMPCS-Br})_3$. The α -alkyne PBLG was prepared by the ROP of Bz-L-GluNCA initiated by the commercially available propargylamine. GPC results in DMF/LiBr, in which LiBr was added to minimize polymer aggregation, verify the successful synthesis of the polymer, and the M_n and PDI of PBLG determined by GPC are $1.51 \times 10^4\text{ g/mol}$ and 1.25, respectively.

The triarm star-shaped BCP was prepared by the click reaction, which was performed in DMF at $35\text{ }^\circ\text{C}$ using CuBr complexed by PMDETA in a Schlenk flask. GPC measurements in DMF (LiBr, 1 g/L) and $^1\text{H-NMR}$ experiments (CDCl_3/TFA with 15% of TFA) were carried out to verify the completion of the coupling reaction. The GPC traces of the star-shaped BCP and the corresponding precursors, $(\text{PMPCS-N}_3)_3$ and alkyne-PBLG, are shown in Fig. 2. There is a monomodal peak of the triarm BCP, with a clear shift to the higher MW region compared with the two precursors, indicating a quantitative click reaction primarily leading to the target star-shaped BCP $(\text{PMPCS-}b\text{-PBLG})_3$. The $^1\text{H-NMR}$ spectrum (Fig. 1C) also reveals the existence of protons from both PMPCS and PBLG blocks in the BCP. The molecular characteristics of $(\text{PMPCS-N}_3)_3$, alkyne-PBLG and the $(\text{PMPCS-}b\text{-PBLG})_3$ BCP are summarized in Table 1. The MWs of PBLG and $(\text{PMPCS-}b\text{-PBLG})_3$ were also calculated from the M_n of triarm $(\text{PMPCS-N}_3)_3$ and the areal ratio of characteristic resonance (methyl group) of PMPCS to that (methylene group of benzyl) of the PBLG block in $^1\text{H-NMR}$ spectra. And the volume fraction of PMPCS was calculated to be 54%.

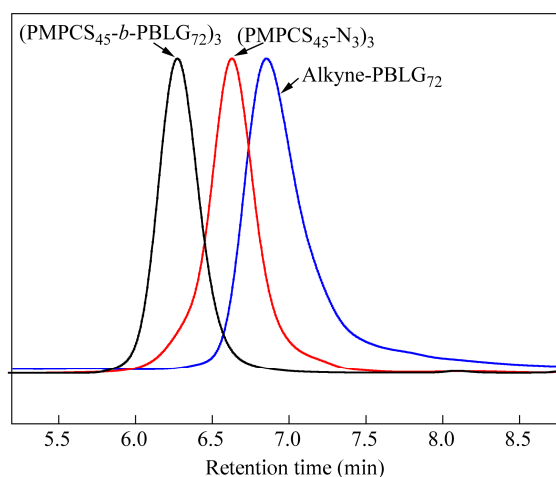
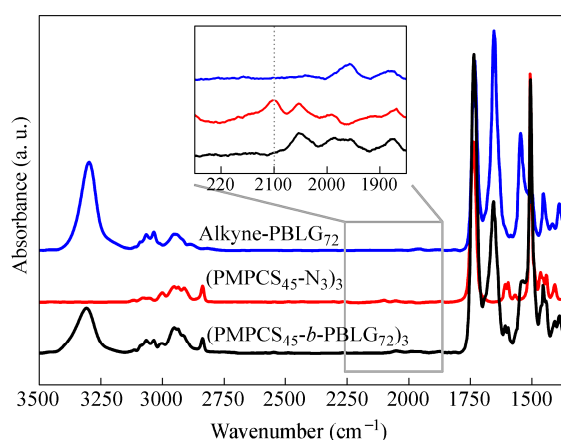


Fig. 2 GPC curves of $(\text{PMPCS-N}_3)_3$, alkyne-PBLG, and $(\text{PMPCS-}b\text{-PBLG})_3$ using DMF in presence of LiBr at 1 g/L as the eluent

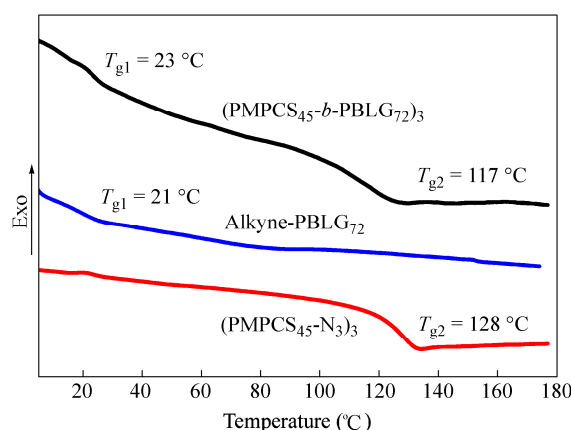
Moreover, FTIR was also used to verify the completion of the click coupling reaction by monitoring the azide vibrational band. The spectra are shown in Fig. 3. The disappearance of the azide band (2098 cm^{-1}) in the spectrum of the block copolymer evidences the completion of the coupling reaction. On the other hand, the appearance of the amide I and amide II bands at 1655 and 1550 cm^{-1} , respectively, and the absence of the amide I at $1636\text{--}1640\text{ cm}^{-1}$ and $1622\text{--}1632\text{ cm}^{-1}$ for the parallel and antiparallel β -sheets, respectively, demonstrate that the PBLG block in the star-shaped BCP takes the peptidic α -helical secondary structure^[51].

Table 1. Molecular characteristics and properties of alkyne-PBLG, triarm (PMPCS- N_3)₃, and the star-shaped BCP

Samples	M_n^a ($\times 10^4$ g/mol)	PDI ^a	M_n^b ($\times 10^4$ g/mol)	f_{PMPCS}^c (%)	L^d (nm)	d^e (nm)
Alkyne-PBLG ₇₂	1.51	1.25	1.58	0	10.8	19
(PMPCS ₄₅ - N_3) ₃	3.20	1.22	5.51	100	11.3	24
(PMPCS ₄₅ - <i>b</i> -PBLG ₇₂) ₃	5.99	1.25	10.2	54	—	43

^a Determined by GPC using DMF in presence of LiBr at 1 g/L as the eluent;^b Determined by 400 MHz ¹H-NMR;^c Volume fraction of PMPCS; calculated with the following densities: PMPCS, $\rho = 1.26$ g/cm³[49]; PBLG, $\rho = 1.28$ g/cm³[50];^d Calculated molecular length; the length of PMPCS was calculated using the zig-zag model, $L_{\text{PMPCS}} = 45 \times 0.25$ nm, where 45 is the DP of PMPCS and 0.25 nm is the bond length of one monomer unit; and the length of PBLG was calculated on the basis of the 18/5 α -helical structure, $L_{\text{PBLG}} = 5/18 \times 72 \times 0.54$ nm, where 72 is the DP of PBLG and 0.54 nm is the pitch of the α -helical structure of PBLG.^e Obtained from the lamellar spacing of the BCP and those of the PMPCS and PBLG sublayers in TEM**Fig. 3** FTIR spectra of the star-shaped (PMPCS-*b*-PBLG)₃ BCP and the precursor polymers**Phase Structure and Self-assembly in Bulk**

The phase behaviors of the star-shaped (PMPCS₄₅-*b*-PBLG₇₂)₃ and the corresponding precursors were analyzed by DSC, as shown in Fig. 4. The DSC thermograms were recorded during the second heating cycle at a rate of 10 K/min under a nitrogen atmosphere. The curve of the BCP clearly demonstrates the glass transitions at ~ 23 °C for the PBLG block and ~ 117 °C for the PMPCS block. The observation of the two glass transition

**Fig. 4** DSC thermograms of (PMPCS- N_3)₃, alkyne-PBLG, and (PMPCS₄₅-*b*-PBLG₇₂)₃ during the second heating cycle at a rate of 10 K/min under a nitrogen atmosphere

temperatures (T_g 's) of the two blocks indicates that the PMPCS and PBLG blocks are microphase-separated in the BCP.

In our previous study, we have found that the liquid crystalline (LC) behaviors of MJLCPs are dependent on their MWs^[5, 47]. LC phases can form when M_n (measured by GPC using THF as the eluent) exceeds 1.00×10^4 g/mol for the linear PMPCS and 2.70×10^4 g/mol for the triarm PMPCS, 0.90×10^4 g/mol for each arm^[5]. In this work, the M_n of the triarm PMPCS is 3.00×10^4 g/mol, which makes it possible to study the effect of LC properties on the phase structure of the BCP. PLM was first used to study the LC properties of the star-shaped polymers. Sample films were cast from THF solutions, dried at ambient temperature and then heated to 200 °C. Both of the PBLG and PMPCS blocks can form LC phases, and the ordering of the LC phases can be improved at high temperatures. However, a small amount of the PBLG segment may decompose above 200 °C. Thus, 200 °C was chosen to thermally treat the samples. The PLM micrographs taken at 200 °C are shown in Fig. 5. Both (PMPCS₄₅-N₃)₃ and (PMPCS₄₅-*b*-PBLG₇₂)₃ are birefringent, which indicates that they are in their LC phases. The textures remain the same when the samples are cooled to ambient temperature, which implies that the LC phases are retained upon cooling.

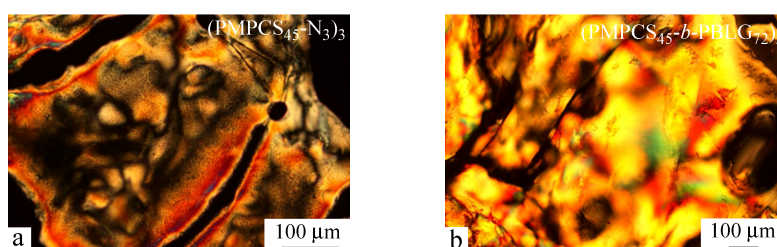


Fig. 5 PLM micrographs of (PMPCS₄₅-N₃)₃ (a) and (PMPCS₄₅-*b*-PBLG₇₂)₃ (b) at 200 °C

One-dimensional WAXD was also applied to study the LC property of the star-shaped BCP. The sample film was prepared by solution-casting from a THF solution and then dried at ambient temperature. Results are shown in Fig. 6. For the star-shaped (PMPCS₄₅-*b*-PBLG₇₂)₃, because the positions of the low-angle peak from PMPCS and the first-order peak from PBLG are very close to each other, these two diffraction peaks overlap to some extent. Upon heating, the two second-order diffractions from the hexagonal columnar (Φ_H) arrangement of the α -helical PBLG appear at q values of 8.05 and 9.32 nm⁻¹, in addition to the first-order peak at $q = 4.63$ nm⁻¹ (with the three peaks having a scattering vector ratio of 1:3^{1/2}:4^{1/2}), at temperatures above 120 °C. The diffraction peak from the columnar nematic (Φ_N) phase of PMPCS at $q = 3.97$ nm⁻¹ (corresponding to a d -spacing of

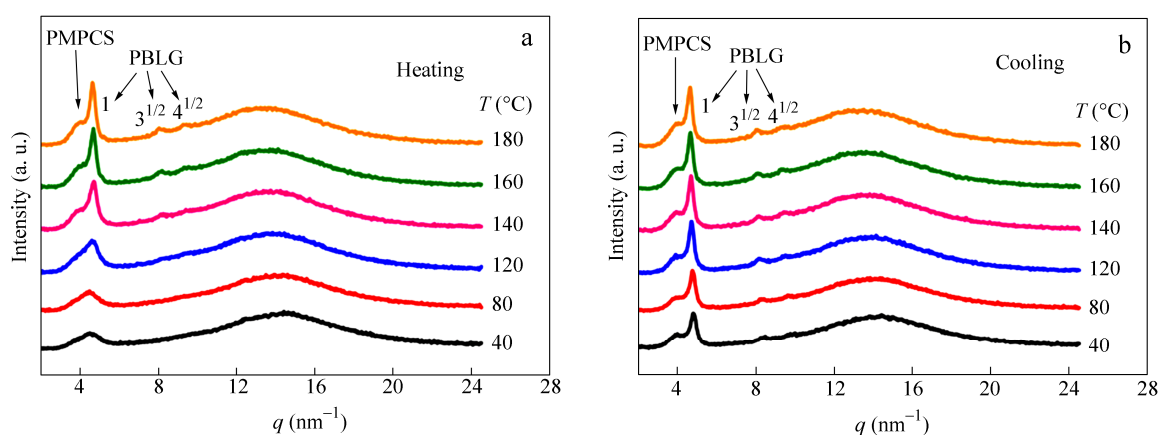


Fig. 6 1D WAXD profiles of the triarm star-shaped (PMPCS₄₅-*b*-PBLG₇₂)₃ during the first heating (a) and the first cooling (b)

1.58 nm) can be gradually seen upon heating from 40 °C to 190 °C. During the cooling process, the Φ_H phase of PBLG remains, with the higher-order diffraction peaks always present (Fig. 6b). The shoulder peak to the left of the first-order peak from PBLG comes from the partly formed Φ_N phase of PMPCS. The halo with q at 14.2 nm^{-1} (corresponding to a d -spacing of about 0.44 nm) is the commonly observed amorphous halo. The 1D WAXD results are consistent with PLM results.

To study the orientation of the two rod-like polymer chains in the BCP, 2D WAXD was used. The experiments were carried out on mechanically sheared samples. Schematic drawing of the shearing geometry is shown in Fig. 7(a), and the shear direction is the X -axis. Parts (b), (c), and (d) of Fig. 7 illustrate the 2D WAXD patterns of the triarm star-shaped (PMPCS₄₅-*b*-PBLG₇₂)₃ with the X-ray beam along Z , Y , and X directions, respectively. As shown in parts (b) and (c) of Fig. 7, there are two pairs of strong diffraction arcs on the meridian direction in the low-angle region, which are attributed to the Φ_N phase of PMPCS and the Φ_H phase of PBLG. Therefore, the PMPCS and PBLG rods are aligned parallel to each other. Figure 7(e) shows the integration at a 30°-angle centered at the meridian from Fig. 7(b). A set of Bragg reflections from the hexagonally ordered packing of PBLG at $q = 4.67, 7.95$, and 9.68 nm^{-1} are observed with a scattering vector ratio of $1:3^{1/2}:4^{1/2}$, and a diffraction peak from the Φ_N phase of PMPCS can also be observed at $q = 3.90 \text{ nm}^{-1}$. The results are consistent

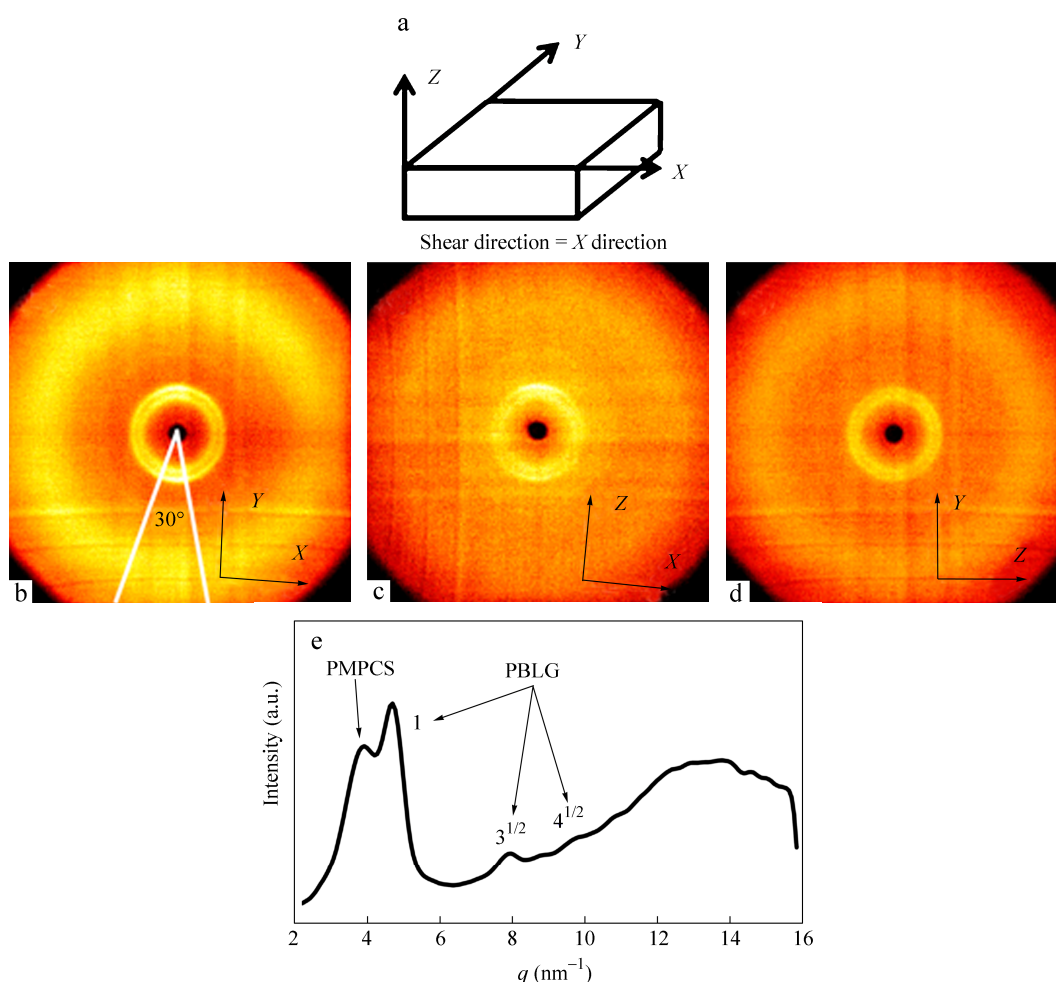


Fig. 7 Schematic drawing of the shearing geometry with the X -axis being the shear direction (a), 2D WAXD patterns of triarm (PMPCS₄₅-*b*-PBLG₇₂)₃ with the X-ray incident beam along Z (b), Y (c), and X (d) directions, and integration at a 30°-angle centered at the meridian (e) from (b)

with those from 1D WAXD experiments. It is necessary to emphasize that because both blocks in the BCP have rigid-rod structures, mechanical shearing for the orientation of the polymer chains is not as effective as in other systems. In Fig. 7(d), the 2D WAXD pattern shows two low-angle diffraction rings from PMPCS and PBLG, indicating the random orientation of the lattices of the two LC phases formed by the two rods in the *Y-Z* plane. The 2D WAXD results demonstrate that the long axes of the PMPCS and PBLG rods are both basically aligned parallel to the shear direction.

The appearance of diffractions from both PMPCS and PBLG in WAXD patterns also indicates the microphase separation of the BCP. TEM was used to directly observe the morphology of the self-assembled structure of the BCP. Observations were performed on solution-cast films from THF solutions at a concentration of 0.5 mg/mL. The triarm BCP was first dissolved in dry THF with stirring at ambient temperature for 12 h. Then the homogeneous solution was cast on carbon-coated Cu grids (T10044) in dry air. The solvent was allowed to evaporate completely at ambient temperature, and then the cast thin films were annealed at 160 °C under a N₂ flow for 3 days. Finally, the film samples were stained by RuO₄ vapor to enhance contrast before measurements. Figure 8(a) shows a typical TEM micrograph. A lamellar structure formed by alternating dark (PBLG) and light (PMPCS) strips is clearly observed, and the average layer spacing is about 43 nm with the PMPCS sublayer of 24 nm and the PBLG sublayer of 19 nm. As shown in the TEM micrograph, defects, such as branching of lamella, exist possibly because of the triarm architecture of the BCP. To figure out the packing scheme in the microphase-separated nanostructure, we calculated the molecular lengths of the two blocks. As both blocks are assumed to be rigid, the zig-zag model was used for the PMPCS segment and the 18/5 α -helical structure was applied for the PBLG block for the calculation. The results are shown in Table 1. Comparing the calculated molecular lengths of the two blocks (about 11.3 nm for PMPCS and 10.8 nm for PBLG) with the estimated layer spacing values from TEM results, we propose that the three arms are packed in two different directions and both rods adopt the stacked bilayer structures. With the combination of the 2D WAXD results, the packing model for the star-shaped BCP can be schematically illustrated in Fig. 8(b).

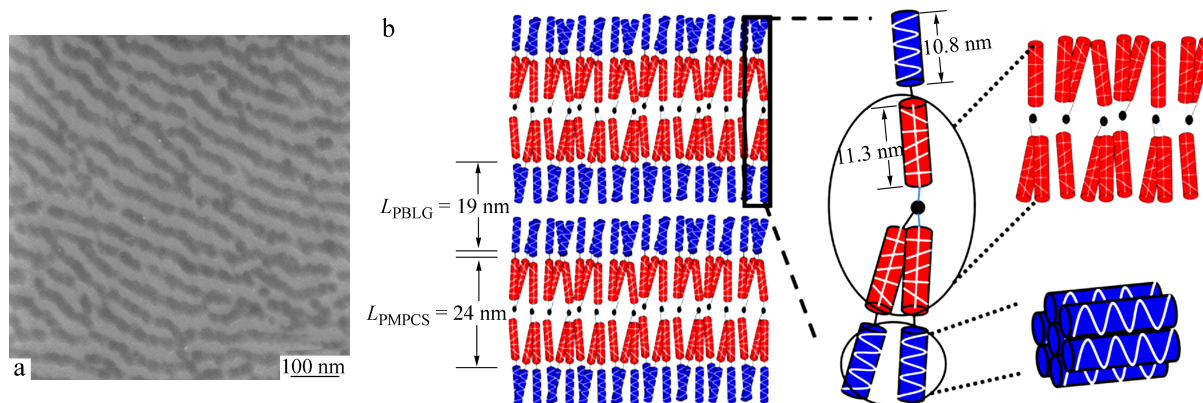


Fig. 8 TEM micrograph of the triarm (PMPCS₄₅-*b*-PBLG₇₂)₃ (a) and the proposed model for the self-assembled structure, including the detailed packing of one BCP and the arrangement of the PMPCS and PBLG blocks (b)

In the triarm star-shaped rod-rod BCP studied herein, the three linear rod-rod arms are connected by chemical bonds, which restrict the PMPCS segment from packing together. As a result, the PMPCS block has to take the bilayer arrangement in its own microdomain, while in the linear rod-rod BCP, the packing of PMPCS is unrestrained. On the other hand, compared with triarm star-shaped rod-coil and coil-coil BCPs, the rigid nature of the rod blocks makes the energy of the bilayer lamellar packing in a high level, and the microstructure may easily transform into cylinders with the change in the composition of the BCP. Therefore, it will be more interesting to know how the self-assembling structure varies with different volume fractions of PMPCS. To this end, further research is currently underway.

CONCLUSIONS

In this work, a triarm star-shaped rod-rod BCP, star-shaped (PMPCS-*b*-PBLG)₃, was successfully synthesized by combining ATRP of MPCS initiated by a trifunctional initiator, ROP of Bz-L-GluNCA, and a subsequent click chemistry to connect the two segments. The click reaction is an efficient method for the synthesis of star-shaped BCPs because both the number of arms and the chemical structures of the two blocks of the BCP can be easily and clearly characterized. The PMPCS and PBLG blocks form Φ_N and Φ_H LC phases, respectively, indicating that the two blocks are microphase-separated. TEM and 2D WAXD results demonstrate that the triarm star-shaped rod-rod BCP self-assembles into a lamellar structure, with the two kinds of rods parallel to each other and the three arms packed in two opposite directions. The PMPCS block arranges in a bilayer manner in its own microdomain owing to the restriction of the chemical bonds in the star-shaped BCP. And the PBLG block also adopts a bilayer packing in the hexagonal columnar phase. Therefore, the BCP self-assembles into a hexagon-in-lamella morphology.

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