

Supporting information

Order-Order Transition Induced by Mesophase Formation in a Novel Type of Diblock Copolymers Based on Poly(isobutyl methacrylate) and Poly[2,5-di(isopropoxycarbonyl)styrene]

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Experimental Section

Materials.

Acetone (A. R.; Beijing Chemical Reagents Co.) was purified by refluxing with KMnO_4 and distilled, dried with anhydrous K_2CO_3 and distilled out just before use. Chlorobenzene (A. R.; Beijing Chemical Reagents Co.) was purified by washing with concentrated sulfuric acid to remove thiophene, followed by washing with water, and then dried and distilled before use. Tetrahydrofuran (THF; A. R.; Beijing Chemical Reagents Co.) was refluxed over sodium under an argon atmosphere and distilled out before use. N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich) was used as received. Cuprous bromide (CuBr; 98%; Aldrich) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol and ether and then dried under vacuum. Isobutyl methacrylate (iBMA; 98%; Fushun Anxin Chemistry Co.) was washed by 5 wt% sodium hydroxide (NaOH) aqueous solution and by deionized water in sequence for three times. After drying over CaH_2 , it was used before distilled twice under vacuum. The synthesis of benzyl 2-bromoisobutyrate (BBiB) was carried out according to the reported method.¹ The monomer 2,5-di(isopropoxycarbonyl)styrene (iPCS) was synthesized following the procedure reported previously.² Other reagents and solvents were purchased from Beijing Chemical Reagents Co. and used as received unless otherwise specified.

Synthesis of the macroinitiator.

The macroinitiator (PiBMAM-Br) was synthesized by ATRP at 40 °C in acetone, and the monomer conversion was controlled below 40% to assure the reactivity of the macroinitiator. PiBMA313-Br as an example: iBMA (7.20 g, 0.05 mol), BBiB (15.5 mg, 0.06 mmol), PMDETA (10.2 mg, 0.06 mmol), CuBr (8.6 mg, 0.06 mmol), and acetone (11.0 g) were introduced into a glass reaction tube equipped with a stirring bar. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum and put into a thermostatic water bath at 40 °C for 6 h. The tube was broken and the reaction mixture diluted with 30 mL of THF was let to pass through a short Al_2O_3 column. The crude product was obtained by adding the filtrate into 600 mL of methanol/water (v/v = 20/1) under rapid stirring and collection of precipitate by filtration.

The operations of dissolution in THF and precipitation in methanol/water (v/v = 20/1) were repeated three times to remove the unreacted monomer. After drying at 40 °C under vacuum, 2.7 g of PiBMA313-Br was obtained. The monomer conversion in weight was 37%. $M_{n,\text{GPC}} = 42,000$, $M_w/M_n = 1.11$.

Synthesis of the block copolymer.

The block copolymers (PiBMAM-PiPCSn) with different molecular weights (MWs) were prepared at 90 °C in chlorobenzene. The initiating system was PiBMAM-Br/CuBr/PMDETA (1:1.5:1.5, molar ratio). The polymerization was allowed to continue for 12 h. The molecular weight was adjusted by changing the molar ratio of monomer to initiator. In a typical run, iPCS (0.55 g, 2.0 mmol), PiBMA313-Br (0.38 g, 0.009 mmol), CuBr (1.9 mg, 0.013 mmol), PMDETA (2.2 mg, 0.013 mmol) and chlorobenzene (1.0 g) were introduced into a glass reaction tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum and put into a thermostatic oil bath at 90 °C for 12 h. The tube was broken and the reaction mixture diluted with 15 mL of THF. After removing the catalysts by passing through a short Al_2O_3 column, the crude product was obtained by adding the filtrate into 300 mL of methanol under rapid stirring and collection of precipitate by filtration. The operations of dissolution in THF and precipitation in methanol were repeated three times to remove the unreacted monomer. To ensure removal of any possible residual PiBMA313-Br, the block copolymers were then extracted with *n*-hexane for 24 h. After drying at 60 °C under vacuum, 0.6 g of PiBMA313-PiPCS168 was obtained. $M_{n,\text{GPC}} = 104,500$, $M_w/M_n = 1.11$.

Instruments and Measurements.

¹H NMR spectra were obtained with a Bruker ARX 400 MHz NMR spectrometer with acetone-*d*₆ as the solvent and tetramethylsilane (TMS) as the internal reference.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI, M_w/M_n) of the resultant macroinitiators and diblock copolymers were estimated on a gel permeation chromatography (GPC) instrument equipped with a Waters 515 HPLC pump and a Waters 2410 refractive-index detector.

Three Waters Styragel columns with 10 μm bead size were connected in series. Their effective molecular weight (MW) ranges were 100-10,000 for Styragel HT2, 500-30,000 for

Styragel HT3, and 5,000-600,000 for Styragel HT4, respectively. The pore sizes were 50, 100, and 1000 nm for Styragels HT2, HT3, and HT4, respectively. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ at 35 °C. The calibration curve was made with polystyrene standards. The densities of PiPCS and PiBMA measured by a floatation technique were 1.069 g cm⁻³ and 1.039 g cm⁻³ at room temperature, respectively.

Differential scanning calorimetry (DSC) thermograms were recorded on a TA DSC Q100 calorimeter in a temperature range of -20 to 150 °C at a heating rate of 20 °C min⁻¹ under continuous nitrogen flow. To observe glass transition easily, all the samples were cooled at a cooling rate of 2 °C min⁻¹ from 150 to -20 °C first.

Thermogravimetric analyses (TGA) were performed on a TA SDT Q600 instrument with a heating rate of 20 °C min⁻¹ up to 600 °C under nitrogen atmosphere.

Mesophase textures were examined on a Leica DML polarized optical microscope (POM) with a Linkam TH-600PM Hot Stage. The sample films were prepared by solution-casting, and the thicknesses were kept at several microns.

One-dimensional wide-angle X-ray diffraction (1D WAXD) powder experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K α) and an X'celerator detector. The sample stage was set horizontally. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). Background scattering was recorded and subtracted from the sample patterns. A temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 10 °C min⁻¹.

Small- and wide-angle X-ray scattering (SAXS and WAXS) experiments were performed with a highflux SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system. The scattering patterns were simultaneously recorded on an imaging plate (IP) with a pixel size of 42.3 $\times$ 42.3 μm^2 which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm⁻¹, $q = 4\pi \sin\theta/\lambda$, where λ is the wavelength of 0.1542 nm and 2θ is the scattering angle). The scattering peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$), respectively. The power of the generator used for the measurement was 40 kV by 40 mA. The distance from the sample to detector was 264.5 mm and the exposure time was 900 s. The processing of original experimental data such as data acquisition, background subtraction, and data reduction, and so on was handled by Anton Paar SAXSquant 1.01 software and the PCG software package. The line smearing effect due to the line-focus X-ray source should be eliminated from the experimental curve (desmearing) and this was performed by using a desmearing program according to Lake's method. A temperature control unit (Anton Paar TCS300) in conjunction with the SAXSess was utilized to study the structure evolution as a function of temperature.

The microphase separation of samples was observed by transmission electron microscope (TEM). Samples were

treated at different testing temperatures for 6h, and then embedded into epoxy, followed by microtoming with an ultramicrotome. The ultrathin sections were stained by RuO₄ vapor at room temperature for 30 min and PiPCS microdomains were preferentially stained to enhance the contrast between the different components. TEM studies were performed on a Hitachi H-800 electron microscope.

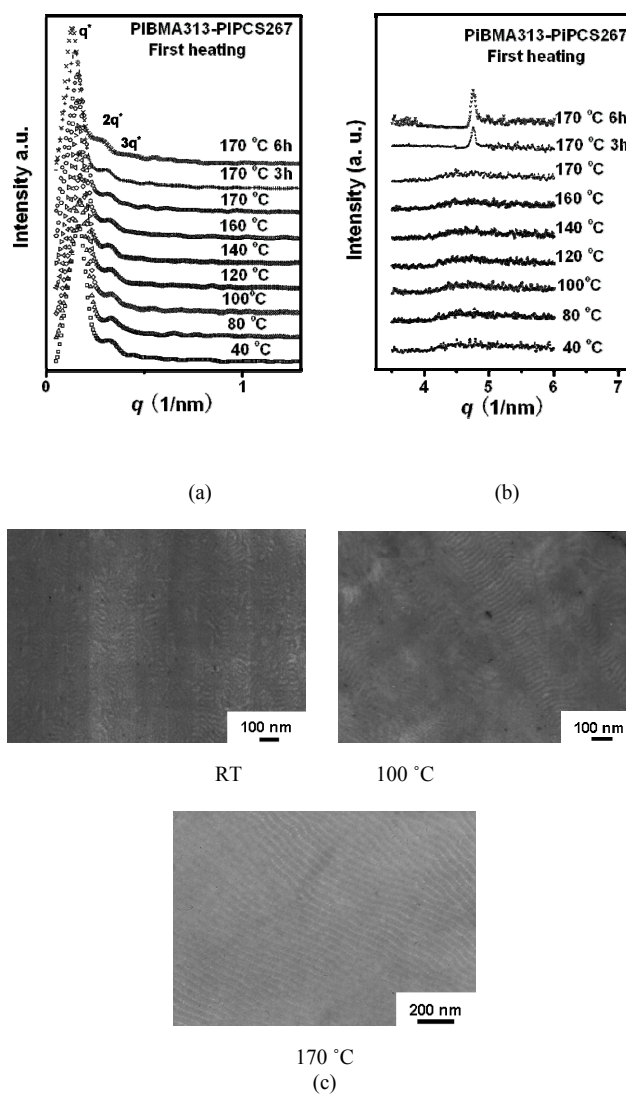


Fig. SI-1 Sets of small-angle X-ray scattering profiles of an unoriented PiBMA313-PiPCS267 sample recorded by using SAXSess at various temperatures during the first heating process in the low- q (a) region and high- q region (b); and transmission electron microscopic images of samples treated at three different temperatures (c).

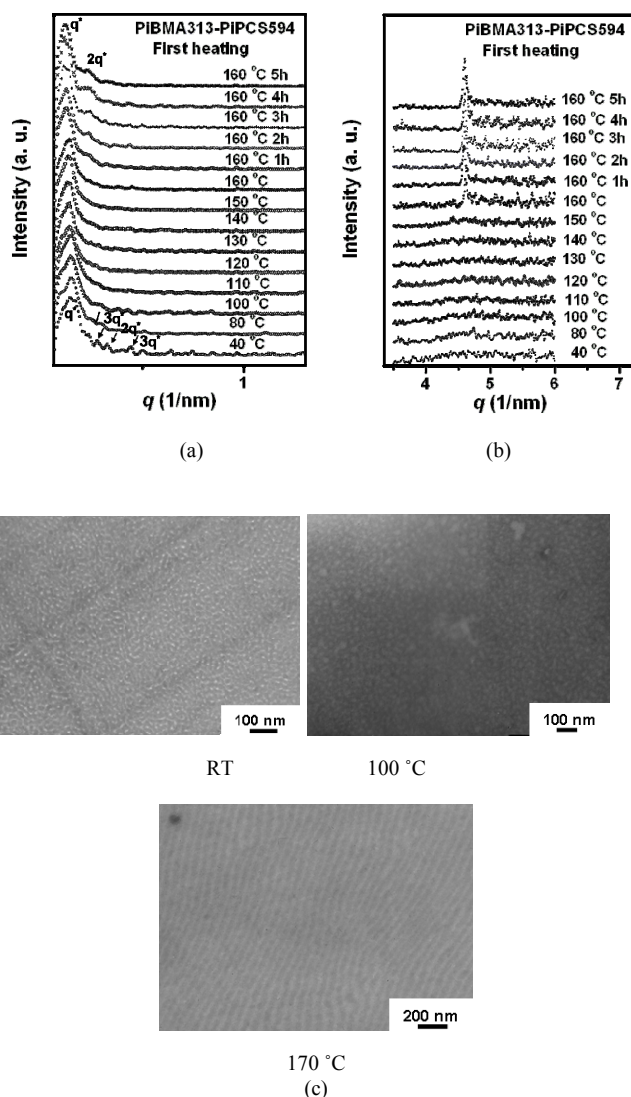


Fig. SI-2 Sets of small-angle X-ray scattering profiles of an unoriented PiBMA313-PiPCS594 sample recorded by using SAXSess at various temperatures during the first heating processes in the low- q region (a) and high- q region (b); and transmission electron microscopic images of samples treated at three different temperatures (c).

1. N. J. Hovestad, G. van Koten, S. A. F. Bon and D. M. Haddleton, *Macromolecules*, 2000, **33**, 4048-4052.
2. X. Y. Yin, E. Q. Chen, X. H. Wan and Q. F. Zhou, *Chin. J. Polym. Sci.*, 2003, **21**, 9-14.