

## [Supporting Information]

### Polymerization-Induced Nanostructural Transitions Driven by *in situ* Polymer Grafting

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#### Materials and molecular characterization

Monomers for living anionic polymerization, styrene and 1,3-butadiene, were purified twice over di-n-butylmagnesium and n-butyllithium, respectively, before initiation. Solvents used for living anionic polymerization, cyclohexane (CHX) and tetrahydrofuran (THF), were purified using solvent columns (JC Myer). Methanol (Fisher Scientific), benzene (Fisher Scientific), 4-hydroxy-2,2,6,6-tetramethylpiperidine (OH-TEMPO, Sigma-Aldrich, 97%), butylated hydroxytoluene (BHT), benzoyl peroxide (BPO, Sigma-Aldrich, 98%), and 2,2'-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, 98%) were used as received without further purification unless stated otherwise. All polymers synthesized were characterized using Tosoh EcoSEC (Tosoh Co.) equipped with a Wyatt Dawn Heleos-II eight angle light scattering detector (Wyatt Technology Corp.) with 2.5 mg/mL samples in tetrahydrofuran at 40 °C.

#### Polymer synthesis

##### *Living Anionic Polymerization*

Poly(styrene)-*block*-poly(butadiene) (PS-PBD) diblock copolymer was synthesized using sequential living anionic polymerization. Monomer purification and reactor setup have been previously reported.<sup>1</sup> In the work described here, we were targeting a 1,2PBD microstructure of ~90%, which was accomplished by adding a THF/sec-butyllithium molar ratio of 100, similar to previously published procedures.<sup>2</sup> Styrene was first polymerized in column purified cyclohexane at 40 °C for 4 h, and an aliquot was taken to determine the  $M_n$  and  $D$  of the first PS block (Figure S1). After the initial 4 h, the reaction mixture was cooled to ~5 °C using an ice bath, THF was added to obtain the ~90% 1,2 microstructure, and then purified 1,3-butadiene was added. The reaction was run for an additional 4 h, and terminated using degassed methanol. The number average molecular weight ( $M_n$ ), volume fraction of PS ( $f_{PS}$ ), dispersity ( $D$ ), and 1,4 vs 1,2 PBD microstructural content for the PS-PBD were 27.5 kg/mol, 0.58, 1.03, and 0.94 1,2 PBD, respectively. The volume fraction of the diblock copolymer was calculated from the molecular weights determined using the multi-angle light scattering detector of the SEC and room temperature density values of 1.04 g/mL and 0.86 g/mL for PS and PBD, respectively (density values used from Sigma-Aldrich). The microstructural content was determined using a Bruker AVIII-HD 500 MHz <sup>1</sup>H NMR (Bruker Corp.) (Figure S2).

Poly(1,2-butadiene) homopolymer (1,2PBD,  $M_n$  = 20.33 kg/mol,  $D$  = 1.04, fraction of 1,2 = 0.90) was also synthesized using living anionic polymerization. A solution of THF and CHX was cooled to ~5 °C using an ice bath before the addition of sec-butyllithium, and then purified 1,3-butadiene. Polymerization was terminated after 4 h via addition of degassed methanol to the reaction mixture. The microstructural content was characterized using 400 MHz <sup>1</sup>H NMR (Figure S3).

Poly(styrene) homopolymer ( $M_n$  = 6.1 kg/mol and  $D$  = 1.03) was synthesized via anionic polymerization of styrene at 40 °C in CHX.

##### *Microwave Nitroxide-Mediated Radical Polymerization*

Poly(styrene) homopolymer (PS,  $M_n = 14.1$  kg/mol,  $\bar{D} = 1.34$ ) was synthesized in bulk using microwave nitroxide-mediated radical polymerization (NMP) with an initiator system consisting of BPO and OH-TEMPO.<sup>3</sup> A typical polymerization procedure consists of combining 14.2 mg of BPO (.0587 mmol) and 6.7 mg of OH-TEMPO (0.0389 mmol) with 1 mL of Styrene in a 10 mL microwave vial. The contents of the vial were agitated until a homogenous mixture was obtained, and the resulting solution was polymerized via microwave radiation for 3 hours using a Discover LabMate with IntelliVent pressure and infrared temperature control system (CEM Co.) in dynamic power mode at 100 W, 125 °C, with a 20 °C/min temperature ramp. The resulting reaction reached approximately 70% conversion for all samples. AIBN poly(styrene) was synthesized using the same molar values as described above with a resulting  $M_n = 8.62$  kg/mol and  $\bar{D} = 1.54$ .

## **Blend Preparation**

### *Polymer/ Styrene Blends*

PS-PBD/styrene, 1,2PBD/styrene, and PS/styrene blends were prepared by dissolving the polymer of interest in a styrene solution containing the same molar ratios of BPO to OH-TEMPO to styrene outlined in the previous polymer synthesis section. A typical blending procedure for a 60% volume PS-PBD and 40% volume styrene solution consisted of combining 0.522 g of PS-PBD with 0.4 mL of styrene/BPO/TEMPO solution. Blends were then heated to 65 °C for approximately 15 min and agitated to promote homogeneous mixing. Reaction conditions for PS-PBD/styrene, 1,2PBD/styrene, and PS/styrene blends were identical to the conditions used for microwave PS homopolymer synthesis.

### *Diblock Copolymer/ Homopolymer Blends*

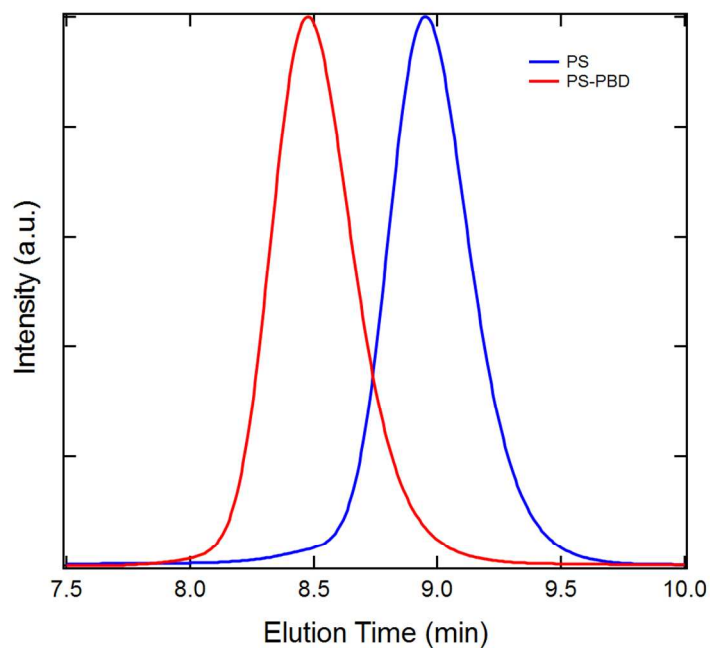
PS-PBD/PS blends, where the volume fraction of PBD-PS was 60%, were prepared by dissolving 1.073 g of PS-PBD, 0.774 g of PS, and 11.8 mg of BHT in 5 mL of benzene at 70 °C. The resulting solution was then frozen in liquid nitrogen and the benzene was sublimed under dynamic vacuum overnight. Once dried, samples were pressed at 150 °C for 30 minutes under vacuum into 1 mm thick films and then annealed overnight at 110 °C under vacuum.

## **Small-angle X-ray scattering (SAXS)**

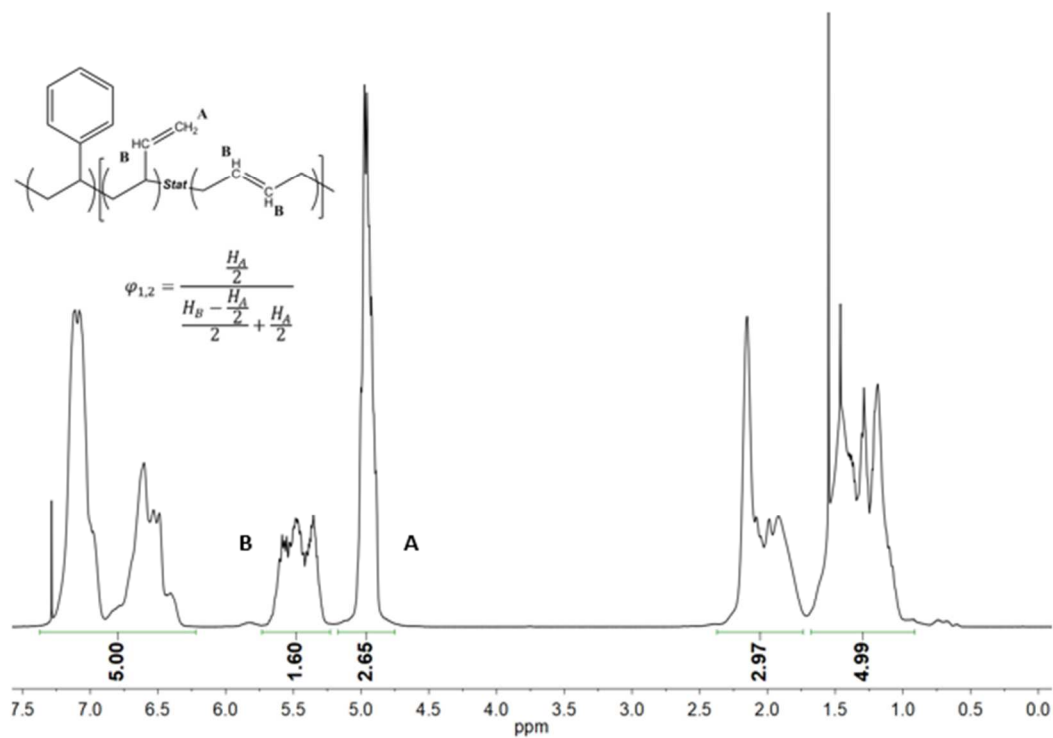
SAXS measurements were performed using a Cu  $K_\alpha$  sourced Xeuss 2.0 beamline (Xenocs) installed with a Pilatus3R 200K-A detector (Dectris). The incident x-ray beam had a wavelength of 1.54 Å and an energy of 8.04 keV. Calibration of the scattering wavevector,  $q$ , was calibrated with powder silver behenate. Samples swollen with residual styrene were prepared in quartz capillaries (1.5 mm thickness, Charles Supper Co.). Dried samples were ran in bulk with approximate thicknesses of 1.5 mm. All measurements were taken under vacuum.

## **Transmission Electron Microscopy (TEM)**

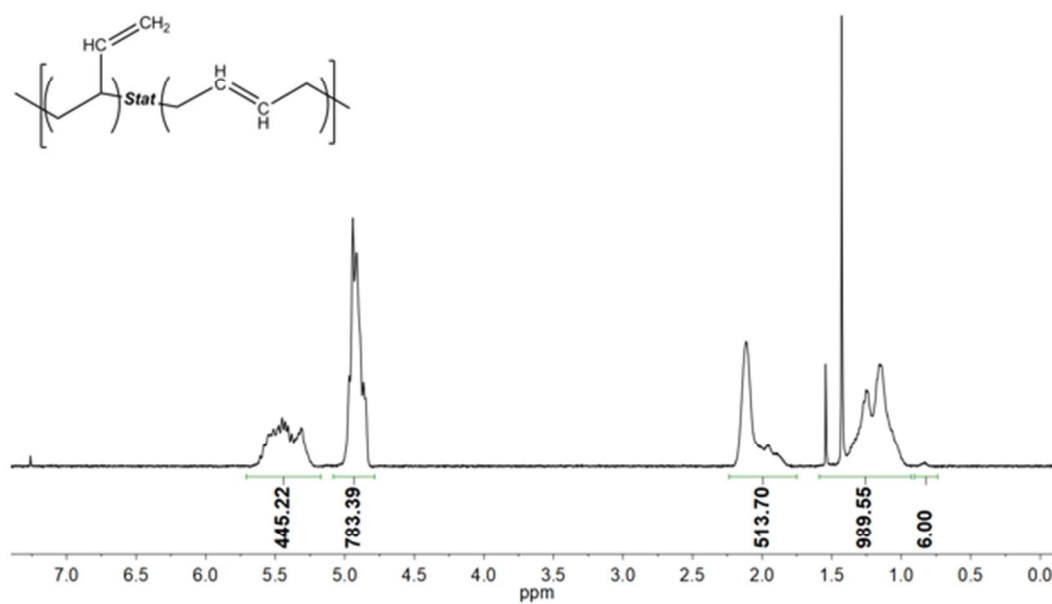
Dried blend samples were cryosectioned into 70 – 90 nm sections using a Leica UC6 ultramicrotome with a FC6 cryo-attachment at –120 °C. Sections were then stained with OsO<sub>4</sub> for 15 min. Samples were imaged under an FEI Tecnai G2 Spirit BioTwin TEM.



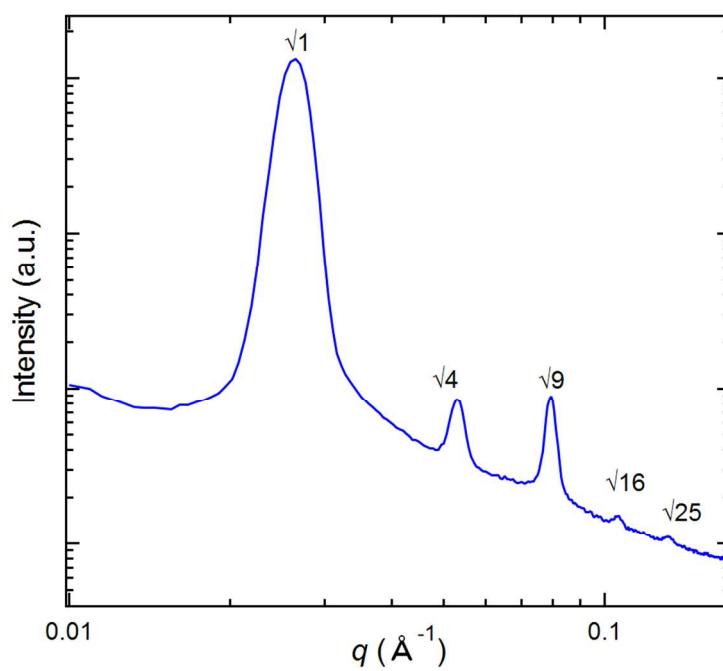
**Figure S1.** SEC traces of the homopolymer PS obtained by taking an aliquot before the sequential addition 1,3-butadiene and the resulting PS-PBD diblock copolymer.



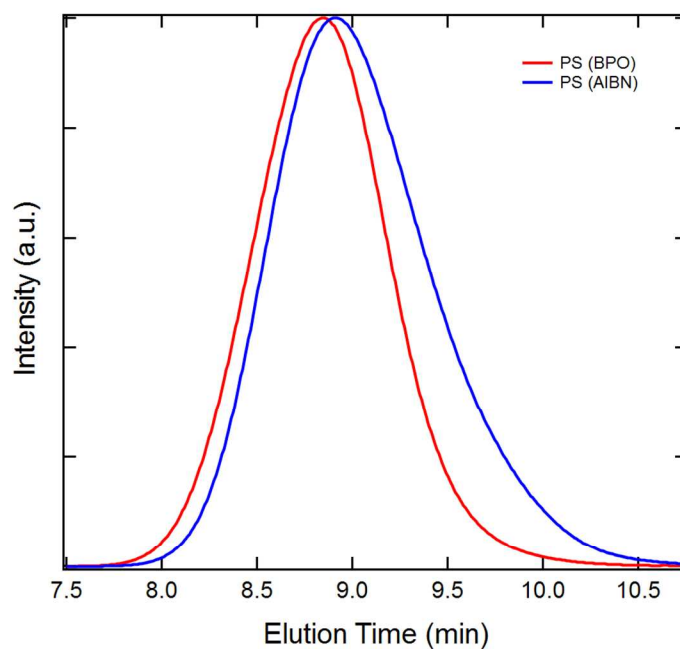
**Figure S2.** 500 MHz  $^1\text{H}$  NMR spectra for PS-PBD synthesized via sequential living anionic polymerization. Displayed in the spectra is the equation used to determine the 1,2 content.



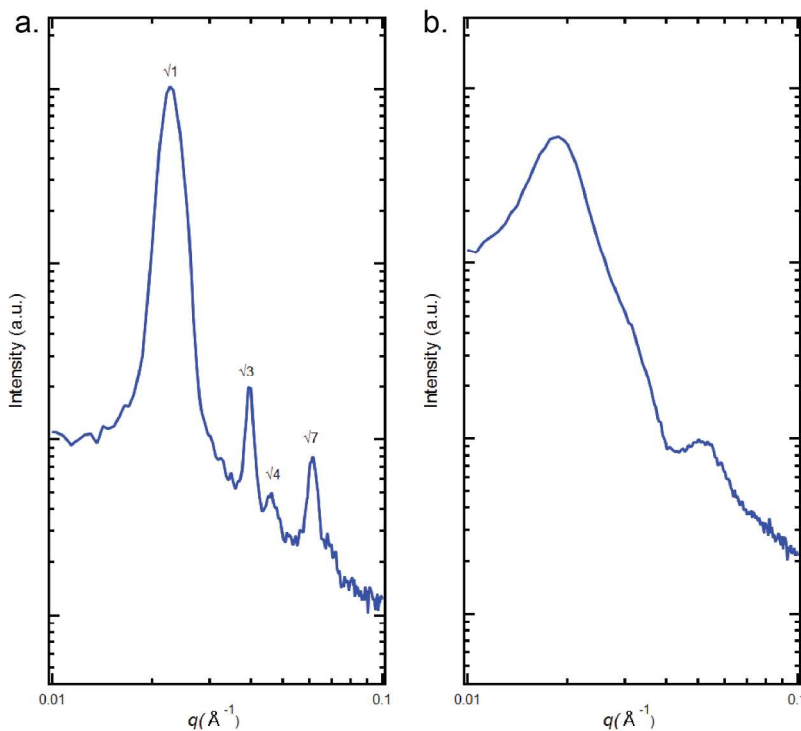
**Figure S3.** 400 MHz <sup>1</sup>H NMR spectra for 1,2PBD synthesized via living anionic polymerization.



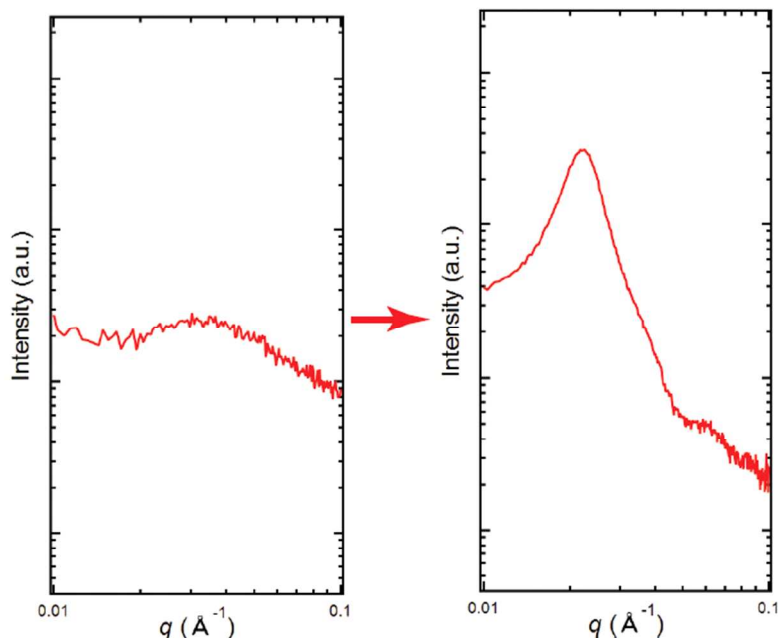
**Figure S4.** Room temperature SAXS pattern of the PS-PBD diblock copolymer.



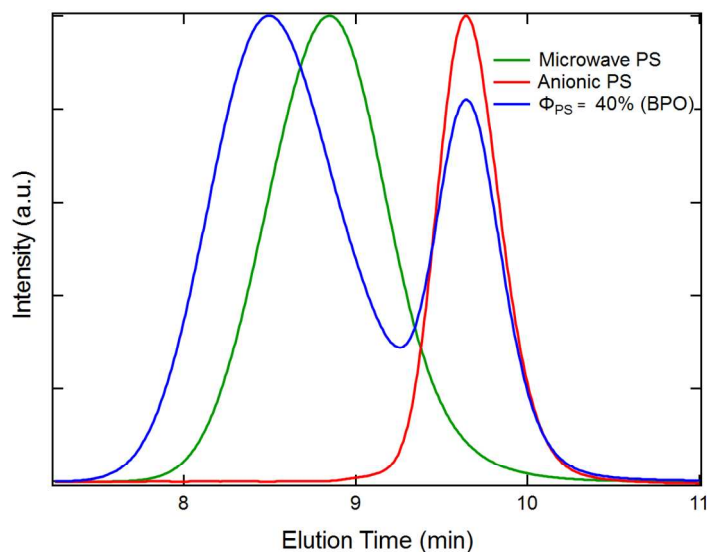
**Figure S5.** SEC traces of the homopolymer PS synthesized using microwave heating with either BPO or AIBN as the initiator.



**Figure S6.** Room temperature SAXS pattern of the PS-PBD/PS binary polymer blends for (a)  $\phi_{\text{PS-PBD}} = 60\%$  and (b)  $\phi_{\text{PS-PBD}} = 40\%$ . The PS homopolymer was synthesized using living anionic polymerization.



**Figure S7.** Room temperature SAXS pattern of the for the polymerization-induced morphology transitions in PS-PBD/styrene blends when  $\phi_{\text{PS-PBD}} = 80\%$ . The left and right SAXS patters are for the sample before and after microwave heating.



**Figure S8.** SEC traces of PS homopolymers synthesized using living anionic polymerization (red trace) and microwave heating (green trace), and the PS homopolymer synthesized in the presence of PS homopolymer synthesized using living anionic polymerization (blue trace). The molecular weight of the original anionically synthesized PS homopolymer does not change, which indicates that there is no PS grafting. There is a slight increase in the synthesized PS homopolymer molecular weight, as compared to the PS synthesized using microwave heating. We attribute the increase in the molecular weight to the slight differences in the experimental conditions due to the addition of anionically synthesized PS homopolymer to reaction mixture.

## References

- (1) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K. Laboratory-Scale Setup for Anionic Polymerization under Inert Atmosphere. *Rev. Sci. Instrum.* **1995**, *66*, 1090-1095.
- (2) Mansour, A. S.; Johnson, L. F.; Lodge, T. P.; Bates, F. S. Thermodynamic Characteristics of Poly(Cyclohexylethylene-*b*-Ethylene-*co*-Ethylethylene) Block Copolymers. *J. Polym. Sci. B* **2010**, *48*, 566-574.
- (3) Li, J.; Zhu, X.; Zhu, J.; Cheng, Z. Microwave-Assisted Nitroxide-Mediated Radical Polymerization of Styrene. *Radiat. Phys. Chem.* **2006**, *75*, 253-258.