

Competition between liquid crystallinity and block copolymer self assembly in core shell rod-coil block copolymers

Kishore K. Tenneti,^a Xiaofang Chen,^{a,b} Christopher Y. Li,^{*a} Xinhua Wan,^b Xinghe Fan,^b Qi-Feng Zhou,^{*b} Lixia Rong,^c and Benjamin S. Hsiao^c

Supporting information

Experimental Section

Materials. Styrene was purchased from Beijing Chemical Company and was distilled over calcium hydride. Chlorobenzene was purified by washing with concentrated sulfuric acid to remove thiophene, followed by washing with water, and then dried and distilled. *N, N, N', N'*-Pentamethyldiethylenetriamine (PMDETA) (>98%, TCI) and 1-bromoethylbenzene (BEB) (97%, Acros) were used as received without further purification. Cuprous bromide (CuBr) was purified by stirring in glacial acetic acid, filtering and washing with ethanol, and was then dried under vacuum.

Synthesis of diblock copolymer. Monomer TBOS was synthesized according to the literature.¹ The chemical structure and synthesis of the PS-*b*-PTBOS are shown in Scheme S1. All block copolymers were synthesized by sequential atom transfer radical polymerization.

Synthesis of PSt-Br macroinitiators. Macroinitiator PSt-Br was synthesized as follows. Typically, styrene (8.012 g, 0.077 mol), BEB (0.071 g, 0.38 mmol), and PMDETA (0.066 g, 0.38 mmol) were added sequentially into a 50 mL reaction tube containing a magnetic stir bar. The reaction mixture was purged with nitrogen and subjected to two freeze-thaw cycles to remove any dissolved oxygen. Then, CuBr (0.055 g, 0.38 mmol) was added. After another two freeze-thaw cycles, the tube was sealed under vacuum. Polymerization was carried out at 90 °C for 4-5 h. After the polymerization was terminated by putting the tube into ice/water mixture, the tube was broken. The polymerization mixture was then diluted with 20 mL THF and passed through a basic Al₂O₃ column to remove copper complex. The collected polymer solution was precipitated into methanol. The precipitate was dried under vacuum. The molecular weight and polydispersity of macroinitiators were measured by Gel Permeation Chromatography (GPC) with Polystyrene standard.

Synthesis of PS-*b*-PTBOS. Block copolymers were synthesized as follows. Typically, TBOS (0.55 g, 0.54 mmol), PSt-Br (0.57 g, 0.027 mmol), PMDETA (0.0047 g, 0.027 mmol) and 1.3 g of chlorobenzene were added sequentially into a 10 mL reaction tube containing a magnetic stir bar. The reaction mixture was purged with nitrogen and subjected to two freeze-thaw cycles to remove any dissolved oxygen. Then, CuBr (0.0039 g, 0.027 mmol) was added. After another two freeze-thaw cycles, the tube was sealed under vacuum. The tube was put into an oil bath preset at 110 °C for ~10 h. After the polymerization was terminated by putting the tube into ice/water mixture, the tube was broken. The polymerization mixture was then diluted with 5 mL of THF and passed through a basic Al₂O₃ column to remove copper complex. After removing the solvent, the product was purified using column chromatography with dichloromethane as the eluent to remove unreacted monomers. Then it was concentrated and precipitated into a large amount of methanol. The crude product was collected, the BCPs were extracted with cyclohexane for 24 h to remove possible unreacted PS. The absence of the monomer from the polymer product was confirmed by the disappearance of the peaks associated with the vinyl protons at 5.35, 5.81 and 6.70 ppm in the ¹H nuclear magnetic resonance (NMR) spectra of the monomer. The absence of unreacted polystyrene was confirmed by GPC.

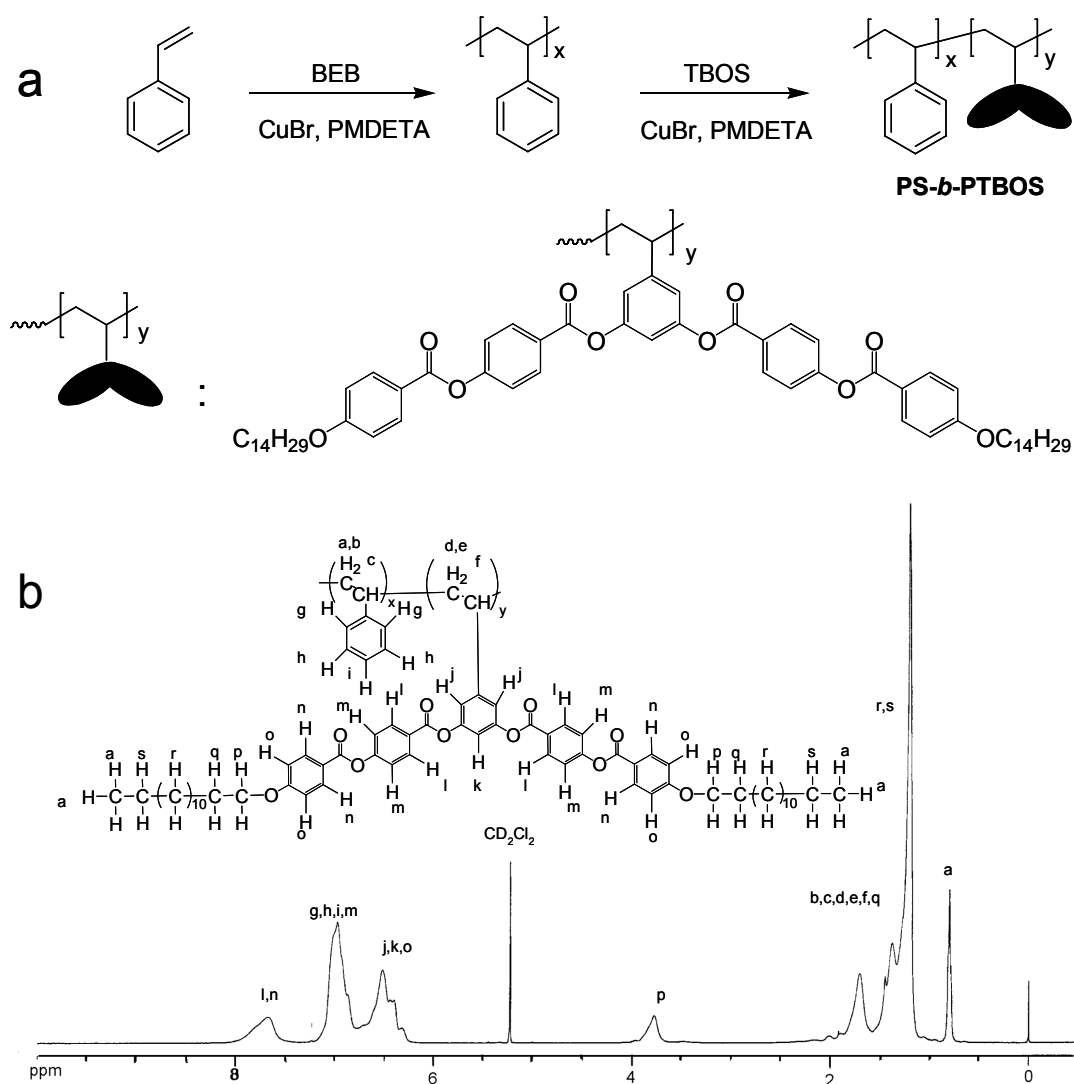
The number-average molecular weight (*M_n*) and the polydispersity (*M_w/M_n*) were estimated from GPC (Waters 150C) profiles and were calibrated with standard PS. The copolymer composition was determined by NMR spectroscopy (¹H NMR, 400 MHz) with dichloromethane-*d*² as solvent. The block length was estimated from the intensity ratio of the alkoxy groups ($\delta = 3.3$ -3.8) and the aromatic groups ($\delta = 6.3$ -7.2). One NMR spectrum for PS-*b*-PTBOS is shown in Scheme S1. Sample information such as molecular weights, polydispersity, and volume fraction are listed in Table S1.

Blends preparation. PS homopolymer was blended with PS₅₆₇-*b*-PTBOS₂₄. Monodispersed PS with *M_n* = 5,000 g/mol was dissolved in chloroform with PS₅₆₇-*b*-PTBOS₂₄ and co-solution cast to obtain polymer blends. Two blend samples were prepared and the PTBOS volume fractions were controlled to be 20% and 14%, respectively (PS₅₆₇-*b*-PTBOS₂₄-20 and PS₅₆₇-*b*-PTBOS₂₄-14). Low *M_w* PS is anticipated to mix in the PS domains and reduce the splaying stress field of the coils. No evidence of macrophase separation of low *M_w* PS was observed either in the differential scanning calorimetry experiments or in the TEM experiments.

Equipment and experiments. Sheared samples were obtained by solution-casting thick polymer films (thickness ~ 0.5-1 mm) from 5% (w/w) chloroform solutions. The solvent was allowed to evaporate at room temperature for 2 days. Residual solvent was removed under vacuum at 80 °C, and the sample was then annealed at 260 °C for 3 days to allow microphase separation. To achieve uniform shear alignment of the microdomains, the microphase-separated samples were then subject to a large-amplitude reciprocating shear at ~260 °C for 40-60 min. The shear frequency was ~0.5 Hz, and the shear amplitude was 150%. The resulting polymer film was then taken out of the shearing apparatus and quenched to room temperature. The samples were then annealed at ~260 °C for 1 day to release residue shear stress. The final film thickness was ~0.2-0.3 mm.

Differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and polarized light microscopy (PLM) were employed to characterize structure and morphology of the block copolymer. The thermal transitions were detected using a Perkin-Elmer DSC-7. The temperature and heat flow were calibrated using standard materials at different cooling and heating rates between 5 and 40 °C/min. Samples with a typical mass of 3 mg were encapsulated in sealed aluminum pans. A controlled cooling experiment was always carried out first, and a subsequent heating was performed at a rate that was equal to or faster than the previous cooling. Figure S1 shows the DSC thermograms and PLM results obtained on the samples. Two-dimensional (2-D) SAXS experiments were carried out at the synchrotron X-ray beam line X-27C at the National Synchrotron Light Source in Brookhaven National Laboratory. The zero pixel of the 2-D SAXS pattern was calibrated using silver behenate, with the first-order scattering vector *q* being 1.076 nm⁻¹. The air scattering for WAXD was subtracted. The X-ray beam spot was ~0.1 mm in diameter. The X-ray beam was along all the three directions of the sheared sample. 2-D WAXD patterns were also recorded at room temperature in the same set up with the sample to detector distance of ~ 15-19 cm.

TEM experiments were conducted on JEOL 2000FX TEM with an accelerating voltage of 120 kV. A Reichert Ultracut cryo-ultramicrotome was used to microtome the sheared BCP sample. Thin sections of the BCP (~50 nm thick) were obtained at room temperature and collected on TEM grids, followed by staining in RuO₄ vapor for approximately 40 mins.



Scheme S1. a) Synthetic route for PS-*b*-PTBOS BCPs b) ¹H NMR of PS-*b*-PTBOS with CD₂Cl₂ as solvent.

Table S1. Molecular analysis and X-ray data of PS-*b*-PTBOS BCPs.

Sample	Mn ^a (PS)	Mn ^b (PTBOS)	Total Mn	PDI ^c	f_{PTBOS} ^d	d ^e (nm)
		Symmetric				
PS ₂₀₂ - <i>b</i> -PTBOS ₃₅	21000	35300	56300	1.17	0.58	27.6
		Asymmetric				
PS-rich						
PS ₅₆₇ - <i>b</i> -PTBOS ₂₄	59000	24300	83300	1.3	0.25	52.7
PTBOS-rich						
PS ₁₆₀ - <i>b</i> -PTBOS ₁₂₆	16600	126800	143400	1.39	0.86	37.9

^a Mn, number average molecular weight, of PS was measured by GPC, and ^c polydispersity were measured using tetrahydrofuran as an eluent at 35 °C, polystyrene as the standard. ^b PTBOS molecular weight and ^d volume fraction were estimated using NMR. ^e d-spacing was measured using small-angle X-ray scattering.

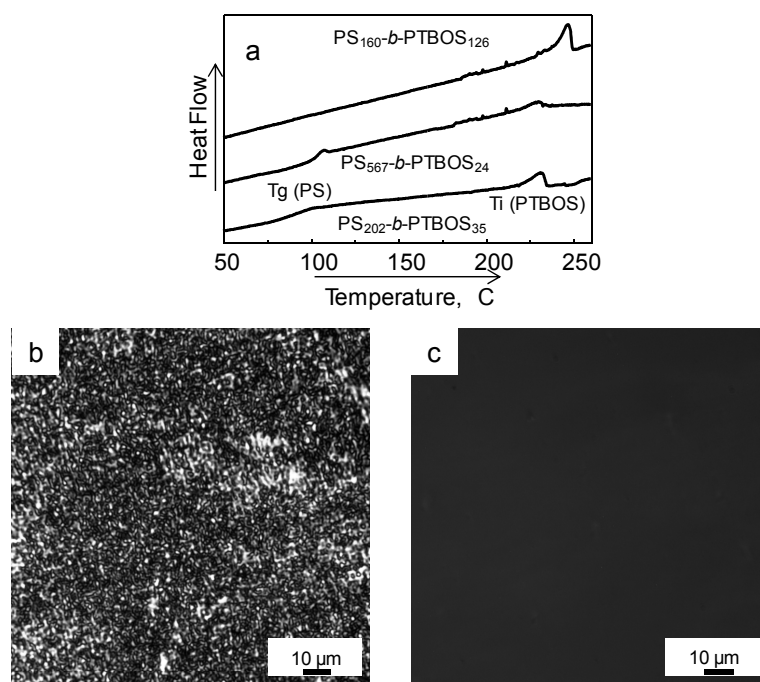


Figure S1. a) DSC thermograms of symmetric and asymmetric PS-*b*-PTBOS BCPs. b) Representative polarized light micrograph of PS₂₀₂-*b*-PTBOS₃₅ LC texture at 150°C (b) and isotropic phase at 240°C (c).

References

1. X. Chen, K. K. Tenneti, C. Y. Li, Y. Bai, R. Zhou, X. H. Wan, X. Fan, Q. F. Zhou, *Macromolecules*, 2006, **39**, 517-527.