

Supporting Information for “Mixing Thermodynamics of Ternary Block-Random Copolymers Containing a Polyethylene Block” (by Bryan S. Beckingham, Adam B. Burns, and Richard A. Register, submitted as Article ma-2013-00311p to *Macromolecules*)

Thermal Characterization

For the block-random copolymers, both E block melting endotherms and VCHrhI or SrhI glass transitions could be observed, with relevant values given in the article’s Table 1. Figure S-1 shows a representative second-heat DSC thermogram, for E-(VCHrhI)₄₉₋₆₈.

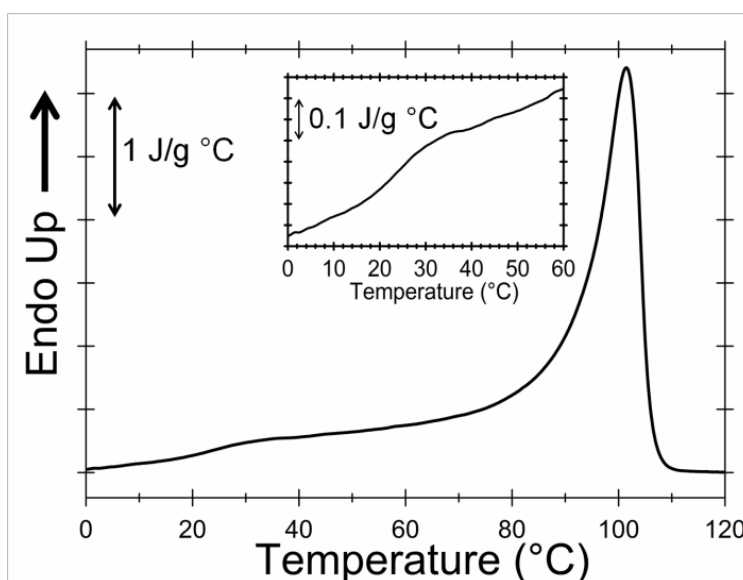


Figure S-1. DSC heating thermogram of E-(VCHrhI)₄₉₋₆₈. A distinct polyethylene melting peak, $T_m = 101$ °C, and glass transition for the VCHrhI block, $T_g = 23$ °C, are observed.

Polymer Specific Volumes (Mass Densities)

To precisely determine block volume fractions and interaction energy densities, accurate expressions for the mass densities of the various polymers are required. A quadratic expression for $\ln V$ was employed, Equation [S-1], where V is the specific volume (cm^3/g), T_r is a reference temperature, and A , B , and C are polymer-dependent constants:

$$\ln V = A + B(T-T_r) + C(T-T_r)^2 \quad [\text{S-1}]$$

Equation [S-1] implies a linear dependence of thermal expansion coefficient, α , on temperature:

$$\alpha \equiv d(\ln V)/dT = B + 2C(T-T_r) \quad [\text{S-2}]$$

One can thus obtain values of A, B, and C either from a quadratic fit of $\ln V$ vs. T, using Equation [S-1], or a linear fit of α vs. T, using Equation [S-2], coupled with a value of V at a single temperature (typically at 23 °C, V_{23}). Parameters for the polymers of interest in the present work, as well as the sources of the data used in the fits, are summarized in Table S-1, with $T_r = 160$ °C. 50SPI is a saturated polyisoprene whose precursor contained 37% 1,4-addition; the parameters for hI (54% 1,4-addition) were thus simply obtained by linear interpolation in 1,4-content between 50SPI and EP (poly(ethylene-*alt*-propylene), 93% 1,4-addition in precursor).

Table S-1. Temperature Parameters Describing Specific Volumes for Polymers of Interest ($T_r = 160$ °C)

Polymer	T Range Fit (°C)	A	$B \times 10^4$ (K ⁻¹)	$C \times 10^8$ (K ⁻²)	Data Source
EP	27-167	0.2519	7.18	23	[1] for α , [2] for V_{23}
50SPI	27-167	0.2508	7.33	16	[1] for α , [2] for V_{23}
hI		0.2511	7.28	18	interpolation
S	100-210	0.0079	5.79	1	[3]
VCH	171-277	0.0890	5.75	8	[4]
E	140-270	0.2567	7.60	12	[5], [6]

For copolymers, values of V were calculated as the weight-fraction-weighted average of the values of V for the copolymers' constituents.

Additional SAXS Patterns and T_{ODT} Determination

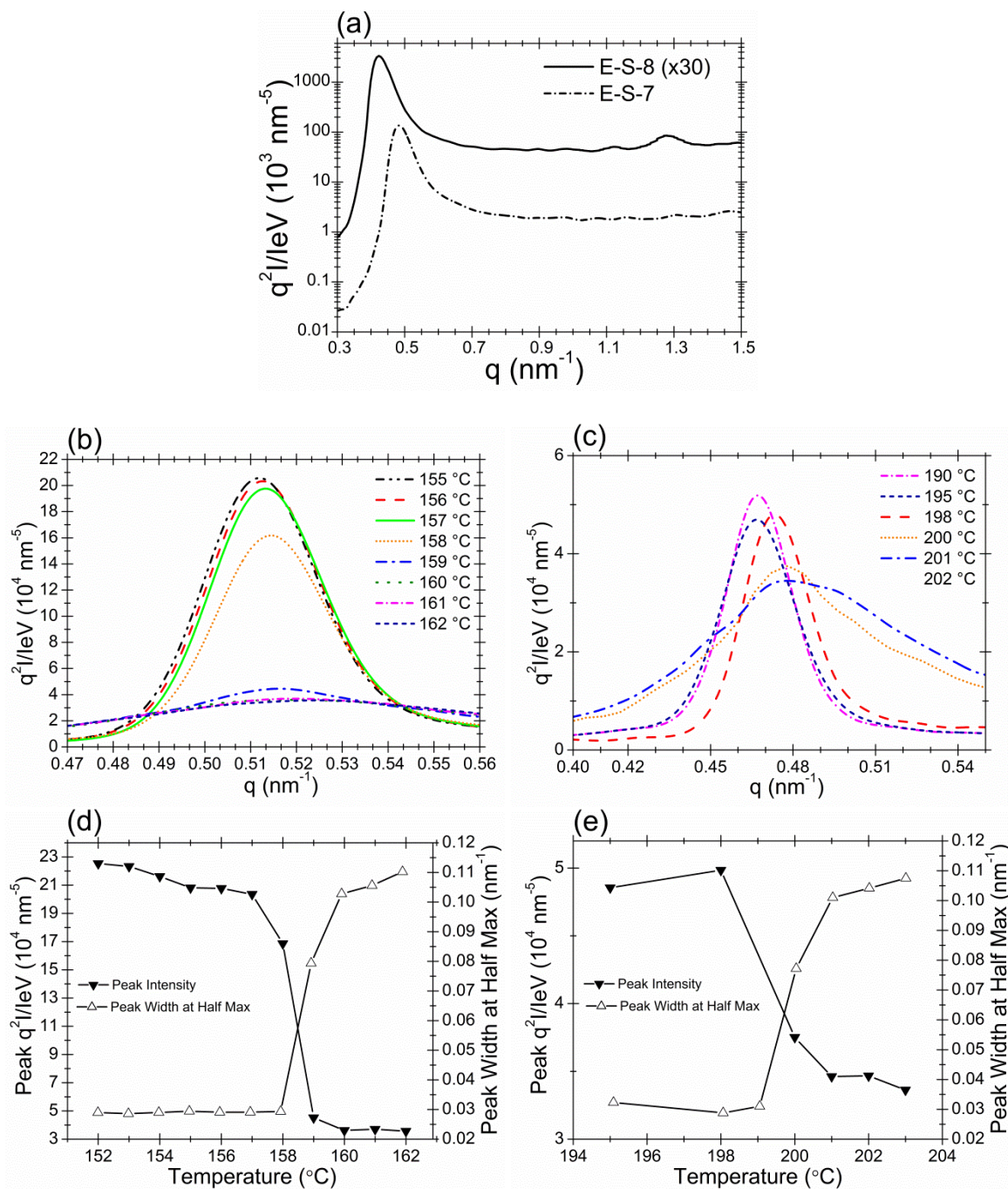


Figure S-2. (a) SAXS patterns for E-S-7 and E-S-8 at 120 °C; intensities for the latter have been multiplied through by 30 for clarity. SAXS patterns for (b) E-S-7 and (c) E-S-8 near T_{ODT} and (d) and (e) the corresponding primary peak intensities and peak widths, indicating $T_{ODT} = 159$ and 200 ± 1 °C, respectively.

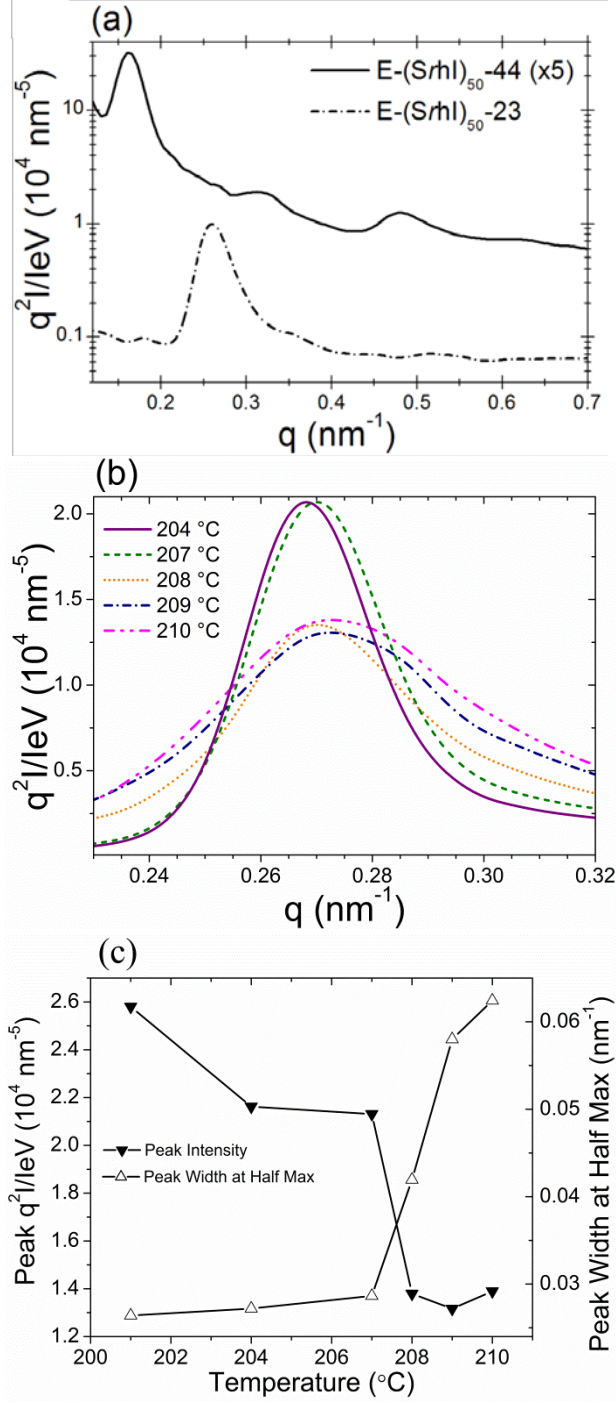


Figure S-3. (a) SAXS patterns for E-(Srhl)₅₀-44 and E-(Srhl)₅₀-23 at 185 ± 5 °C; intensities for the former have been multiplied through by 5 for clarity. (b) E-(Srhl)₅₀-23 near its order-disorder temperature, T_{ODT} . (c) E-(Srhl)₅₀-23 SAXS peak intensity (▼, left axis) and full width at half-maximum (Δ, right axis) plotted against temperature, indicating $T_{\text{ODT}} = 208 \pm 1^\circ\text{C}$.

References

- [1] Krishnamoorti, R.; Graessley, W. W.; Dee, G. T.; Walsh, D. J.; Fetters, L. J.; Lohse, D. J. *Macromolecules* **1996**, *29*, 367-376.
- [2] Krishnamoorti, R. *Ph.D. Thesis*; Princeton University, 1994.
- [3] Richardson, M. J.; Savill, N. G. *Polymer* **1977**, *18*, 3-9. This reference contains correlations of V (not $\ln V$) as quadratic equations in T . The correlation for the “liquid” density for a PS with $M_w = 111$ kg/mol, $M_w/M_n < 1.1$, was used to calculate V at every 1 °C from 100-210 °C, corresponding roughly to the range over which the V measurements were made, and those values were fit to Equation [S-1] to obtain the values of A , B , and C in Table S-1.
- [4] Reichart, G. C. *Ph.D. Thesis*; Princeton University, 1997.
- [5] Zoller, P.; Walsh, D. J. *Standard Pressure-Volume-Temperature Data for Polymers*; Lancaster, PA: Technomic Publishing Co., 1995.
- [6] This equation is assumed also to hold for lightly-branched polyethylenes, such as hydrogenated low-vinyl polybutadiene. This assumption is bolstered by the limited thermal expansion coefficient data presented in Graessley, W. W.; Krishnamoorti, R.; Balsara, N. P.; Butera, R. J.; Fetters, L. J.; Lohse, D. J.; Schulz, D. N.; Sissano, J. A. *Macromolecules* **1994**, *27*, 3896 (1994): $\alpha = 7.45 \times 10^{-4} \text{ K}^{-1}$ at 121 °C and $7.65 \times 10^{-4} \text{ K}^{-1}$ at 167 °C, which interpolate to $7.62 \times 10^{-4} \text{ K}^{-1}$ at 160 °C. Data given by Zoller and Walsh in reference [5] for branched (low-density) polyethylene yield slightly higher melt densities: $A = 0.2564$, $B \times 10^4 = 7.32 \text{ K}^{-1}$, $C \times 10^8 = 27 \text{ K}^{-2}$). Note that the fit parameters in Table S-1 yield a density for amorphous polyethylene at 23 °C of 0.860 g/cm³.