

[Electronic Supplementary Information]

**Controlling Nanostructure and Mechanical Properties in Triblock Copolymer/Monomer
Blends via Reaction-Induced Phase Transitions**

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Macromolecular Characterization using NMR and SEC

¹H NMR was used to determine critical molecular characteristics such as PS wt% and ratio of 1,2 vs 1,4 PBD content in the SBS triblock copolymer. The PS wt% was calculated to be 35%, which by using bulk densities of 1.04 g cm⁻³ for PS and 0.91 g cm⁻³ for PBD, the resulting density of the SBS triblock was calculated to be 0.95 g cm⁻³. Similarly, the dn/dc value of the polymer was approximated using the PS wt% by using dn/dc values of 0.185 for PS and 0.13 for PBD, resulting in a dn/dc to be approximately 0.1495. It was determined that the SBS triblock was 89% 1,4- PBD. By using the above dn/dc value, the number-average molecular weight (M_n) of the copolymer was determined to be 62 kg mol⁻¹.

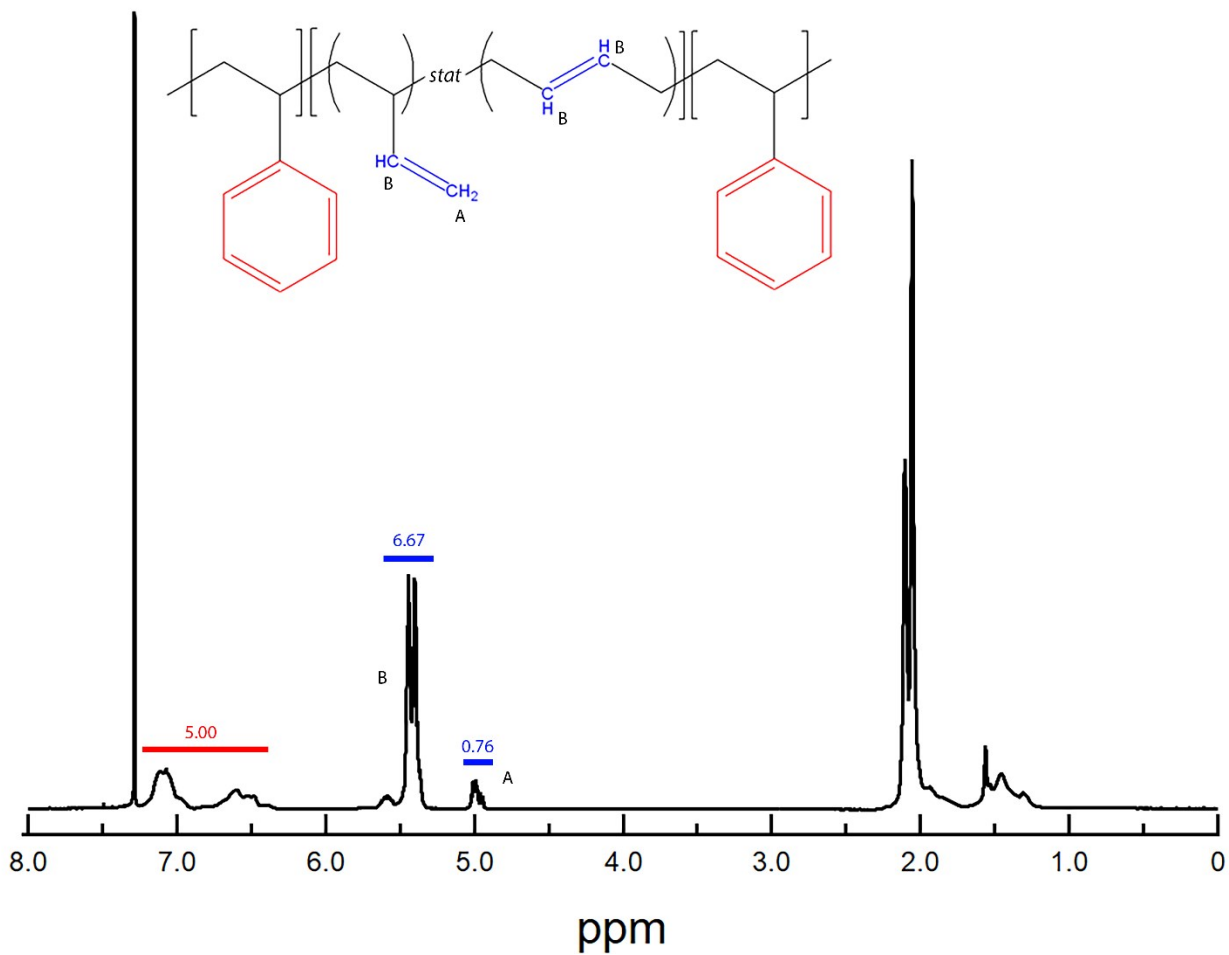


Figure S1. 500 MHz ^1H NMR spectrum for $\phi_{\text{SBS}} = 100\%$. The PS wt% was calculated by comparing the relative mole amounts for PS and PBD. The relative 1,4 vs 1,2- PBD content was calculated by comparing group A and B hydrogens as shown in the spectrum.

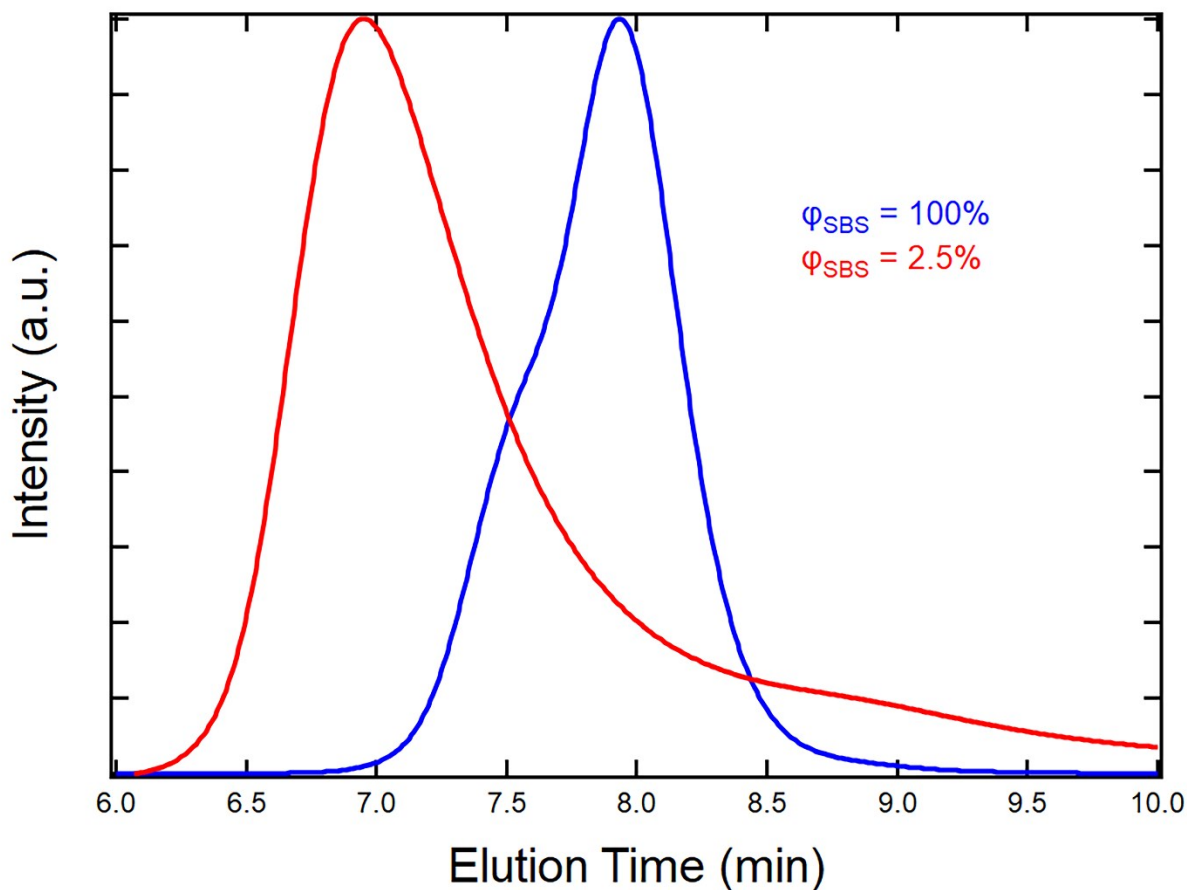


Figure S2. SEC trace of $\phi_{\text{SBS}} = 100\%$ (blue) and $\phi_{\text{SBS}} = 2.5\%$ (red). The large shift in elution time indicates the large increase in molecular weight due to grafting of the SBS. The small hump at later elution times in the $\phi_{\text{SBS}} = 2.5\%$ SBS trace shows that homopolymer PS is being formed in the reaction. For $\phi_{\text{SBS}} = 100\%$, the M_n and D were determined to be 62 kg mol^{-1} and 1.11, respectively. For $\phi_{\text{SBS}} = 2.5\%$, the M_n and D were determined to be $6,400 \text{ kg mol}^{-1}$ and 1.34, respectively.

Glass Transition Temperature (T_g)

Glass transition temperatures (T_g) were measured using a TA Instrument DSC 250. 10-20 mg of each sample were pressed into aluminum pans, heated to 120 °C at 20 °C/min, cooled to -160 °C at 20 °C/min, and heated again to 120 °C at 20 °C/min. The T_g of both the PBD and PS domains were acquired on the second heating cycle.

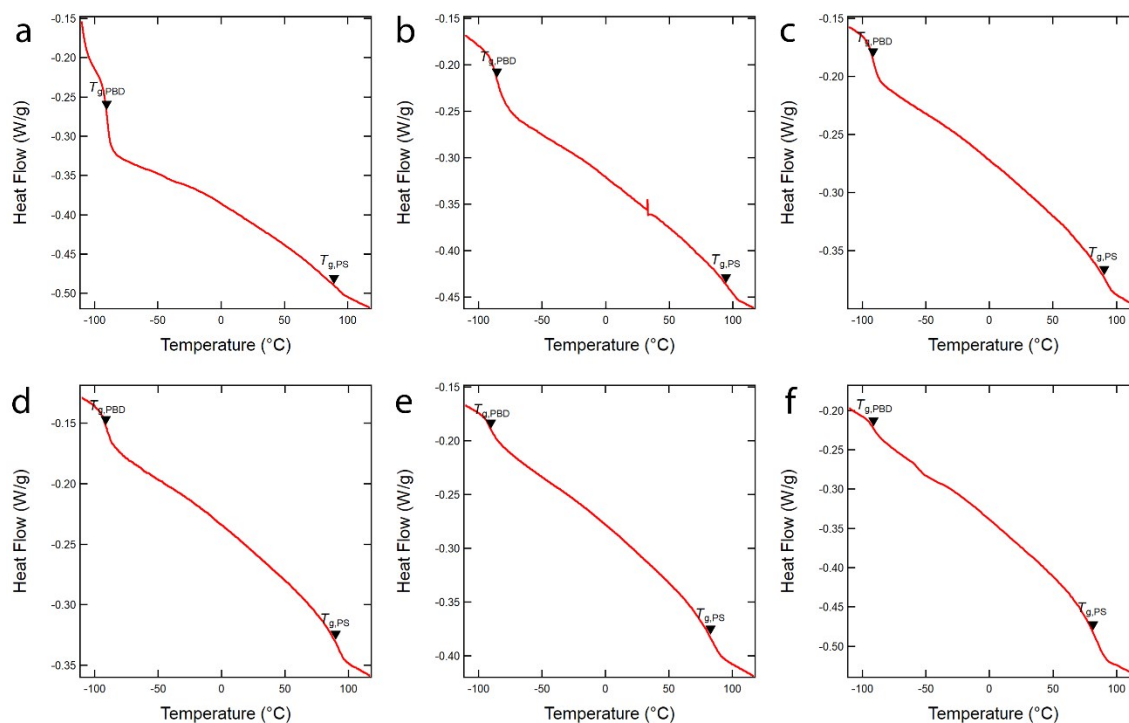


Figure S3. DSC traces for the dog bone samples after polymerization and vacuum drying. a) $\phi_{SBS} = 100\%$, b) $\phi_{SBS} = 50\%$, c) $\phi_{SBS} = 40\%$, d) $\phi_{SBS} = 30\%$, e) $\phi_{SBS} = 20\%$, and f) $\phi_{SBS} = 10\%$.

Table S1. Results from DSC experiments

Sample	$T_{g, \text{PBD}}$ (°C)	PS wt% in PBD^a	$T_{g, \text{PS}}$ (°C)	PBD wt% in PS^a
$\varphi_{\text{SBS}} = 100\%$	-91	9	89	3
$\varphi_{\text{SBS}} = 50\%$	-85	14	95	1
$\varphi_{\text{SBS}} = 40\%$	-92	8	91	2
$\varphi_{\text{SBS}} = 30\%$	-91	9	90	2
$\varphi_{\text{SBS}} = 20\%$	-90	10	82	4
$\varphi_{\text{SBS}} = 10\%$	-91	9	81	5

^aCalculated using the Fox equation.

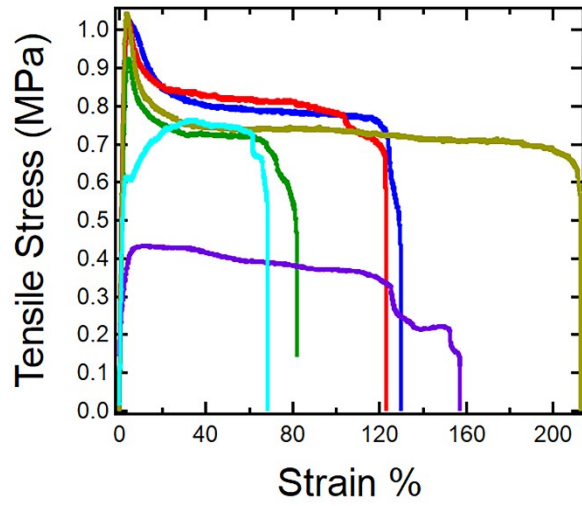


Figure S4. Tensile measurements for all the $\phi_{\text{SBS}} = 100\%$ samples. The applied rate of strain was 5 mm/min.

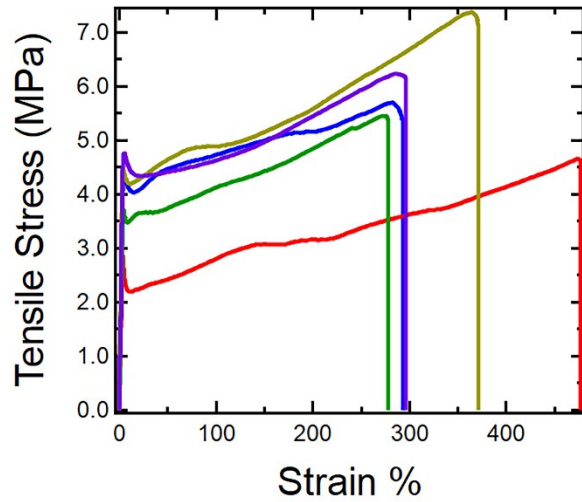


Figure S5. Tensile measurements for all the $\phi_{\text{SBS}} = 50\%$ samples. The applied rate of strain was 5 mm/min.

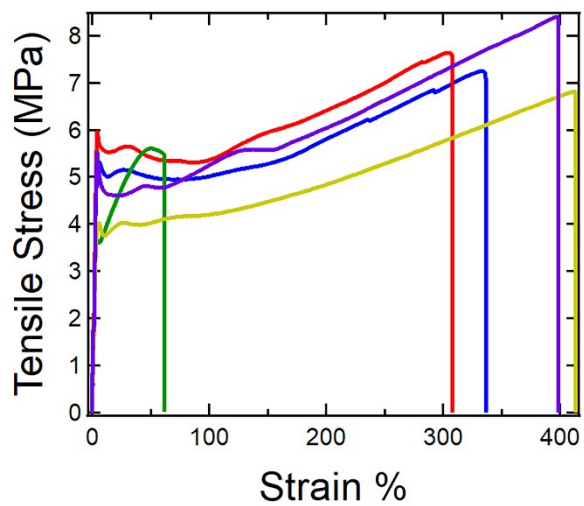
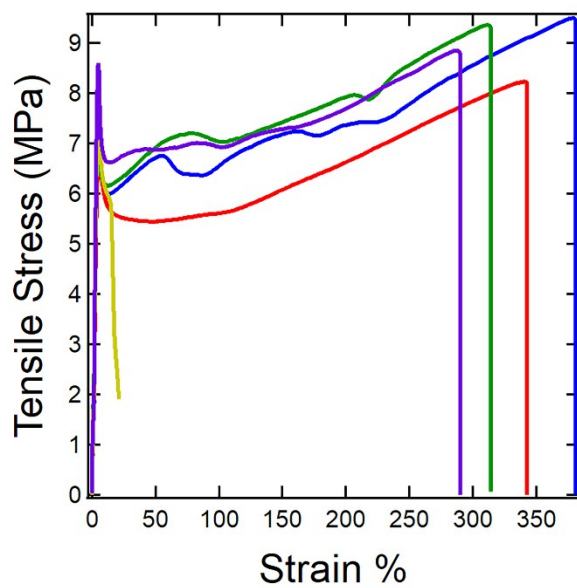


Figure S6. Tensile measurements for all the $\phi_{\text{SBS}} = 40\%$ samples. The applied rate of strain was 5



mm/min.

Figure S7. Tensile measurements for all the $\phi_{\text{SBS}} = 30\%$ samples. The applied rate of strain was 5 mm/min.

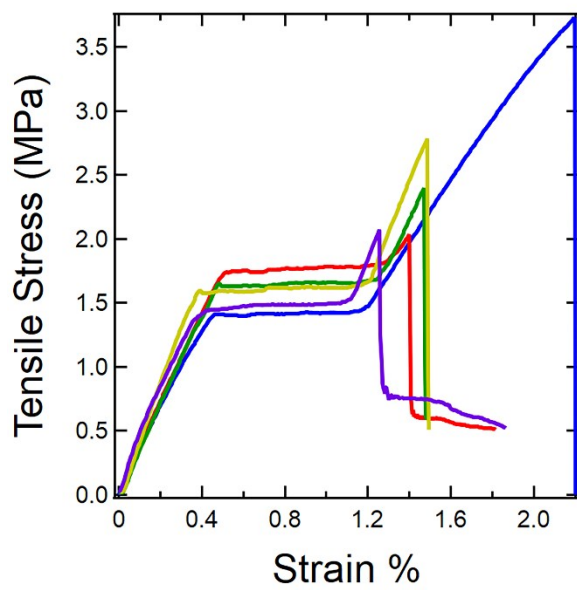


Figure S8. Tensile measurements for all the $\phi_{\text{SBS}} = 20\%$ samples. The applied rate of strain was 5 mm/min.

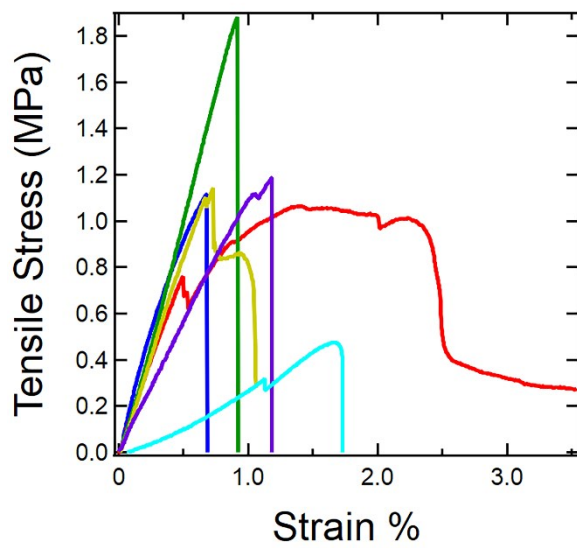


Figure S9. Tensile measurements for all the $\phi_{\text{SBS}} = 10\%$ samples. The applied rate of strain was 5 mm/min.