

Synthesis and Self-assembly of a Linear Coil-Coil-Rod ABC Triblock Copolymer*

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Abstract An interesting order-order transition between two different complex nanostructures was observed in a new liquid crystalline linear coil-coil-rod ABC triblock copolymer (triBCP). First, the ABC triBCP, poly(dimethylsiloxane)-*b*-polystyrene-*b*-poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PDMS-*b*-PS-*b*-PMPCS), was synthesized through sequential atom transfer radical polymerization. The degrees of polymerization of PDMS, PS, and PMPCS blocks are 58, 159, and 106, and the corresponding volume fractions of PDMS, PS, and PMPCS are 0.09, 0.29, and 0.62, respectively. The phase behaviors of the PDMS-*b*-PS diblock copolymer precursor and the final triblock copolymer were studied by small-angle X-ray scattering, one-dimensional wide-angle X-ray scattering, and transmission electron microscopy experiments. The PDMS-*b*-PS precursor self-assembles into hexagonally packed cylinders with a relatively small periodic size after thermal annealing. When the triblock copolymer is annealed at a relatively low temperature (120 °C) at which the PMPCS block is in the amorphous state, the triBCP forms core-shell hexagonally packed cylinders (CSH) with a relatively large periodic size. After the triBCP is annealed above 140 °C at which the PMPCS block transforms to the liquid crystalline (LC) phase, the nanophase-separated structure transforms to a three-phase four-layer lamellar structure (LAM-3P4L). Thus, accompanied with the transition of the PMPCS blocks from the amorphous state to the LC phase, the order-order transition from CSH to LAM-3P4L occurs in the PDMS-*b*-PS-*b*-PMPCS ABC triBCP.

Keywords: Coil-coil-rod triblock copolymer; Self-assembly; Order-order transition; Liquid crystalline polymer; Complex nanostructures.

INTRODUCTION

The self-assembly of most diblock copolymers (diBCPs) investigated can only provide a very limited number of stable morphologies including lamellae (LAM), gyroid, *Fddd*, cylinders, and spheres^[1–4]. Compared with diblock copolymers^[1, 5], linear ABC triblock copolymers (triBCPs) with three distinct polymer sequences can form various more intricate nanostructures which are not accessible from diblock copolymers, and therefore, dramatically broaden the types of nanophase-separated morphologies^[6, 7]. Thus, linear ABC triblock copolymers as one type of the simplest multicomponent block copolymers have great potentials to be used as nanomaterials^[7, 8]. The parameters which determine the nanophase separation behavior of linear ABC triBCPs include three different Flory-Huggins interaction parameters (χ_{AB} , χ_{BC} , χ_{AC}), two independent volume fractions (f_A , f_B), and the total degree of polymerization (N)^[9]. Most theoretical and experimental studies on linear ABC triblock copolymers are focused on coil-coil-coil ones. Computer simulations on linear coil-coil-coil ABC

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triblock copolymers reveal a great set of complex nanostructures^[9–11], some of which have been found in experimental studies such as three-phase four-layer lamellae (LAM-3P4L), ordered tricontinuous double-diamond, core-shell hexagonally packed cylinders (CSH), core-shell double gyroid, and double square-packed cylinders^[6, 12–14].

The phase behavior of rod-like polymer-containing AB rod-coil diblock copolymers and ABA triblock copolymers have been extensively studied^[15–20], and the additional geometrical asymmetry between the rod and coil blocks and the rod-rod aligning interaction play important roles in forming the final morphologies^[18, 21]. However, coil-coil-rod (or rod-coil-coil) ABC triblock copolymers with one rod-like block on one end have been less frequently studied. Coil-coil-rod ABC triblock copolymers have the capability of forming more complicated hierarchical structures consisting of the complex nanophase-separated structure and the liquid crystalline (LC) structure. For theoretical research, only Xia *et al.* studied the self-assembly of linear ABC coil-coil-rod triBCP melt by applying self-consistent field lattice techniques in three-dimensional (3D) space and found seven stable structures including “two-color” lamellae, “three-color” lamellae, “two-color”-perforated lamellae, “three-color”-perforated lamellae, core-shell hexagonal lattice phase, strips, and micelles^[22]. For experimental research, only Chang *et al.* reported that the π -conjugated poly(diethylhexyloxy-pphenylenevinylene)-*b*-poly(2-vinyl pyridine)-*b*-polystyrene (PPV-*b*-PVP-*b*-PS) rod-coil-coil triblock copolymers with low or high volume fractions of the PPV block formed triple-lamellar phases when the PPV block was in the smectic C phase^[23], and the order-disorder transition occurred when the PPV blocks transformed to the isotropic phase. Thus, they concluded that the rod-rod interaction of the PPV blocks was important for forming and stabilizing the lamellar structure of the PPV-*b*-PVP-*b*-PS triBCP. For ABC triblock copolymers containing mesogen-jacketed LC polymers (MJLCPs), only Zhang *et al.* reported the LC phase behavior of the MJLCP in the synthesized poly(ethylene oxide)-block-poly(methyl methacrylate)-block-poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl] styrene} (PEO-*b*-PMMA-*b*-PMPCS) triblock copolymer^[24]. Moreover, rod-like blocks possess mesophase transitions with varying temperatures, and some order-order transitions of the rod-coil diblock copolymers are triggered by such mesophase transitions^[25, 26]. However, as far as we know, there has been no report on the order-order transitions among the different complex nanostructures of linear coil-coil-rod ABC triblock copolymers induced by the mesophase transitions of the rod-like blocks.

In this work, a new structurally well-defined coil-coil-rod ABC triblock copolymer, poly(dimethylsiloxane)-*b*-polystyrene-*b*-poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PDMS-*b*-PS-*b*-PMPCS), was synthesized by atom transfer radical polymerization (ATRP). And the nanophase separation behaviors of the PDMS-*b*-PS precursor and the final PDMS-*b*-PS-*b*-PMPCS triBCP were studied by small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and transmission electron microscopy (TEM) techniques. Significantly, an irreversible order-order transition between two complex nanostructures was observed in the PDMS-*b*-PS-*b*-PMPCS triBCP accompanying the amorphous-to-LC phase transition of the PMPCS blocks.

EXPERIMENTAL

Materials

N,N,N',N'',N'''-Pentamethyl diethylenetriamine (PMDETA, TCI, 98%), *n*-hexane, and methanol were used as received. Styrene, triethylamine (98%), and tetrahydrofuran (THF, Beijing Chemical Reagents Co., A.R.) were used after being distilled. Chlorobenzene was purified by washing with concentrated sulfuric acid to remove residual thiophene, followed by washing with a 5% sodium carbonate solution and with water, and then dried with anhydrous calcium chloride before it was 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.

Synthesis of the Macroinitiator 2-Bromoisobutyrate-terminated PDMS (PDMS-Br)

The macroinitiator 2-bromoisobutyrate-terminated PDMS was synthesized as previously reported^[27].

Synthesis of PDMS-*b*-PS-*b*-PMPCS through Sequential Atom Transfer Radical Polymerization

PDMS-Br (0.200 g, 44.4 μmol), styrene (1.38 g, 13.3 mmol) and PMDETA (7.70 mg, 44.4 μmol) were charged into a polymerization tube. After stirring and degassing by two freeze-pump-thaw cycles, CuBr (6.37 mg, 44.4 μmol) was charged into the frozen polymerization tube. Then, after stirring and degassing by three freeze-pump-thaw cycles again, the tube was sealed under vacuum and subsequently immersed into an oil bath thermostated at 90 °C for 3 h. It was then quenched in liquid nitrogen and taken out to ambient condition. The solution was passed through a neutral alumina column in order to remove copper salt. Finally, the copolymer was precipitated in a large volume of methanol and dried in vacuum overnight.

The PDMS-*b*-PS block copolymer (0.200 g, 9.56 μmol), the monomer {2,5-bis[(4-butoxyphenyl)oxycarbonyl]styrene} (MPCS, 0.554 g, 1.37 mmol), CuBr (1.38 mg, 9.56 μmol), and PMDETA (1.65 mg, 9.56 μmol) were charged into a polymerization tube for polymerization similar to the preparation of PDMS-*b*-PS. After the triblock copolymer was precipitated out and dried, it was extracted by reflux of *n*-hexane in a Soxhlet extractor for 48 h to remove the unreacted PDMS-*b*-PS block copolymer.

Characterization Techniques

The molecular weights of the PDMS-*b*-PS diblock copolymer and the PDMS-*b*-PS-*b*-PMPCS triblock copolymer were determined with the combination of gel permeation chromatography (GPC), $^1\text{H-NMR}$, and the absolute molecular weight of the macroinitiator^[27]. GPC experiments were conducted on a Waters 2410 instrument equipped with a Waters 2410 RI detector, with pure THF 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.

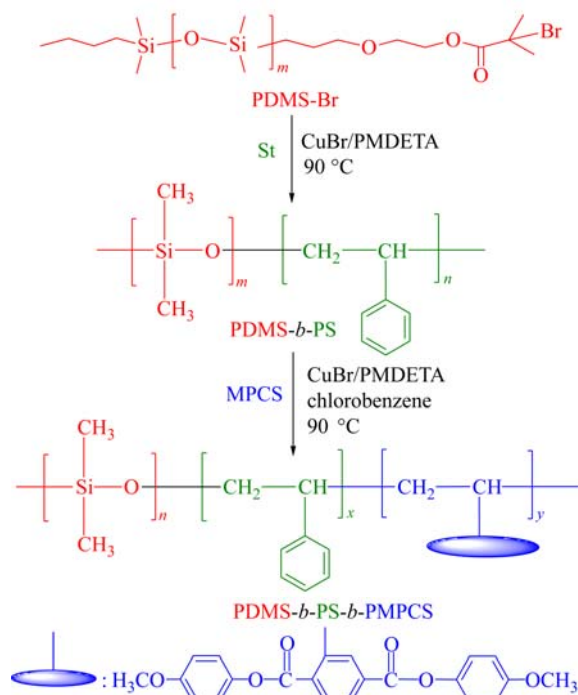
Differential scanning calorimetry (DSC) measurements were carried out on a TA Q100 DSC calorimeter in a nitrogen atmosphere. SAXS experiments were carried out on a Bruker Nanostar SAXS instrument using Cu K α radiation at a wavelength of 0.154 nm. The working voltage and current were 40 kV and 0.65 mA, respectively. The scattering vector q is defined as $q = 4\pi/\lambda \sin\theta$, where the scattering angle is 2θ , and the d -spacing (d) is given by $2\pi/q$. And the q values which can be collected from the SAXS experiment range from 0.09 nm $^{-1}$ to 2.80 nm $^{-1}$. One-dimensional wide-angle X-ray scattering (1D WAXS) experiments were performed on an SAXSess instrument (Anton Paar) with the working voltage and current of 40 kV and 40 mA, respectively. The scattering patterns were recorded on an imaging plate (IP) with a pixel size of 42.3 $\mu\text{m} \times 42.3 \mu\text{m}$ which extended to the high-angle range (the q range covered by the IP was from 0.06 nm $^{-1}$ to 29 nm $^{-1}$). The scattering peak positions in the wide-angle region were calibrated with silicon powder. TEM bright field images were obtained with a Tecnai T20 TEM instrument using an accelerating voltage of 120 kV.

RESULTS AND DISCUSSION

Synthesis and Characterization of PDMS-*b*-PS-*b*-PMPCS TriBCP

As shown in Scheme 1, the PDMS-*b*-PS-*b*-PMPCS ABC triblock copolymer was synthesized through sequential ATRP from the PDMS macroinitiator prepared as described in our previous work^[27]. The number-average molecular weight, degree of polymerization (DP), and polydispersity index (PDI) of the PDMS-Br macroinitiator are 4332 g/mol, 58, and 1.02 (determined by MALDI-TOF mass spectrometry), respectively^[27]. PDMS-*b*-PS was first synthesized using PDMS-Br as the initiator, and then PDMS-*b*-PS-*b*-PMPCS was synthesized from PDMS-*b*-PS. The chemical structures, molecular weights, and polydispersities of PDMS-*b*-PS and PDMS-*b*-PS-*b*-PMPCS were characterized by GPC (Fig. 1 and Table 1) and $^1\text{H-NMR}$ (Fig. 2). The absolute molecular weight of PDMS-*b*-PS is calculated to be 20900 g/mol from the $^1\text{H-NMR}$ result in Fig. 2(a). As shown in the NMR spectrum of PDMS-*b*-PS-*b*-PMPCS triBCP (Fig. 2b), the ratio of the integral of the absorption peak of the H (f and f') on the phenyl group of the PS block to that of the H (a) on the OCH $_3$ group of PDMS is 1.36, and the ratio of the integral of the absorption peak of the H (c) on the OCH $_3$ group of PMPCS to that of the H (a) on the OCH $_3$ group of PDMS is 1.83. Thus, the DP of PS (DP $_{\text{PS}}$) is calculated to be 158 (DP $_{\text{PS}} = 1.36 \times 2 \times 58 \approx 158$), and the DP of PMPCS (DP $_{\text{PMPCS}}$) block is calculated to be 106 (DP $_{\text{PMPCS}} = 1.83 \times 1 \times 58 \approx 106$). From the

$^1\text{H-NMR}$ results and the densities of PDMS (0.97 g/cm^3), PS (1.05 g/cm^3), and PMPCS (1.28 g/cm^3)^[28], the volume fractions of PDMS (f_{PDMS}) and PS (f_{PS}) in the PDMS-*b*-PS diblock copolymer are calculated to be 0.23 and 0.77, respectively, and the volume fractions of PDMS (f_{PDMS}), PS (f_{PS}), and PMPCS (f_{PMPCS}) in PDMS-*b*-PS-*b*-PMPCS are 0.09, 0.29, and 0.62, respectively. The glass transition temperatures of PS ($T_{\text{g,PS}}$) and PMPCS ($T_{\text{g,PMPCS}}$) blocks are $103\text{ }^\circ\text{C}$ and $111\text{ }^\circ\text{C}$, respectively, obtained from DSC measurements. The molecular weights and volume fractions of different blocks in PDMS-*b*-PS and PDMS-*b*-PS-*b*-PMPCS as well as the glass transition temperatures of the PS and PMPCS blocks are listed in Table 1.



Scheme 1 Synthesis of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer

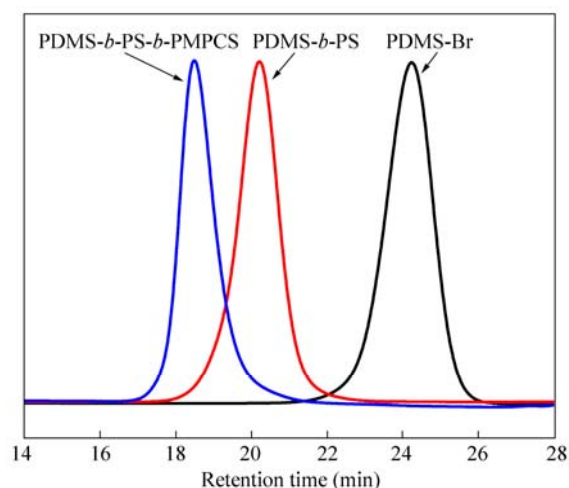
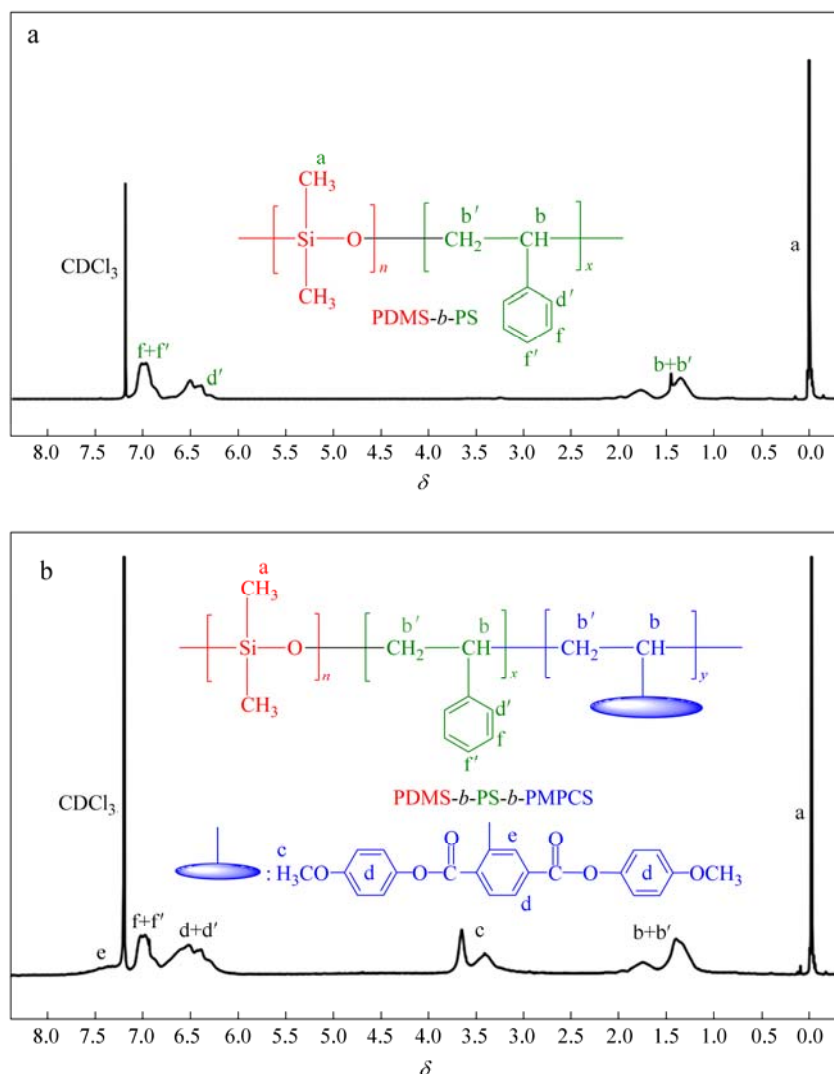


Fig. 1 GPC curves of the macroinitiator, the PDMS-*b*-PS diblock copolymer and the PDMS-*b*-PS-*b*-PMPCS triblock copolymer synthesized

Table 1. Molecular weights of all blocks, polydispersity indexes, and volume fractions of PDMS and PS in the diBCP and the triBCP as well as T_g values of the PS and PMPCS blocks

sample	$M_{n,PDMS}^a$ (g/mol)	$M_{n,PS}^a$ (g/mol)	$M_{n,PMPCS}^a$ (g/mol)	PDI ^b	f_{PDMS}^a (%)	f_{PS}^a (%)	$T_{g,PS}^c$ (°C)	$T_{g,PMPCS}^c$ (°C)
PDMS- <i>b</i> -PS	4500	16400	— ^d	1.09	23	77	103	— ^d
PDMS- <i>b</i> -PS- <i>b</i> -PMPCS	4500	16400	42800	1.13	9	29	103	111

^a Determined from ^1H -NMR results of the PDMS macroinitiator and the block copolymers;^b Determined from GPC results using linear polystyrene standards;^c Determined from DSC results;^d Not applicable**Fig. 2** ^1H -NMR spectra of the PDMS-*b*-PS diblock copolymer (a) and the PDMS-*b*-PS-*b*-PMPCS triblock copolymer (b)**Nanophase-separated Structure of PDMS-*b*-PS**

Firstly, the nanophase separation behavior of the PDMS-*b*-PS diblock copolymer which is the precursor of the ABC triblock copolymer was investigated. As shown in Fig. 3(a), the diffraction peaks in the SAXS profile of the PDMS-*b*-PS diBCP sample after thermal annealing at 140 °C for 3 days have a scattering vector ratio of 1: $3^{1/2}$:2: $7^{1/2}$ which is characteristic of the hexagonally packed cylinders (HEX). The primary reflection is at $q^* = 0.330 \text{ nm}^{-1}$, corresponding to a d -spacing value of 19.0 nm. The TEM micrograph (Fig. 3b) also confirms the

HEX morphology. The cylinder-to-cylinder distance (a) in the TEM micrograph is about 21 nm which agrees well with the calculated value ($a = 2d/3^{1/2} = 21.9$ nm) from the SAXS result within the range of errors. When the annealing temperature is increased to 180 °C, similar SAXS and TEM results are obtained. Thus, the PDMS-*b*-PS diBCP forms a stable HEX structure after annealing above the glass transition temperature of the PS block. And the model of the HEX structure is schematically shown in Fig. 3(c).

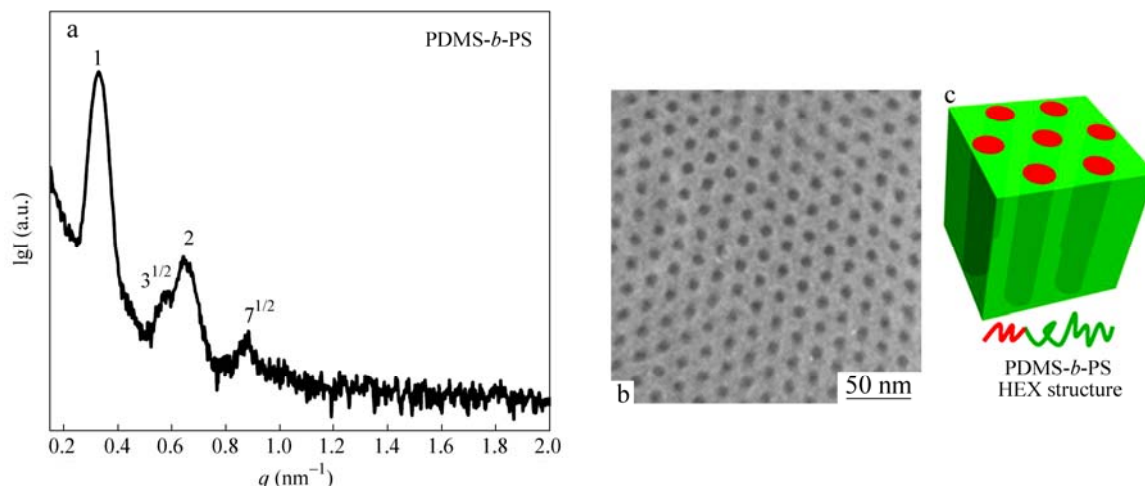


Fig. 3 SAXS profile (a) and TEM micrograph (b) of the PDMS-*b*-PS sample after thermal annealing at 140 °C for 3 days and the model of the HEX structure formed by the PDMS-*b*-PS diBCP (c)

Nanophase-separated Complex Nanostructures of PDMS-*b*-PS-*b*-PMPCS after Annealing above $T_{g,PMPCS}$ but below $T_{LC,PMPCS}$

Subsequently, the phase behavior of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer was investigated. The PMPCS block in the triBCP has a relatively high molecular weight and can transform from the amorphous state to the LC phase after annealing at a relatively high temperature^[28]. All triBCP samples were first slowly dried from concentrated THF solutions. Then three different temperatures (120, 140, and 180 °C) were chosen to anneal the triBCP samples, and the annealing time at each temperature was 5 days. After thermal annealing, the nanophase-separated nanostructures of the triBCP samples were examined by SAXS and TEM techniques, and the LC phase of the PMPCS block was characterized by 1D WAXS. The 1D WAXS and SAXS profiles of the triBCP samples after annealing at different temperatures are shown in Figs. 4(a) and 4(b), respectively.

When the triBCP sample is annealed at 120 °C which is just above the glass transition temperatures of the PS and PMPCS blocks but below the LC phase formation temperature of the PMPCS blocks ($T_{LC,PMPCS}$), the PMPCS blocks are in the amorphous state indicated by the absence of any reflection peaks in the 1D WAXS profile (the bottom curve in Fig. 4a). And the diffraction peaks in the SAXS profiles (the bottom curve in Fig. 4b) have a scattering vector ratio of 1:3^{1/2}:2:7^{1/2}:13^{1/2} which is characteristic of the HEX structure. The primary reflection is at $q^* = 0.214$ nm⁻¹, corresponding to a d -spacing value of 29.4 nm. In the TEM micrograph of the thin slice of the corresponding sample, the CSH structure is observed as shown in Figs. 5(a) and 5(b), in which the darkest core is the PDMS domain because PDMS has the highest electron density^[29], the lightest shell is the PS domain which has the lowest electron density, and the relatively dark matrix is the PMPCS domain^[30]. The cylinder-to-cylinder distance in the TEM micrograph is about 35 nm which is consistent with the calculated value ($2d/3^{1/2} = 34.0$ nm) from the SAXS result within the range of errors. Thus, the PDMS-*b*-PS-*b*-PMPCS triblock copolymer forms a CSH structure after annealing at 120 °C. However, the PMPCS blocks are amorphous and have no orientational ordering in the PMPCS matrix. And the model of the core-shell HEX structure with PMPCS rods in the amorphous state in the matrix is shown in Fig. 5(c).

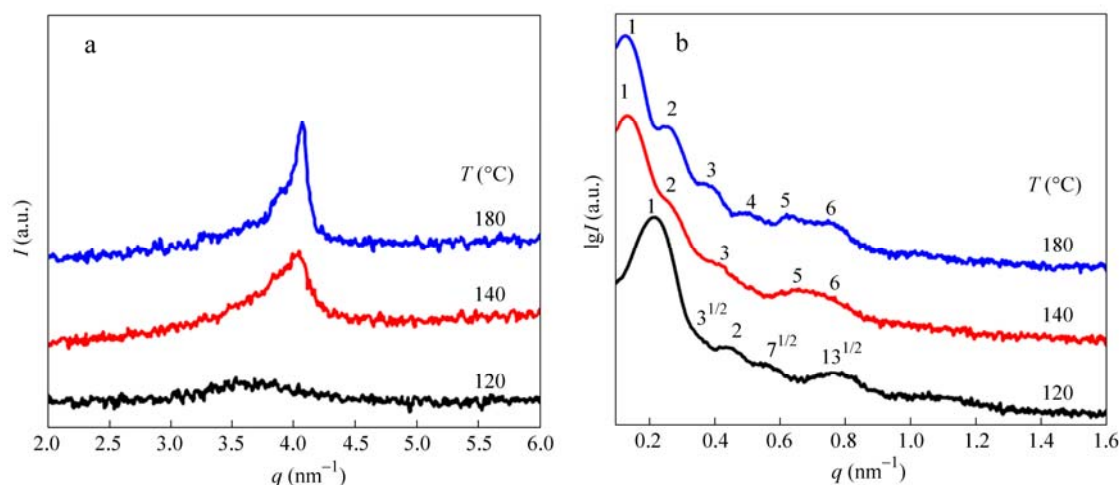


Fig. 4 1D WAXS (a) and SAXS (b) profiles of PDMS-*b*-PS-*b*-PMPCS samples after thermal annealing at indicated temperatures for 5 days

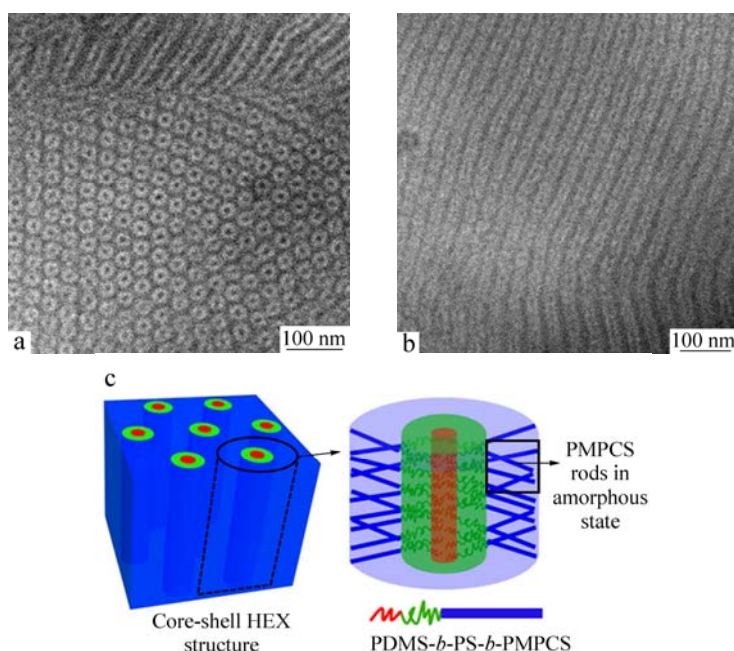


Fig. 5 TEM micrographs of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer after thermal annealing at 120 °C (a and b) and the model of the core-shell HEX structure with PMPCS rods in the amorphous state in the matrix (c)

Nanophase-separated Complex Nanostructures of PDMS-*b*-PS-*b*-PMPCS after Annealing above $T_{LC,PMPCS}$

After the triBCP sample is annealed at 140 °C, the 1D WAXS profile exhibits a reflection peak at $q = 4.03 \text{ nm}^{-1}$ (the middle curve in Fig. 4a), which indicates that the PMPCS blocks enter into the LC phase. The diffraction peaks in the SAXS profile (the middle curve in Fig. 4b) of the corresponding sample have a scattering vector ratio of 1:2:3:4:5:6 which is the typical ratio of the LAM structure, and the primary reflection is at $q^* = 0.131 \text{ nm}^{-1}$ corresponding to a d -spacing of 48.0 nm. Comparison of the SAXS results of the triBCP after annealing at 140 °C and at 120 °C shows a clear change of the scattering vector ratio and a significant change of q^* , indicating that an order-order transition occurs. When the triBCP is annealed at 180 °C, the reflection peak in the 1D WAXS profile (the top curve in Fig. 4a) becomes more intense, indicating that more PMPCS is in the LC

phase, and the scattering vector ratio and the q^* value in the SAXS profile remain the same as those of the SAXS profile of the sample after annealing at 140 °C. And the reflection peaks in the SAXS profile of the sample after annealing at 180 °C (the top curve in Fig. 4b) become sharper, indicating that the nanophase-separated structure is also more ordered.

In order to determine the lamellar thicknesses of different blocks in the LAM structure from the SAXS results, the relative electron density profile across the LAM structure can be plotted using the following equation^[23, 31, 32]:

$$\rho_e(z) \sim \sum_{k=1}^n \sqrt{I(q_k)q_k^2} \phi_k \cos(q_k z)$$

Here n is the total number of diffractions observed, q_k and $I(q_k)$ are the scattering vector and the scattering intensity of the k th diffraction at the peak position, respectively, and ϕ_k is the phase factor of the k th diffraction and is either +1 or -1. For a centrosymmetrical lamellar system, ϕ_k is reasonable to be -1, -1, +1, and +1 when k is 1, 2, 3, and 4, respectively. The SAXS data of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer after annealing at 180 °C are plotted into the Lorentz-corrected SAXS (Iq^2 versus q) profile, as shown in Fig. 6(a). The q_k and $I(q_k)q_k^2$ can be directly obtained from the Iq^2 versus q profile. The relative electron density profile of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer is obtained using the first four reflections of the Iq^2 versus q profile with phase factors of -1, -1, +1, and +1 as shown in Fig. 6(b), in which the region with $\rho_e(z) < 0$ from $z = -13.8$ nm to +13.8 nm represents the PMPCS domain, the transition zones from $z = -13.8$ (+13.8) nm to -21.0 (+21.0) nm represent the PS domains, and the regions from $z = -21.0$ (+21.0) nm to -23.5 (+23.5) nm represent the PDMS domains^[32]. From the above result, the thicknesses of the PMPCS (L_{PMPCS}), PS (L_{PS}), and PDMS (L_{PDMS}) lamellae are 27.6, 7.2, and 5.0 nm, respectively, and the periodic size (L_0) is 27.6 nm + 2 × 7.2 nm + 5.0 nm = 47.0 nm, as indicated in Fig. 6(b). L_0 is a little smaller than the d -spacing due to the small increase of the q^* value in the Iq^2 versus q profile ($q^* = 0.134 \text{ nm}^{-1}$) compared with that in the $\lg I$ versus q profile ($q^* = 0.131 \text{ nm}^{-1}$).

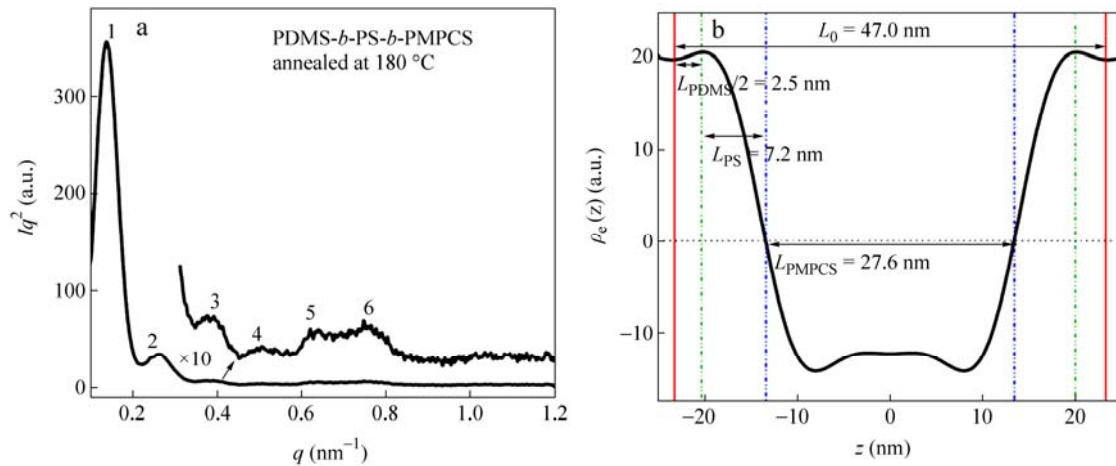


Fig. 6 Lorentz-corrected SAXS (Iq^2 versus q) profile (a) and the relative electron density profile (b) of the PDMS-*b*-PS-*b*-PMPCS triblock copolymer at 180 °C

Moreover, the TEM results of the triBCP sample after annealing at 180 °C are shown in Figs. 7(a) and 7(b), which confirm the morphologies of a LAM-3P4L structure. In the TEM micrographs, the distance between the two neighboring PDMS lamellae is 47 nm, which is consistent with the d -spacing value from the SAXS result. The thickness of the PMPCS lamella in the TEM micrographs is about 27 nm, which is also consistent with both the value calculated from the f_{PMPCS} and the d -spacing in the SAXS result ($f_{\text{PMPCS}}L_0 = 28 \text{ nm}$) and the L_{PMPCS} value (27 nm) obtained from the relative electron density profile of PDMS-*b*-PS-*b*-PMPCS within the range of

errors. Thus, the TEM results and the SAXS results including those from the relative electron density profile are consistent. Moreover, for the PMPCS rod in the LC phase, the length of the rod can be estimated to be 26 nm from the DP of PMPCS (about $0.24N \text{ nm}^{[28]}$, where N is the DP of PMPCS) which is almost equal to the thickness of the PMPCS lamella. Therefore, the PMPCS rods in the PMPCS domain are arranged in an interdigitated manner to form a columnar LC phase. The models of the LAM-3P4L structure, the molecular arrangement in the lamellar structure, and the LC phase of PMPCS are schematically illustrated in Fig. 7(c).

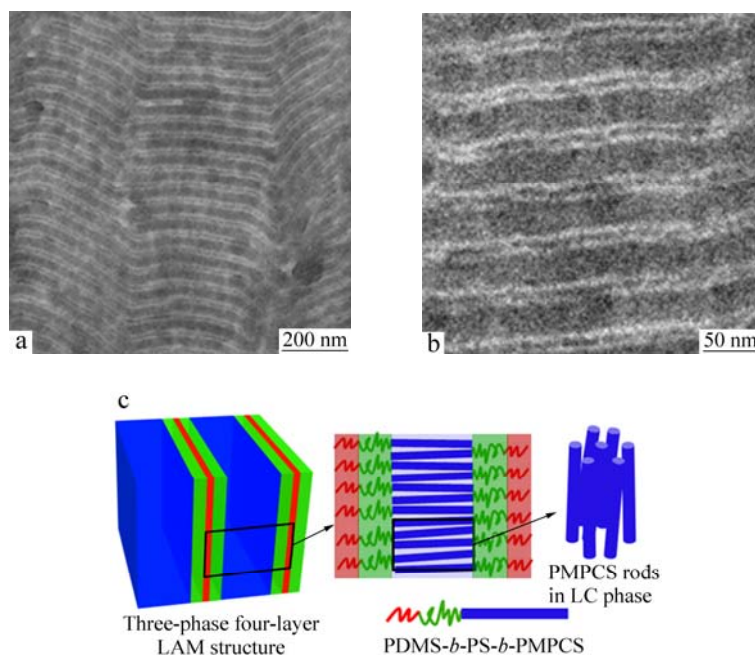


Fig. 7 TEM micrographs of PDMS-*b*-PS-*b*-PMPCS after thermal annealing at 180 °C (a and b) and the model of the LAM-3P4L structure with the interdigitated packing of the LC PMPCS rods in the PMPCS lamella (c)

Discussion on Nanophase-separated Complex Nanostructures and Order-Order Transition of PDMS-*b*-PS-*b*-PMPCS

From the literature^[22], both the CSH and LAM-3P4L structures should be the stable nanostructures for common coil-coil-rod ABC triblock copolymers. However, as revealed by a previous study^[28], the stable state of the PMPCS block at 120 °C is the LC phase formed at temperatures higher than its glass transition temperature because this mesophase will be retained when the polymer is cooled to ambient temperature or annealed again at temperatures below the LC phase formation temperature. Therefore, the CSH structure formed after annealing at 120 °C is not a stable structure, while the LAM-3P4L structure of the triBCP formed after the PMPCS enters into the LC phase is the stable structure. Thus, such an order-order transition is actually between a kinetically trapped structure and a stable one.

From the Hildebrand solubility parameters of PDMS (δ_{PDMS}), PS (δ_{PS}), and PMPCS (δ_{PMPCS}) which are 14.9, 18.9, and 21.8 $\text{J}^{1/2}\text{cm}^{-3/2}$, respectively, the Flory-Huggins interaction parameters among these three blocks have the relationship $\chi_{\text{PDMS-PMPCS}} > \chi_{\text{PDMS-PS}} > \chi_{\text{PS-PMPCS}}$ ^[27, 33]. Thus, the repulsion interactions of the PS block with PDMS and PMPCS blocks are smaller than the interaction between PDMS and PMPCS blocks. Therefore, the domains of the middle PS block of the PDMS-*b*-PS-*b*-PMPCS triBCP in both CSH and LAM-3P4L structures connect the PDMS domains and PMPCS domains to minimize the interfacial energies. The order-order transition of the ABC triBCP induced by the mesophase transition of the PMPCS block may be attributed to two aspects. On one hand, the additional LC interaction of PMPCS increases the effective interaction between the PMPCS block and the PS/PDMS blocks. On the other hand, the LAM structure is more favorable for the triblock copolymer with the major component PMPCS ($f_{\text{PMPCS}} = 62\%$) in the LC phase. Due to the irreversible

transition of the PMPCS block from the amorphous state to the LC phase, the order-order transition of the triBCP is not reversible. In order to obtain reversible order-order transitions of similar ABC triblock copolymers, an LC polymer such as poly{2,5-bis[(4-butoxyphenyl)oxycarbonyl]styrene} (PBPCS) with reversible mesophase transitions will be used in our future research. Furthermore, other complex nanostructures and their phase transitions of these ABC triBCPs are currently under investigation.

CONCLUSIONS

In summary, we have synthesized a well-defined PDMS-*b*-PS-*b*-PMPCS liquid crystalline ABC triblock copolymer. The DPs of the PDMS, PS, and PMPCS blocks are 58, 167, and 110, and f_{PDMS} , f_{PS} , and f_{PMPCS} are 0.09, 0.29, and 0.62, respectively. The PDMS-*b*-PS diblock copolymer precursor self-assembles into a HEX structure with a relatively small d -spacing (19.0 nm). The PDMS-*b*-PS-*b*-PMPCS triBCP forms a core-shell HEX structure with a d -spacing of 29.4 nm after annealing at 120 °C at which the PMPCS block is still in the amorphous state. After annealing above 140 °C, the PMPCS block transforms to the LC phase, and the nanophase-separated structure of the triblock copolymer changes to a three-phase four-layer LAM structure with a d -spacing of 48.0 nm. Therefore, the addition of the PMPCS rod to the PDMS-*b*-PS diblock copolymer forming a coil-coil-rod ABC triBCP results in the formation of complex nanostructures with larger periodic sizes, and the amorphous-to-LC phase transition of the PMPCS rod block induces an order-order transition in the triBCP from the CSH structure to a LAM-3P4L structure.

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