

Mechanical Properties of Star Block Polymer Thermoplastic Elastomers with Glassy and Crystalline End Blocks

Supporting Information

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Gel Permeation Chromatography Traces of Star Polymers

Gel permeation chromatography (GPC) traces of the precursors to the three star polymers are shown in Figures S1–S3. The refractive index signal has been normalized to constant total area and the ordinate is presented on a fixed scale to facilitate comparison. The small peak near 13 min corresponds to the residual uncoupled arm. The GPC trace of hydrogenated (C-EP)₆, also presented in Figure S1, shows minimal arm regeneration during hydrogenation.¹

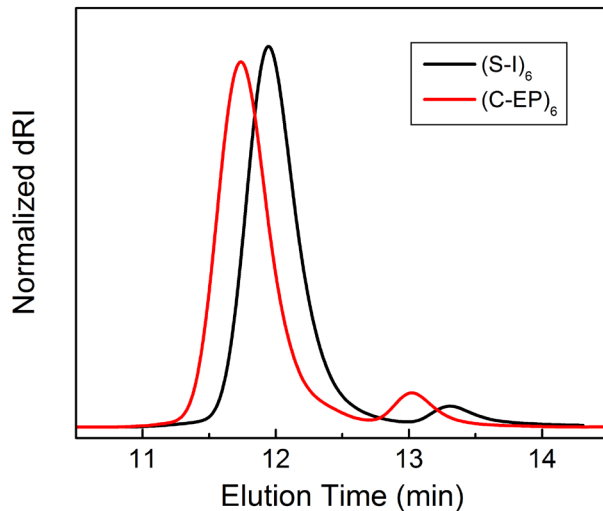


Figure S1. GPC traces of the unsaturated precursor to (C-EP)₆, labeled (S-I)₆, and (C-EP)₆ after hydrogenation.

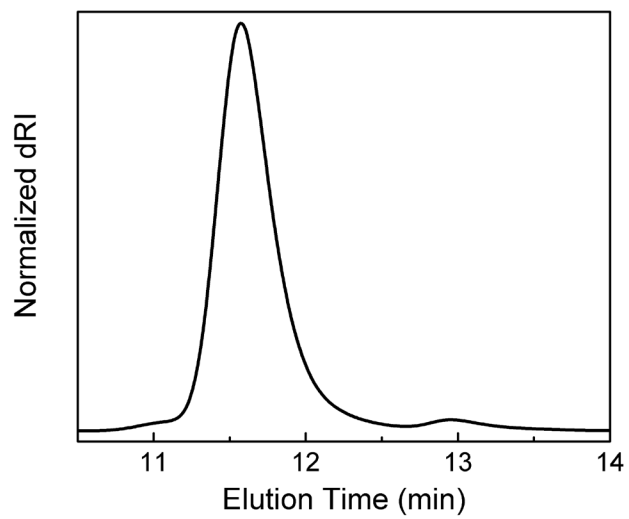


Figure S2. GPC trace of the unsaturated precursor to (E-EP)₆.

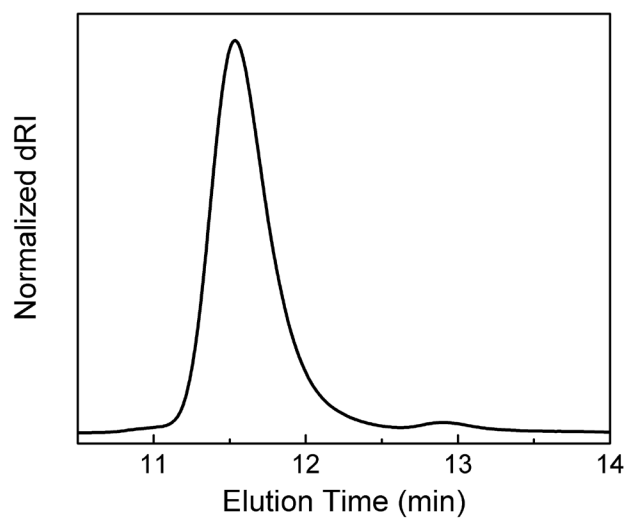


Figure S3. GPC trace of the unsaturated precursor to (E-C-EP)₆.

Form Factor Calculations for (C-EP)₂ and (C-EP)₆

Although the lack of long-range order in (C-EP)₂ and (C-EP)₆ does not allow for a direct determination of the nanoscale structure by SAXS (Figure S4), form factor calculations can aid in the assignment. As mentioned in the main text, the equilibrium morphology is expected to be hexagonally packed cylinders (HEX). Form factor calculations for cylindrical domains based on the primary peak positions (q^*) were compared against the SAXS patterns. The form factor for infinitely long cylinders can be approximated by:²

$$P_{cyl}(q) \cong \frac{1}{q} \left[\frac{2J_1(qR_{cyl})}{qR_{cyl}} \right]^2 \quad [S1]$$

$$R_{cyl} = \frac{2\pi}{q^*} \left[\frac{2}{\sqrt{3}\pi} \phi_C \right]^{1/2} \quad [S2]$$

where q is the scattering vector, $J_1(x)$ is the Bessel function of the first kind, R_{cyl} is the cylinder radius, ϕ_C is the C volume fraction calculated from the weight fractions and mass densities³ ($\phi_C = 0.169$ for (C-EP)₂ and 0.163 for (C-EP)₆ at room temperature). Equation [S2] is derived for a hexagonal packing geometry ($d^* = 2\pi/q^* = d_{10}$); $R_{cyl} = 9.2$ nm for both polymers. The scattered intensity (I) is proportional to the product of the form (P) and structure (S) factors: $I \sim P(q)S(q)$. The structure factor of a well-ordered morphology comprises a series of sharp Bragg reflections, the expected positions of which are indicated by triangles in Figure S4. Thus, minima in $P(q)$ should correspond to minima in I . Figure S4 shows the comparison between $P_{cyl}(q)$ and the SAXS data. The first minimum of $P_{cyl}(q)$ corresponds to a local dip in I for both polymers. Additionally, the expected positions of the $\sqrt{3}$ and $\sqrt{4}$ peaks and the $\sqrt{7}$ and $\sqrt{9}$ peaks correspond to broad local maxima in the scattering patterns, particularly for (C-EP)₂. Therefore, although the long-range order is poor, the morphology of the C domains appears to be cylindrical.

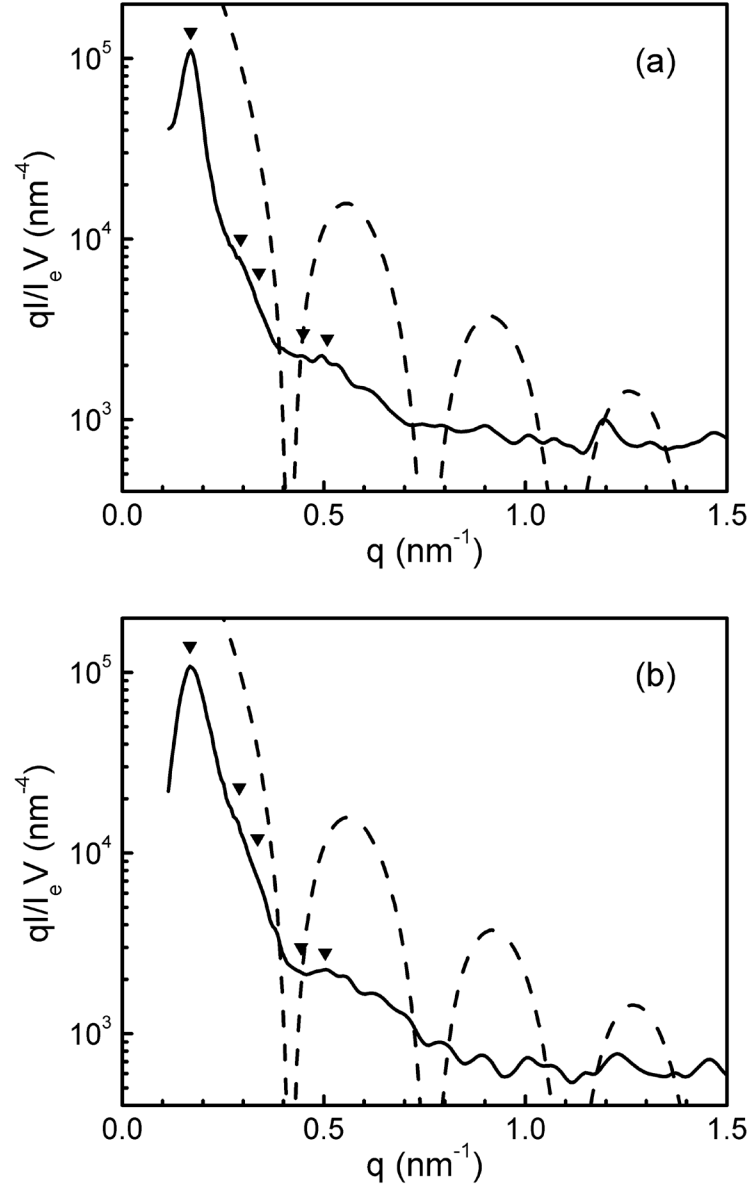


Figure S4. SAXS pattern of (C-EP)₂ (a) and (C-EP)₆ (b) at room temperature (solid curves) with form factor calculations (dashed) for cylinders and expected structure factor peak positions (triangles, $q/q^* = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}$).

Cyclic Strain Testing

The recovery of each polymer was studied in uniaxial extension with an Instron 5865 using the following cyclic strain test:

1. The specimen was elongated to a prescribed strain (ε_a) at a constant cross-head speed of 2 in/min
2. When ε_a was reached, the cross-head was immediately reversed at 2 in/min until the initial position was reached
3. The specimen was allowed to rest for 5 min
4. Steps 1–3 were repeated, increasing ε_a

Individual specimens were serially strained to 25, 50, 100, 150, 200, 300, 400, and 500%; Figure S5a shows an example of the raw data. The “initial” residual strain (ε_s^i) was measured immediately following step 2 and corresponds to the strain at which the stress first went to zero. The “final” set (ε_s^f) was taken as the strain at which the stress first became non-zero on the subsequent advancing cycle following step 3. These two measures of residual strain are illustrated in Figure S5b using the 400% and 500% cycles. The residual strain was then cast in terms of the percent recovery: $R = (1 - \varepsilon_s/\varepsilon_a) \times 100\%$.

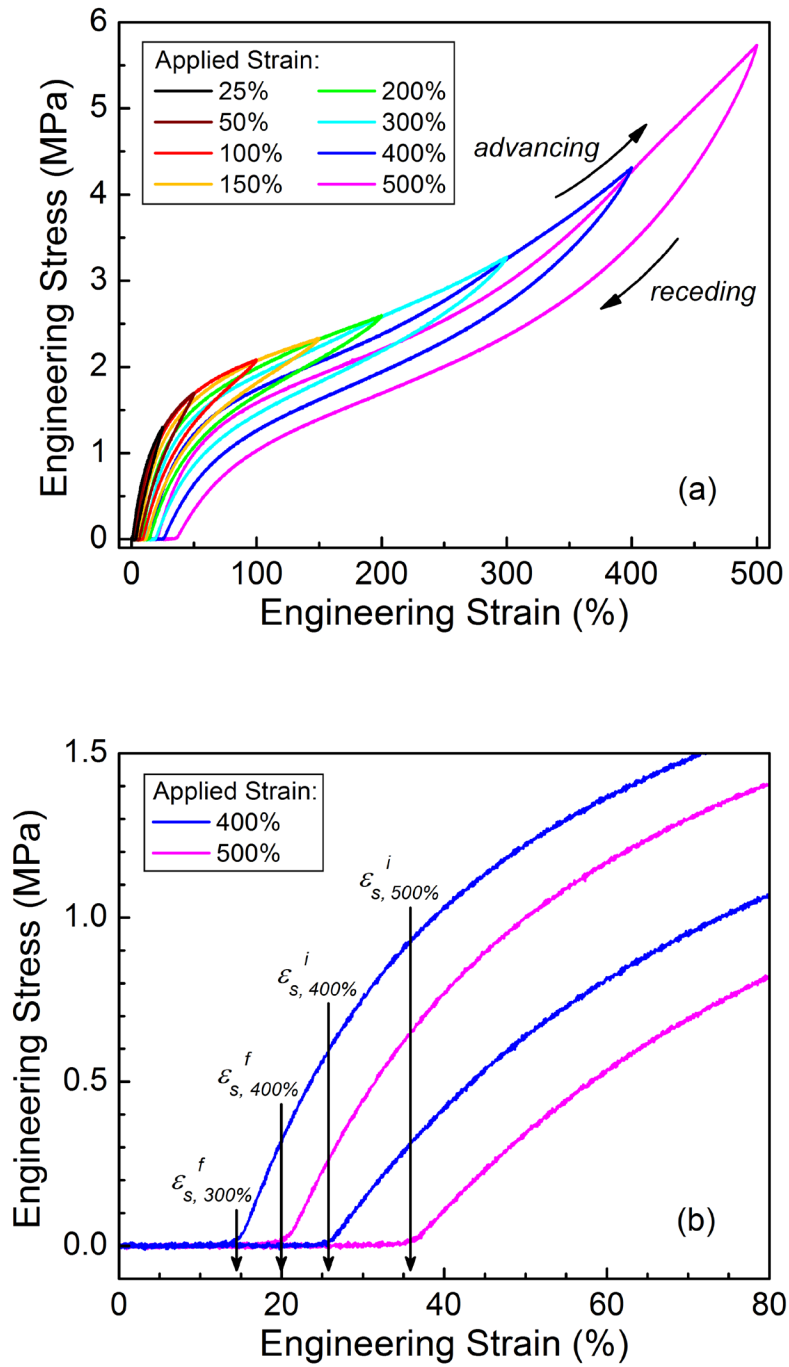


Figure S5. Example of raw cyclic strain test data from (E-EP)₂ (a), and an illustration of the residual strains measured therefrom (b).

Recovery of Kraton[®] D1111

As a reference, the recovery and hysteresis performance of (C-EP)₂ and (C-EP)₆ were compared to a commercial styrenic triblock copolymer TPE. Kraton[®] D1111 was chosen to match the hard block volume fraction of (C-EP)₂. Kraton[®] D1111 is a polystyrene-polyisoprene-polystyrene (S-I-S) triblock with 20 vol% S (compared to 17 vol% C in (C-EP)₂ and 16 vol% C in (C-EP)₆, at 20 °C) and $M_n \approx 130$ kg/mol, and approximately 19% diblock.⁴ Despite differences in the T_g values and entanglement molecular weights of the constituent blocks and the segregation strength, D1111 and (C-EP)₂ perform similarly (see Figure S6).

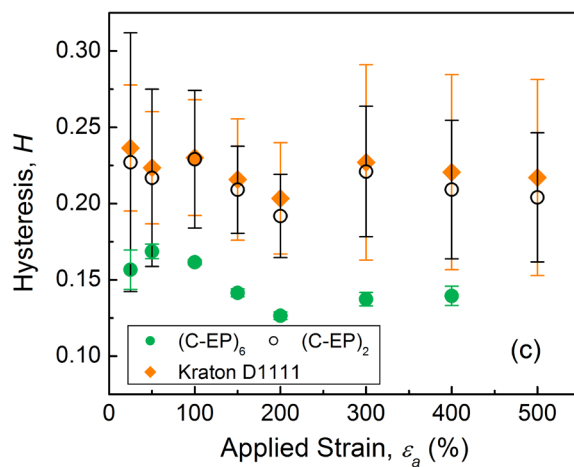
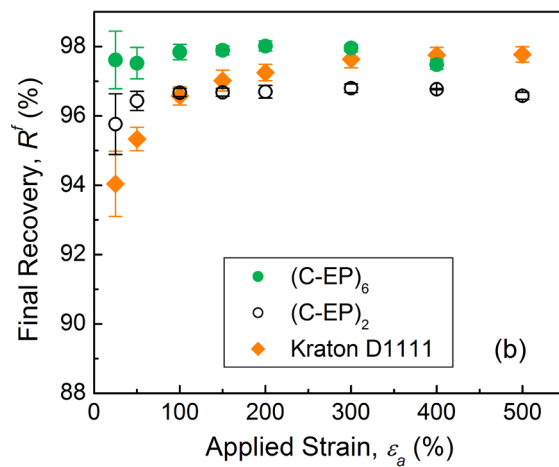
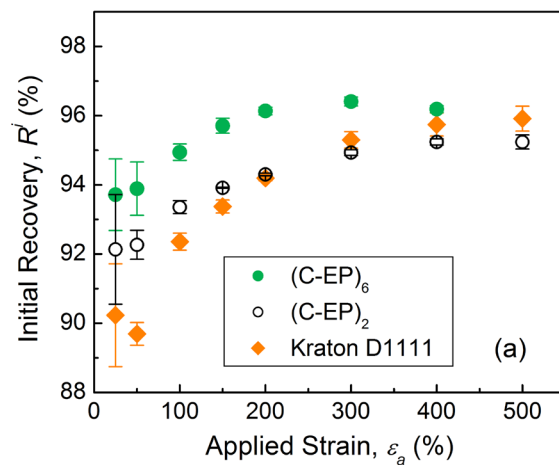


Figure S6. Initial (a) and final (b) recovery and hysteresis (c) of Kraton[®] D1111 compared to (C-EP)₂ and (C-EP)₆.

References

1. Burns, A. B.; Register, R. A. Strategies for the Synthesis of Well-Defined Star Polymers by Anionic Polymerization with Chlorosilane Coupling and Preservation of the Star Architecture during Catalytic Hydrogenation. *Macromolecules* **2016**, *49*, 2063-2070.
2. Porod, G. General Theory. In *Small Angle X-ray Scattering*, Glatter, O.; Kratky, O., Eds.; Academic Press Inc.: London, UK, 1982; pp 17-51.
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4. Balich, J. W. Characterization of Thermoplastic Elastomer Gels: Commercial Triblock Copolymers in Selective Solvents. B.S.E. Thesis, Princeton University, May 2000.