Supporting Information for

Hierarchical Microphase Separation in Bicontinuous Ternary Polymer Blends

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Polymer characterization

^{1}H NMR spectra of the hydrogenated blend components are presented in Figure S1. NMR experiments were conducted in either deuterated chloroform at room temperature (P) or in deuterated toluene at 70 °C (CEC and CECEC–P**)**; solvent peaks are labeled "s" in Figure S1. The absence of peaks from 4.5-5.5 ppm and 6.5-7.5 ppm indicates complete hydrogenation of olefin and styrene groups, respectively.

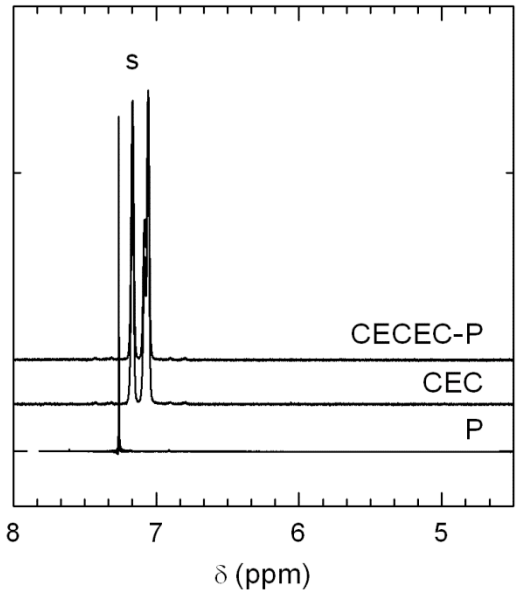


Figure S1. ^{1}H NMR spectra of P, CEC, and CECEC-P; successive curves are shifted vertically for clarity.

Blend rheology

The T_g of C within the blends was measured rheologically by a dynamic temperature ramp experiment conducted at a frequency of 1 rad/s and temperature ramp rate of 0.4 °C/min. Figure S2 shows tan(δ) as a function of temperature for blend XP89; the broad peak indicates T_g.

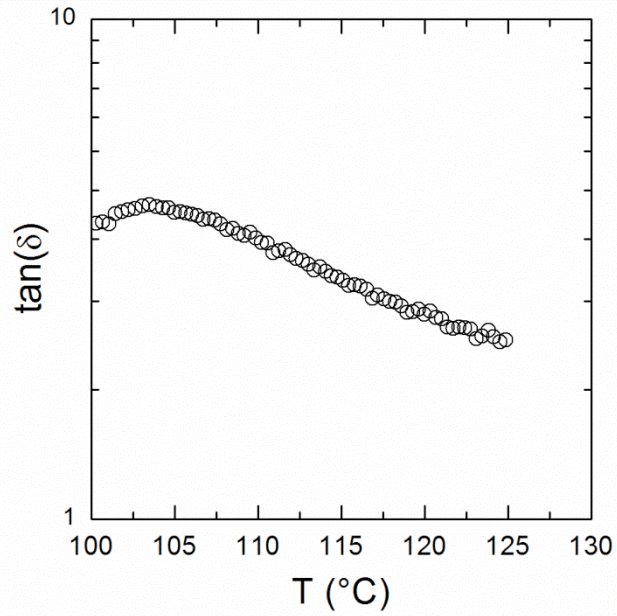
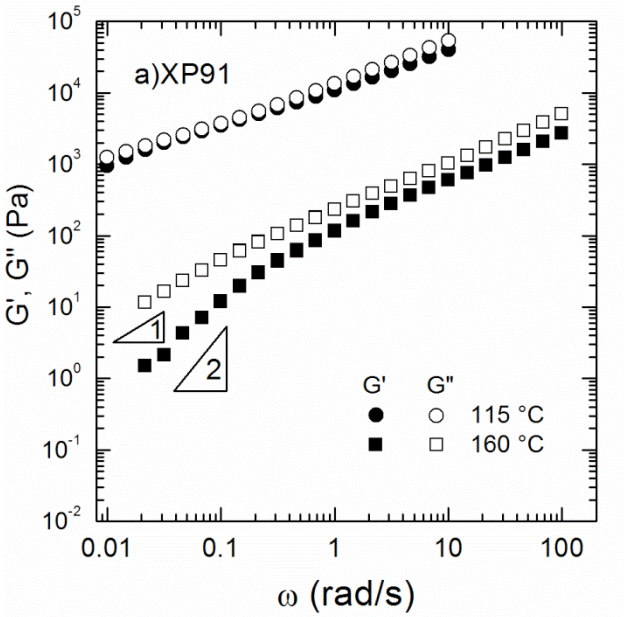
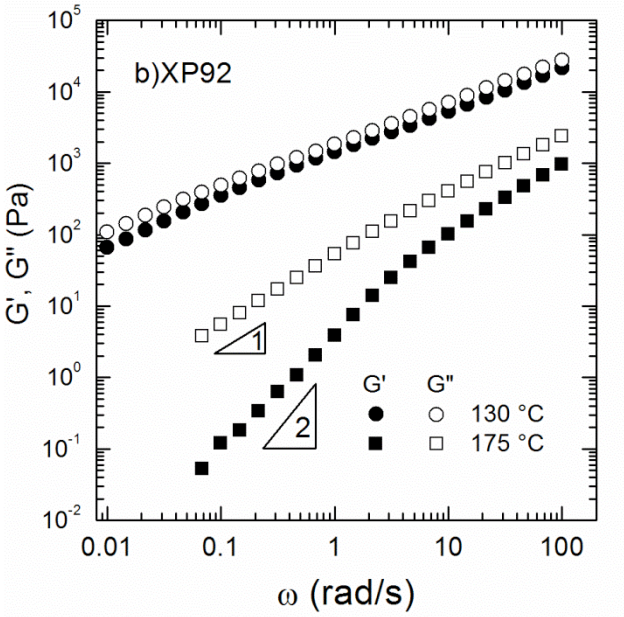


Figure S2. Tan(δ) as a function of temperature for blend XP89.

Dynamic temperature ramps of samples XP91-94 were presented in Figure 3. Figure S3 contains dynamic frequency sweeps for these samples at temperatures above and below the measured T_{ODT}. In each case, terminal melt behavior is observed at high temperature.





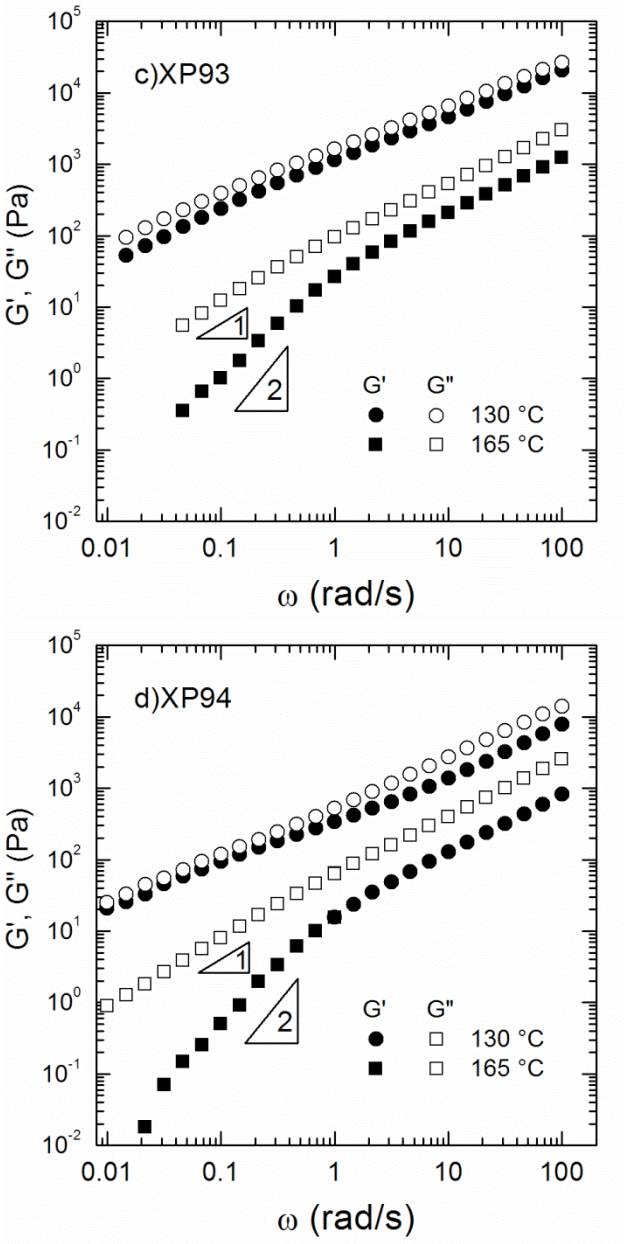
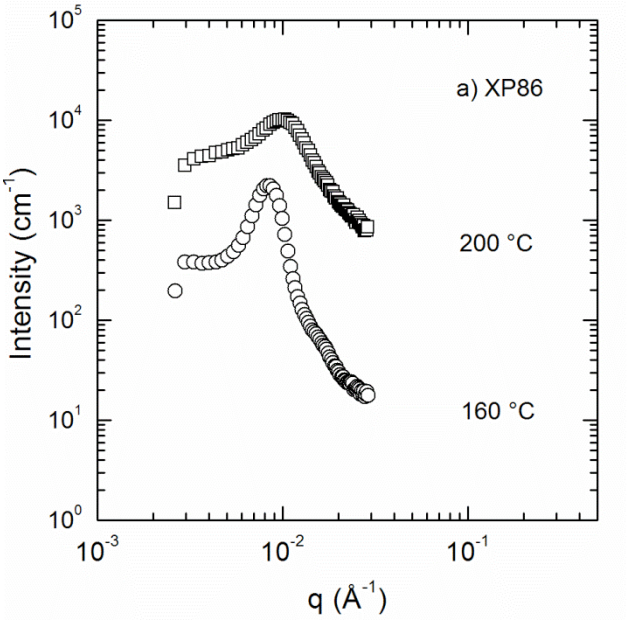


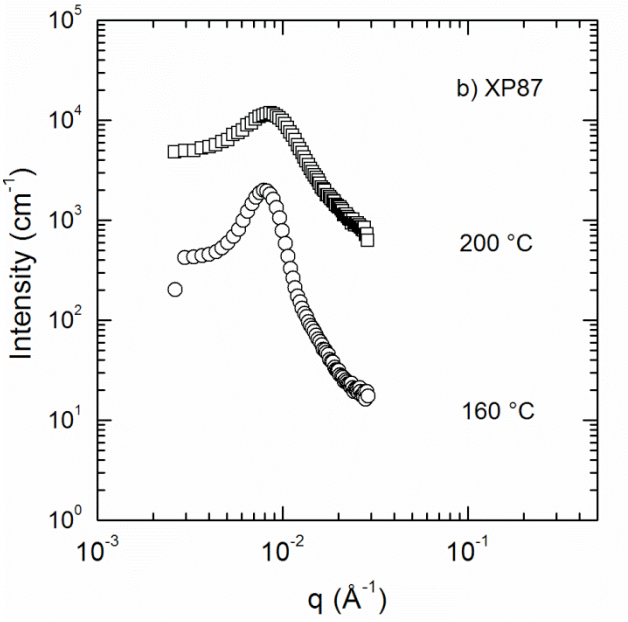
Figure S3. Dynamic frequency sweeps for blends (a) XP91, (b) XP92, (c) XP93, and (d) XP94 at temperatures above and below the blend T_{ODT}.

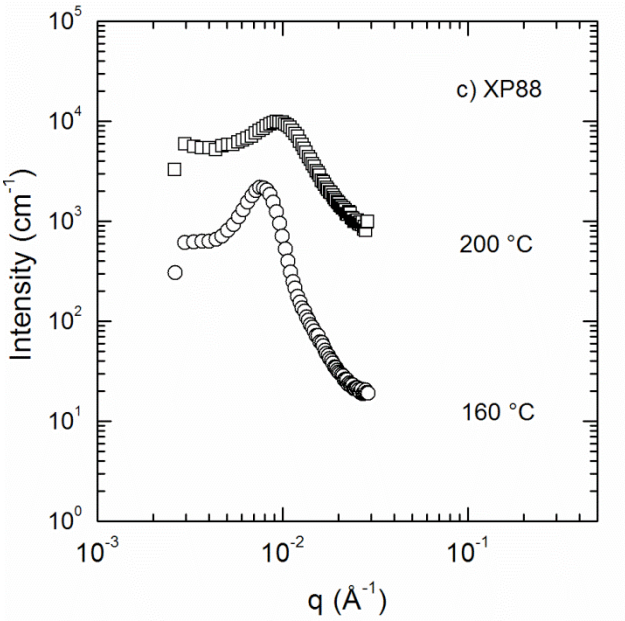
Blend structure

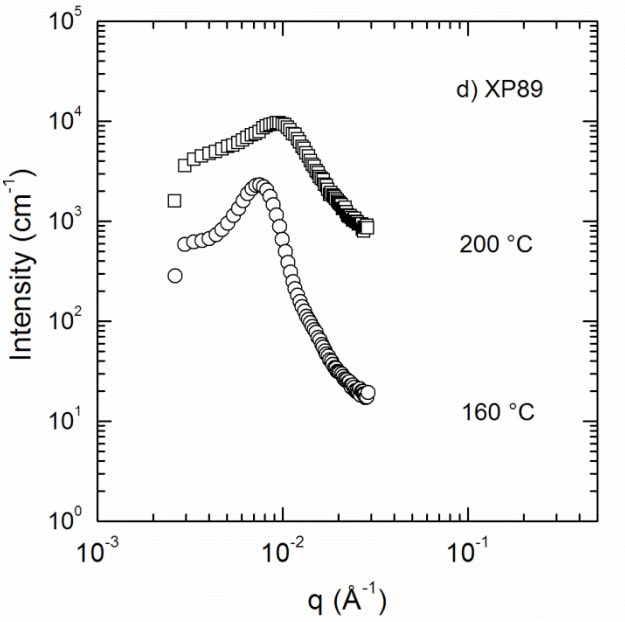
SANS profiles of blends XP86-92 at 116 °C, 140 °C, and 180 °C were presented in Figure 5. SANS data collected at 160 °C and 200 °C are presented in Figure S4. At these temperatures,

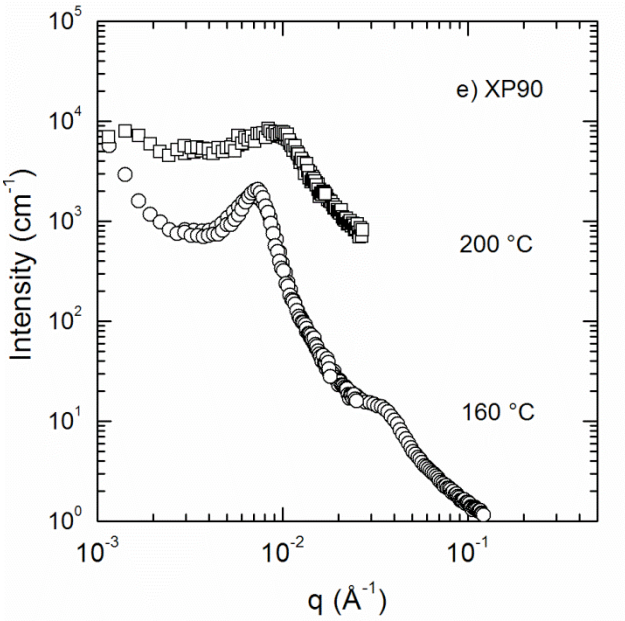
data were not collected at all available sample-to-detector distances, but are presented on the same scale as Figure 5 for ease of comparison.

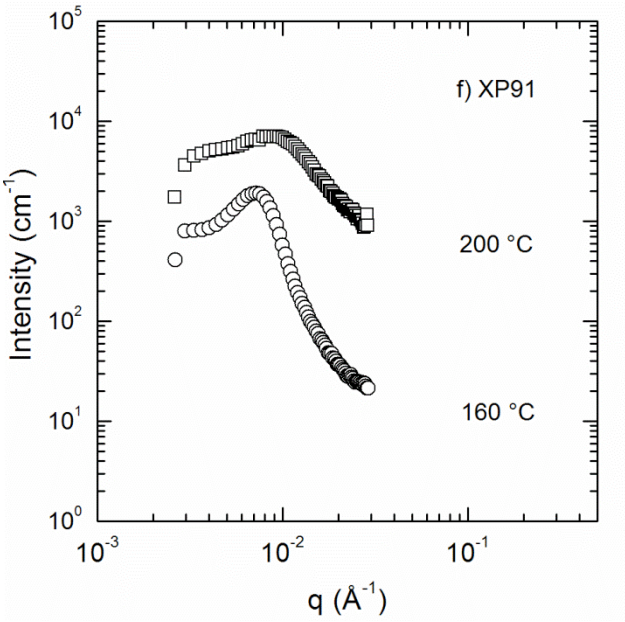












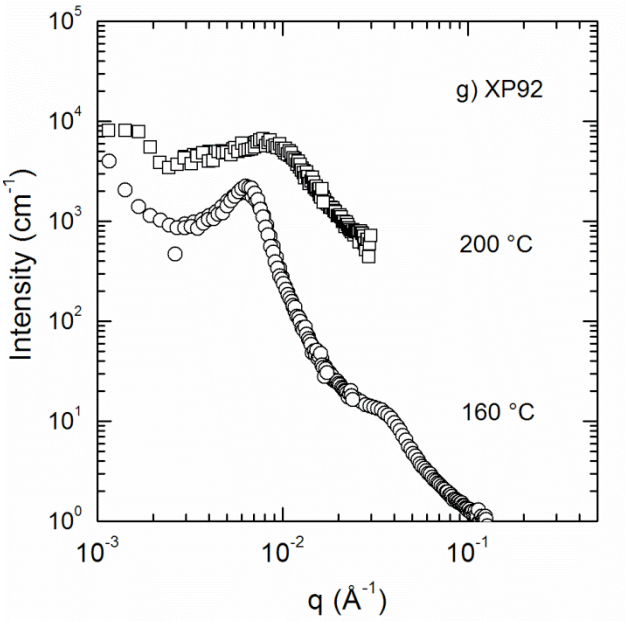


Figure S4. 1-D SANS patterns for samples XP86-92 at 160 °C and 200 °C. Data at 200 °C has been shifted vertically by a factor of 50.

Identification of CEC and P phases in TEM images was aided by comparison with the appearance of disordered bulk CEC, shown in Figure S5. Randomly distributed small dark circles are identified as amorphous E. In some cases, a small white spot can be seen in the center of these circles; these bright spots indicate crystalline E, which resists the diffusing staining agent.[1] Though they cannot be seen at the size and resolution of most TEM images in this publication, these features are present in the phase identified as CEC-rich in all blends which contain disordered CEC.

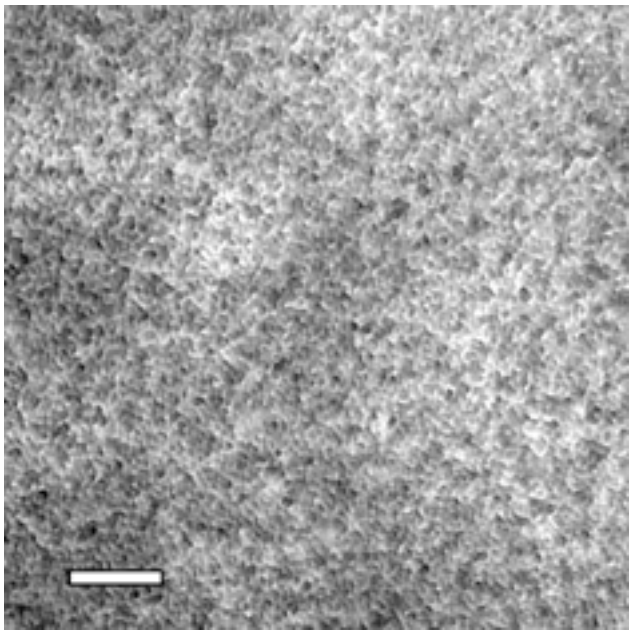


Figure 5. TEM micrograph of CEC quenched from 130 °C – above the T_{ODT}. Scale bar is 25 nm.

Supporting References

1. Loo, Y. L.; Register, R. A.; Adamson, D. H. *Journal of Polymer Science Part B-Polymer Physics* **2000,** 38, (19), 2564-2570.