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 $^1$H NMR spectrum for $\varphi_{\text{SBS}} = 100\%$. 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 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.

![DSC traces for the dog bone samples after polymerization and vacuum drying.](image)

**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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{g,PBD}$ (°C)</th>
<th>PS wt% in PBD⁹</th>
<th>$T_{g,PS}$ (°C)</th>
<th>PBD wt% in PS⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi_{SBS} = 100%$</td>
<td>-91</td>
<td>9</td>
<td>89</td>
<td>3</td>
</tr>
<tr>
<td>$\varphi_{SBS} = 50%$</td>
<td>-85</td>
<td>14</td>
<td>95</td>
<td>1</td>
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<td>$\varphi_{SBS} = 20%$</td>
<td>-90</td>
<td>10</td>
<td>82</td>
<td>4</td>
</tr>
<tr>
<td>$\varphi_{SBS} = 10%$</td>
<td>-91</td>
<td>9</td>
<td>81</td>
<td>5</td>
</tr>
</tbody>
</table>

⁹Calculated using the Fox equation.
Figure S4. Tensile measurements for all the $\varphi_{\text{SBS}} = 100\%$ samples. The applied rate of strain was 5 mm/min.

Figure S5. Tensile measurements for all the $\varphi_{\text{SBS}} = 50\%$ 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.