Supplementary Information I

Blocky Bromination of Syndiotactic Polystyrene via Post-Polymerization Functionalization in the Heterogeneous Gel State

Kristen F. Noble,^a Alexandria M. Noble^b, Samantha J. Talley^a and Robert B. Moore^{*a} ^aDepartment of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA 24061 ^bGrado Department of Industrial and Systems Engineering, Virginia Tech, Blacksburg, VA 24061

¹H NMR spectra were recorded using the following parameters: pulse sequence s2pul, 5 sec relaxation delay, 64 scans, 1.6622 µsec pulse width, and an acquisition time of 2.5559 sec. The full ¹H NMR spectra of the sPS homopolymer, Random R-31%, and Blocky B-29% are shown in **Figure S1**. Between 1.58-1.75 ppm, there are two distinct chemical shifts assigned to H(a') protons based on the heteronuclear single quantum coherence (HSQC) NMR spectra (see **Figure S3**). The two H(a') resonances are indicative of two different nuclei environments of the Br-Sty monomers. Based on the HSQC spectra, the more downfield resonance (H(a'1)) is assigned to a Br-Sty with one neighboring Br-Sty and the more upfield (H(a'2)) resonance is assigned to a Br-Sty with two Br-Sty neighbors. For Blocky B-29%, the relative intensity of the H(a'2) peak to the H(a'1) peak is greater than that of Random R-31%, indicating a greater prevalence of Br-Sty triads in the Blocky copolymer.



Figure S1. Full ¹H NMR spectra of pure sPS and the Blocky B-29% and Random R-31% sPS-co-sPS-Br copolymers. ¹H NMR spectra were recorded at room temperature and are referenced to CDCl₃ and normalized over the range 6.27-6.60 ppm..Asterisks (*) indicate solvent resonances.

The full quantitative ¹³C NMR spectra of the sPS homopolymer, Random R-31%, and Blocky B-29%, recorded using a C13IG pulse program, proton decoupled (NOE–), 6 sec relaxation delay, 7680 scans, O1P of 95, and sweep width of 150 ppm, are shown in **Figure S2**.



Figure S2. Full ¹³C NMR of pure sPS and the Blocky B-29% and Random R-31% sPS-co-sPS-Br copolymers. The spectra were recorded at room temperature and are referenced to TCE- d_2 and normalized over the range 127.0-132.5 ppm. Asterisks (*) indicate solvent resonances.

The gHSQC and band-selective heteronuclear multiple bond correlation (bsgHMBC) spectra of Random R-30% and Blocky B-29%, shown respectively in **Figures S3 and S4**, were used to assign peaks in the ¹H and ¹³C NMR spectra.



Figure S3. ¹H-¹³C gHSQC NMR spectra of (a) Random R-31% and (b) Blocky B-29% referenced to CDCl₃. The spectra are cut to improve the clarity of the aromatic and aliphatic regions.



Figure S4. bsgHMBC NMR spectra of (left) Random R-31% and (right) Blocky B-29% referenced to TCE-d₂. The spectra are cut to improve the clarity of the aromatic and aliphatic regions.

The relationship between melting temperature and degree of bromination for the sPS homopolymer and Random and Blocky copolymers is shown in **Figure S5**. The reported multiple T_m per sample represent each endothermic peak maxima in the differential scanning calorimetry (DSC) heating scans shown in **Figure 4**. Melting point depression is greater in the Random samples, which is consistent with thinner crystallites and supports that the Random copolymers have shorter segments of consecutive styrene units relative to their Blocky analogs.



Figure S5. Melting temperature (T_m) versus degree of bromination for the Random and Blocky copolymers after the samples were rapidly cooled from the melt at -60 °C min⁻¹. The melting temperature is defined here as the temperature in the heating scan at the peak(s) of the melting endotherm. Dashed lines are linear fits to the highest melting temperatures and are shown to guide the eye.

The DSC thermograms of the sPS homopolymer and Random and Blocky copolymers during slow cooling from the melt to 0 °C at -10 °C min⁻¹ are shown in **Figure S6**. For both series, the crystallization exotherm, T_c, decreases in temperature and intensity with increasing Br-content, which reflects a reduction in the rate of crystallization^{1, 2}. For the Blocky samples,

the T_c occur at higher supercooling compared to their Random analogs, demonstrating that these blocky copolymers crystallize at a faster rate. The faster crystallization kinetics is also supported by the ability of Blocky B-21% to crystallize during the slow cooling conditions. In contrast, at and above 16 mol% Br, the Random samples do not crystallize under these conditions.



Figure S6. DSC slow cooling scans (-10 °C min⁻¹) for the sPS homopolymer and the (left) Random and (right) Blocky copolymers.

To further investigate the crystallinity of the copolymers, samples were isothermallycrystallized from the melt at 190 °C for 2 h and analyzed using wide-angle X-ray diffraction (WAXD). **Figure S7** shows the diffraction patterns of the sPS homopolymer and the Random and Blocky copolymers after isothermal crystallization. Observed in the diffractograms of the Random copolymers with 6-16 mol% Br-content and the Blocky copolymers with 6-21 mol% Br-content are crystalline reflections that are consistent with the diffraction pattern of the meltcrystallized sPS homopolymer sample. For the highly brominated Random samples, above 16 mol% Br, the copolymers are completely amorphous. Observed in the diffraction pattern of Blocky B-29% is a new crystalline reflection at 19.3°, which we discuss in further detail in the Morphological characterization subsection.



Figure S7. Wide-angle X-ray diffractograms of the (left) sPS homopolymer and the (center) Random and (right) Blocky copolymers, after 2 h isothermal crystallization at 190 °C. The powder samples were heated to 300 °C, held for 5 min to erase the thermal history, cooled to 190 °C at -60 °C min⁻¹, held for 2 h, then cooled to 0 °C at -60 °C min⁻¹, and held for 5 min. The WAXD profiles are vertically offset to facilitate a comparison of the peak positions and arranged top to bottom in order of increasing Br-content.

The WAXD profiles of an sPS quenched film, prepared from sPS pellets by melt pressing between Kapton sheets at 300 °C followed by quenching in ice water to prevent sPS crystallization, and a 10 w/v% sPS/CCl₄ gel that was dried under vacuum at 80 °C for 24 h, are shown in **Figure S8**. Microsoft Excel software with Solver was used to fit the amorphous and crystalline components of the diffractograms to Gaussian distributions. The fit of the amorphous component of the sPS film was used to fit the amorphous component of the 10 w/v% sPS/CCl₄ gel by keeping the position of the Gaussian peaks constant and adjusting the peak amplitude and width. The percentage of the crystalline component in the gel was calculated from the total area of the crystalline component relative to the area of the full diffractogram and found to be 44%.



Figure S8. In black, diffractograms of (left) an sPS quenched film and (right) a 10 w/v% sPS gel from CCl_4 dried under vacuum at 80 °C for 24 h. Red curve = overall curve fitting; green curve = fit of the amorphous component; Blue curves = individual Gaussian distributions composing the amorphous component.

The probability of selecting a Br-Sty monomer that exists in a sequence of at least three consecutive Br-Sty monomers (i.e., BBB triads) in the simulated random and blocky copolymer chains of 0-30 mol% Br is shown in **Figure S9**. For the simulated 30 mol% Br random copolymer, the percentage of Br-Sty monomers in BBB triads or longer is less than 5%. In contrast, the simulated 30 mol% Br blocky copolymer has a significantly higher prevalence of Br-Sty monomers in sequences of at least three consecutive Br-Sty, demonstrating that the simulated blocky copolymer chains have segments that are densely brominated.



Figure S9. Probability that a Br-Sty monomer selected at random exists in a segment of at least three consecutive Br-Sty units from simulations of the theoretical blocky (gel state) or random (solution state) copolymer microstructures. Results based on 1000 polymer chains of 1442 monomer units each. Error bars represent one standard deviation.

The dimensions of the scattering features in the USAXS/SAXS profiles of the Blocky copolymer samples (Figure 6) were calculated using the Unified Fit model and are summarized in Table S1.

Table S1. Dimensions of the scattering features in the USAXS/SAXS profiles of semicrystalline sPS and the Blocky copolymers.

Sample	low <i>q</i> (nm)	high q (nm)
sPS (semicrystalline) ^a		5.1
	04.0.0.4	
B-15%	31.9 ± 0.1	
B-21%	29.7 ± 0.2	
B-29%	34.4 ± 0.2	5.12 ± 0.02

^aObtained from Wang et al.³

The low q feature is between 0.0003 - 0.001 nm⁻¹ and the high q feature is between 0.001 - 0.01 nm⁻¹.

Notes and references

- 1. L. Annunziata, Y. Sarazin, M. Duc and J. F. Carpentier, Macromol. Rapid Comm., 2011, 32, 751-757.
- Y. Gao and H. M. Li, *Polym. Int.*, 2004, 53, 1436-1441.
 H. Wang, C. Wu, D. Cui and Y. Men, *Macromolecules*, 2018, 51, 497-503. 2. 3.