

Melt Miscibility in Diblock Copolymers Containing Polyethylene and Substituted Hydrogenated Polynorbornenes

William D. Mulhearn and Richard A. Register*

Department of Chemical and Biological Engineering, Princeton University,
Princeton, New Jersey 08544, United States

* corresponding author: tel +1 609 258 4691; fax +1 609 258 0211; e-mail register@princeton.edu

Diimide Hydrogenation of Polynorbornenes

Polymers containing aromatic groups were hydrogenated using the olefin-selective diimide method.¹ The polymer, 0.5 wt% of BHT to polymer, and 2 molar equivalents each of *p*-toluenesulfonyl hydrazide (TSH) and tripropylamine (TPA) per olefinic site in the polymer, were dissolved in xylenes and heated under reflux. Subsequent charges of TSH and TPA were added if necessary.

The two species of aromatic-containing polymers studied here, poly(phenyl norbornene) (PPhN) and poly(phenyl ethyl norbornene) (PPhEN), undergo complete saturation of olefinic sites after a single charge of TSH and TPA as described above. ¹H NMR spectra illustrating the diimide hydrogenation of PPhN are shown in Figure S1. The unhydrogenated polymer contains aromatic, olefinic, and aliphatic protons in a ratio of 5.05 : 2.00 : 7.06 (the repeat unit structure implies a ratio of 5 : 2 : 7). These small deviations (~1%) from the expected intensities are typical, and can be attributed to imperfect baseline subtraction and the difficulty of precisely removing peaks corresponding to small molecules (*e.g.*, water is nearly always present in the

NMR solvents). The hydrogenated polymer contains aromatic and aliphatic protons in a ratio of 5.00 : 11.14 (hPPhN with no loss of aromatic protons should have a ratio of 5 : 11). The measured excess of aliphatic protons implies that slightly less than 1% of aromatic rings in the PPhN were hydrogenated; however, this value is within the ^1H NMR measurement uncertainty.

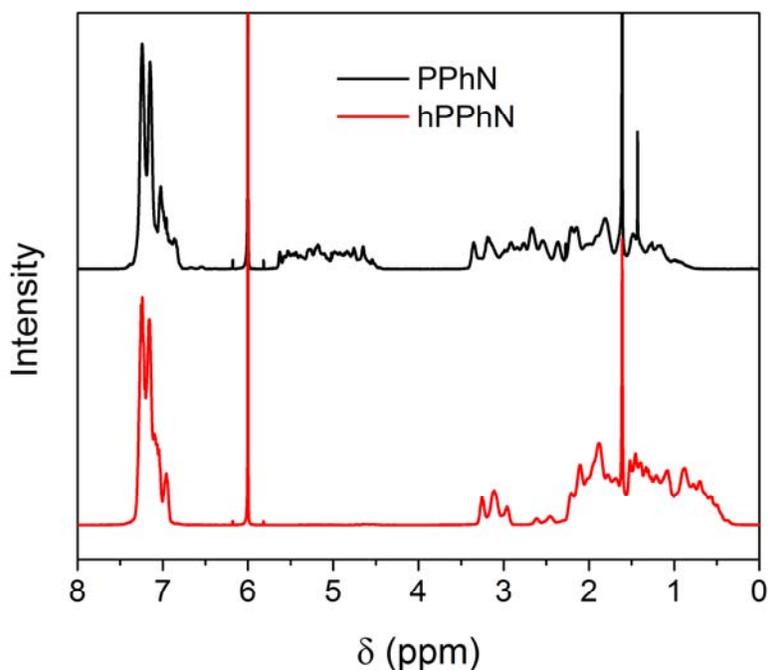


Figure S1. ^1H NMR spectra in 1,1,2,2-tetrachloroethane- d_2 (solvent $\delta = 6.0$ ppm) of PPhN before (black) and after (red) diimide hydrogenation (1 charge) to hPPhN. Aromatic protons appear at $\delta = 6.5\text{--}7.5$ ppm, olefinic protons at $\delta = 4.5\text{--}5.5$ ppm, and aliphatic protons at $\delta = 0.4\text{--}3.5$ ppm. Small-molecule impurities appear as narrow, intense peaks: water at $\delta = 1.6$ ppm and cyclohexane at $\delta = 1.4$ ppm.

Diimide hydrogenation of certain other ROMP polynorbornenes proceeded more slowly. For example, poly(norbornyl norbornene) (PNbN) required 9 charges of TSH and TPA before

residual olefinic protons became undetectable. The diimide hydrogenation of PNbN is illustrated by the ^1H NMR spectra in Figure S2.

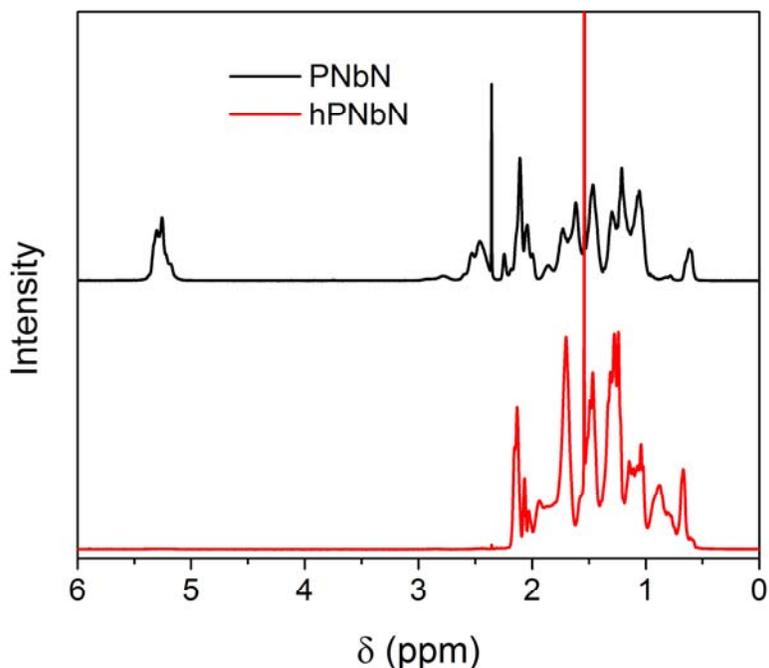


Figure S2. ^1H NMR spectra in chloroform- d of PNbN before (black) and after (red) diimide hydrogenation (9 charges) to hPNbN. Olefinic protons at $\delta = 5\text{--}5.5$ ppm, and aliphatic protons at $\delta = 0.5\text{--}3$ ppm. Small-molecule impurities appear as narrow, intense peaks: toluene at $\delta = 2.4$ ppm and water at $\delta = 1.6$ ppm.

Diimide hydrogenation does not result in measurable degradation or coupling of the polymer. GPC chromatograms for the PPhN/hPPhN and PNbN/hPNbN samples described above are shown in Figure S3. The elution times of the unhydrogenated and hydrogenated species are shifted for PNbN/hPNbN, reflecting a difference in hydrodynamic volume following backbone saturation, but the peak shapes and breadths remain unchanged in both cases. Both PPhN and PNbN contain small amounts of coupled polymer (secondary population at shorter elution time),

which remains in the hydrogenated samples. This is likely attributable to small amounts of difunctional monomer species or to trace amounts of oxygen introduced during termination.²

Elemental analysis for sulfur was performed by Galbraith Laboratories (Knoxville, TN) on the hydrogenated hPPhN and hPNbN samples. The hPPhN contained 125 ppm of sulfur and the hPNbN contained 697 ppm of sulfur, associated with a side reaction in which the *p*-toluene sulfinate fragment from decomposition of TSH to diimide adds to an olefinic site in the polymer.¹ These levels of sulfur addition are small and not expected to significantly alter the mixing thermodynamics of the hydrogenated product. For example, considering a 50 kg/mol polymer, 125 ppm of sulfur corresponds to an average of 1 sulfur per 5 chains and 697 ppm of sulfur corresponds to an average of 1 sulfur per chain.

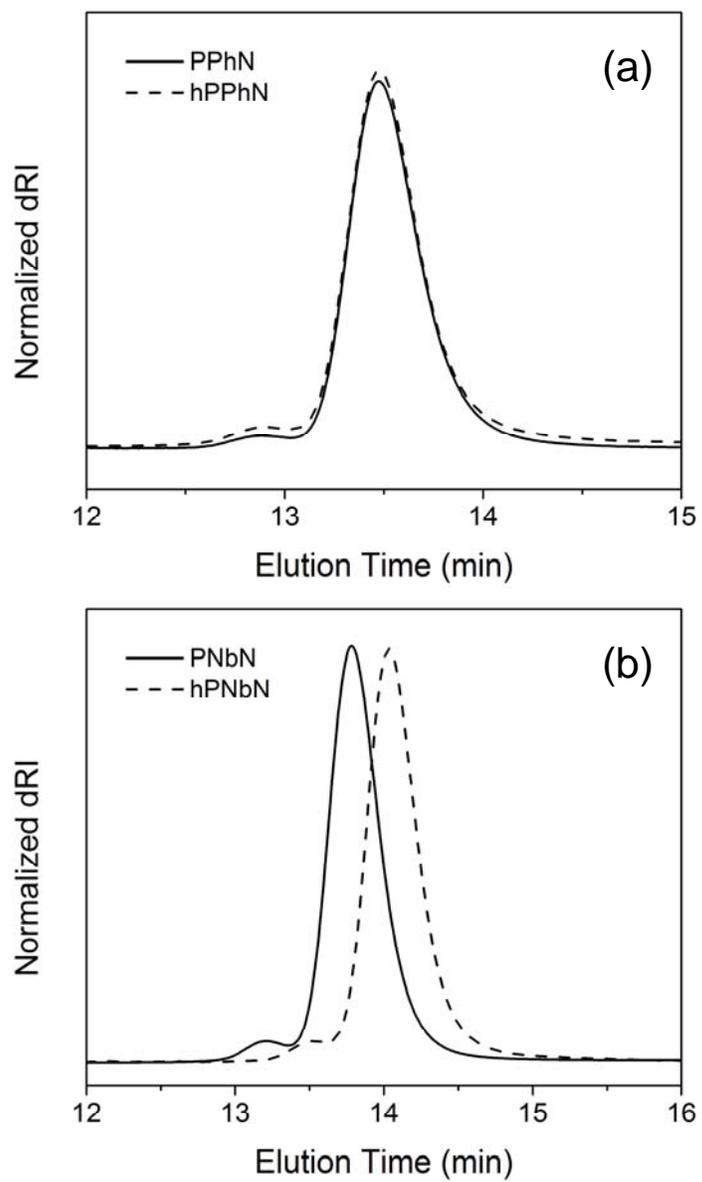


Figure S3. GPC chromatograms of (a) PPhN ($M_n = 56$ kg/mol) and (b) PNbN ($M_n = 57$ kg/mol) before (solid) and after (dashed) diimide hydrogenation.

Ellipsometry

Thermal expansion coefficients, α , were measured via ellipsometry (Woollam M-2000 spectroscopic ellipsometer) on polymer films. After annealing under vacuum above T_g for 6 h, films were cooled from ~ 50 °C above T_g to ~ 50 °C below T_g at a rate of 10 °C/min, and then heating back to ~ 50 °C above T_g at a rate of 2 °C/min. (Polymers with T_g much less than ambient temperature were instead cooled to 23 °C and then heated.) Glass and melt thermal expansion coefficients were calculated from the heating curve, by a best fit of the data far from T_g to the equation

$$h = h_0 e^{\alpha t} \quad (\text{S1})$$

Here, t is the temperature in °C and h is the film thickness, where h_0 is the extrapolated film thickness at $t = 0$ °C. The measured α values were corrected to account for very minor thermal expansion of the silicon substrate³ and data for the glassy state were corrected to account for thermal stresses imparted to the film upon heating,³ estimating that Poisson's ratio was $\sim 1/3$. As an example, the heating curve for an hPNbN film ($M_n = 57$ kg/mol, $D = 1.06$) is shown in Figure S4. Fits to the glass and melt portions of the data are shown, and the extrapolated intersection of these nearly linear ranges (120 °C) is close to the measured T_g by DSC for hPNbN (115 °C).

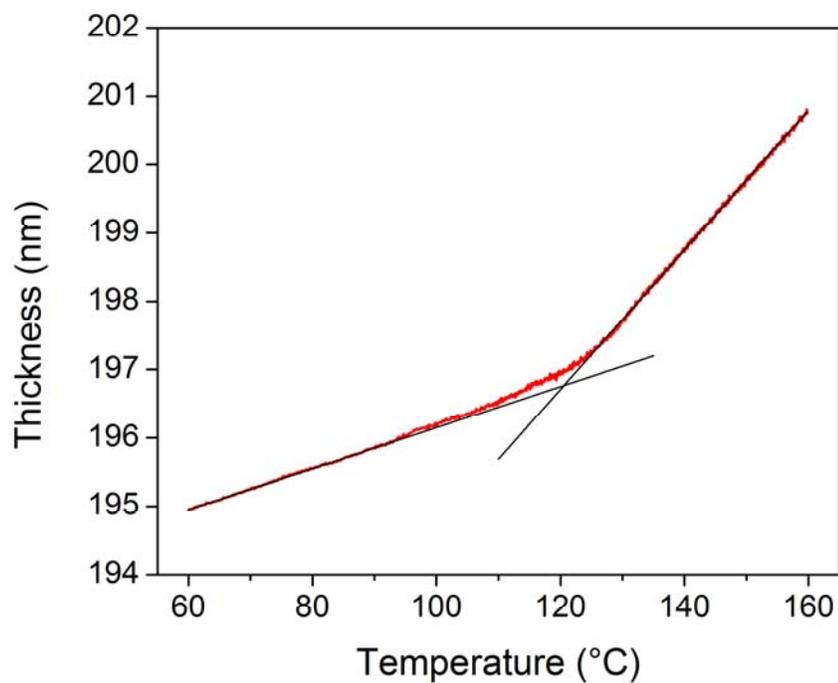


Figure S4. Ellipsometry of hPNbN ($M_n = 57$ kg/mol, $D = 1.06$), collected on heating at 2 °C/min. Fits to the glass and melt portions of the data are shown as solid black lines, corresponding to $\alpha_{\text{glass}} = 1.58 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_{\text{melt}} = 5.14 \times 10^{-4} \text{ K}^{-1}$. These values were subsequently corrected³ to $\alpha_{\text{glass}} = 2.42 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_{\text{melt}} = 5.20 \times 10^{-4} \text{ K}^{-1}$, in order to account for substrate expansion and thermal stresses imparted to the glassy polymer.

Plateau Modulus Measurements

Plateau moduli were measured using a Rheometrics RSA-3 dynamic mechanical analyzer, in a shear-sandwich geometry. The plateau modulus, G_0 , was identified as the value of G' at which G'' was at its minimum.^{4,5}

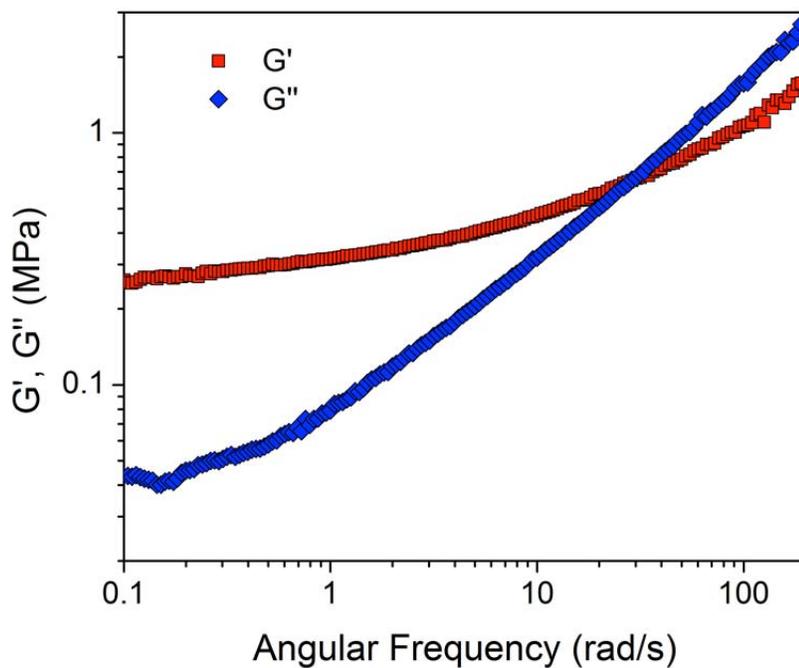


Figure S5. Dynamic mechanical analysis of hPCyN ($M_n = 252$ kg/mol, $\mathcal{D} = 1.23$) at 120 °C. The minimum in G'' occurs at $\omega = 0.15$ rad/s, corresponding to $G' = 0.27$ MPa.

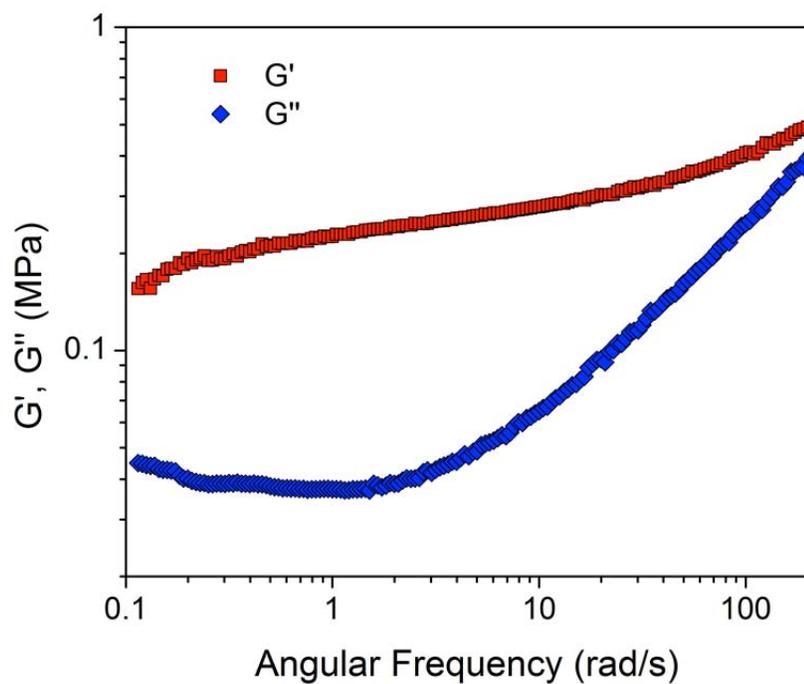


Figure S6. Dynamic mechanical analysis of hPNbN ($M_n = 247$ kg/mol, $D = 1.14$) at 160 °C. The minimum in G'' occurs at $\omega = 1.14$ rad/s, corresponding to $G' = 0.22$ MPa.

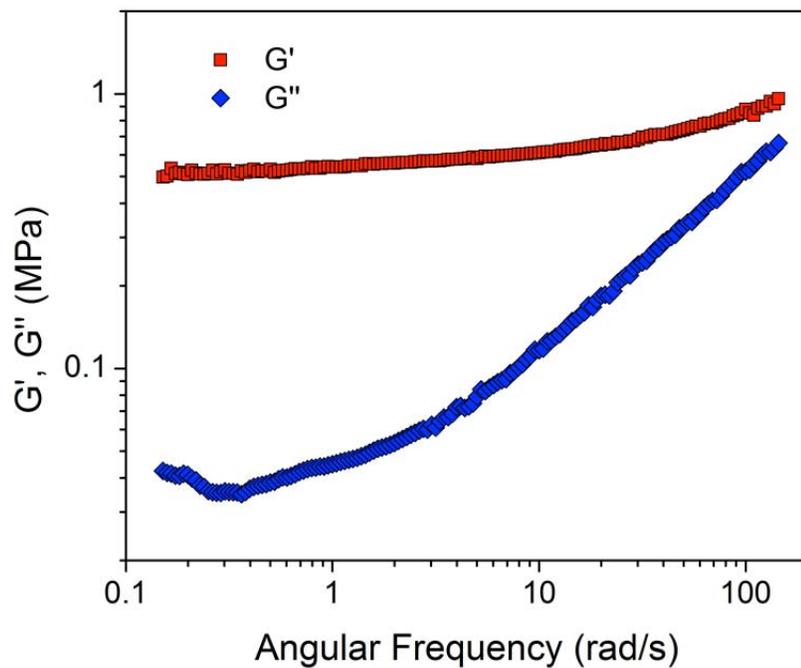


Figure S7. Dynamic mechanical analysis of hPPhN ($M_n = 278$ kg/mol, $D = 1.09$) at 100 °C. The minimum in G'' occurs at $\omega = 0.36$ rad/s, corresponding to $G' = 0.52$ MPa.

Additional SAXS Patterns Upon Heating Through T_{ODT}

Two additional sets of small-angle X-ray scattering patterns upon heating through the order-disorder transition temperature are shown below. These were collected following the same procedure described in the Article, and are analogous to Figure 2. The patterns correspond to hPiPrN-PE (Figure S8) as an example of a high-molecular-weight diblock copolymer ($M_n = 127$ kg/mol), and hPDcN-hPPhN (Figure S9) as an example of a low-molecular-weight diblock copolymer ($M_n = 13.7$ kg/mol). In both cases, T_{ODT} was identified by a sharp decrease in primary peak intensity and increase in primary peak breadth with changing temperature.

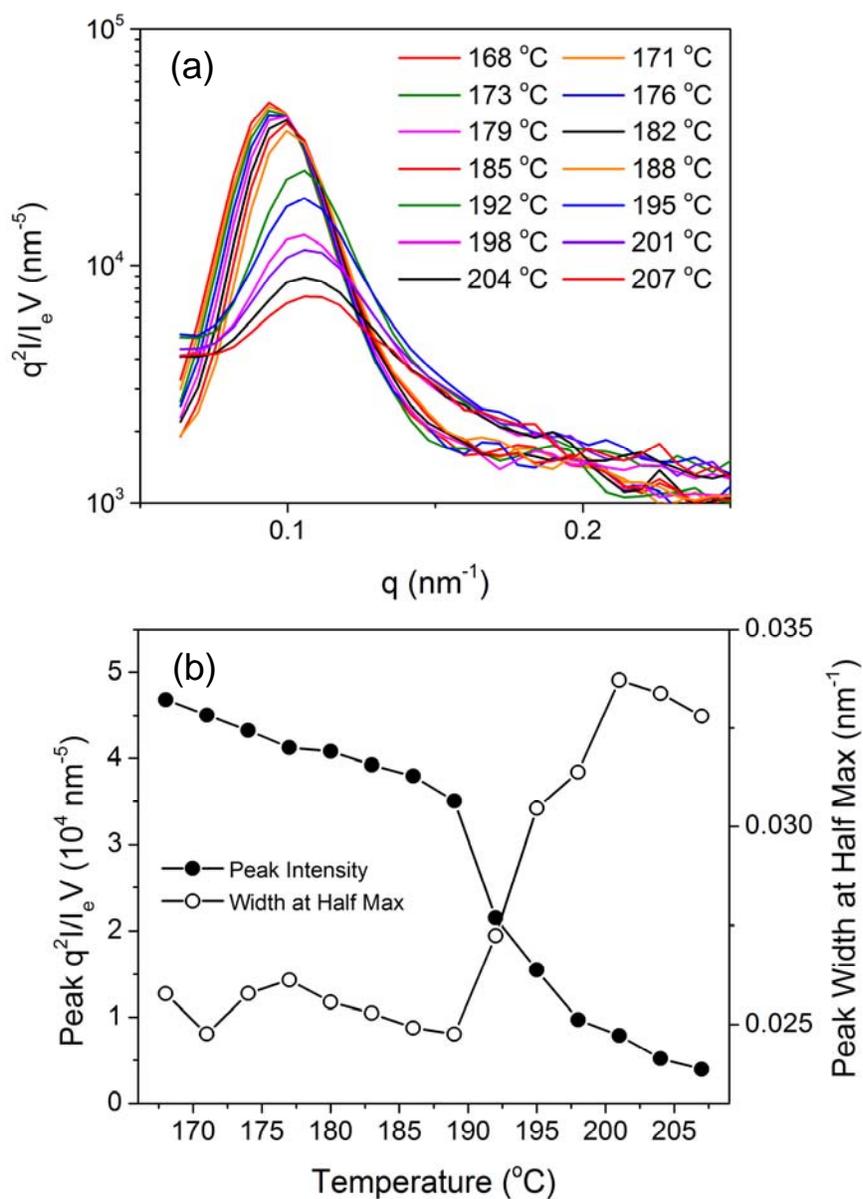


Figure S8. Order-disorder transition determined for a 127 kg/mol hPiPrN-PE diblock by SAXS;

$T_{ODT} = 190 \pm 3$ °C. (a) SAXS patterns in the region of the primary peak, on heating through T_{ODT} . (b) SAXS primary peak intensity (left axis) and full width at half maximum (right axis) on heating through T_{ODT} .

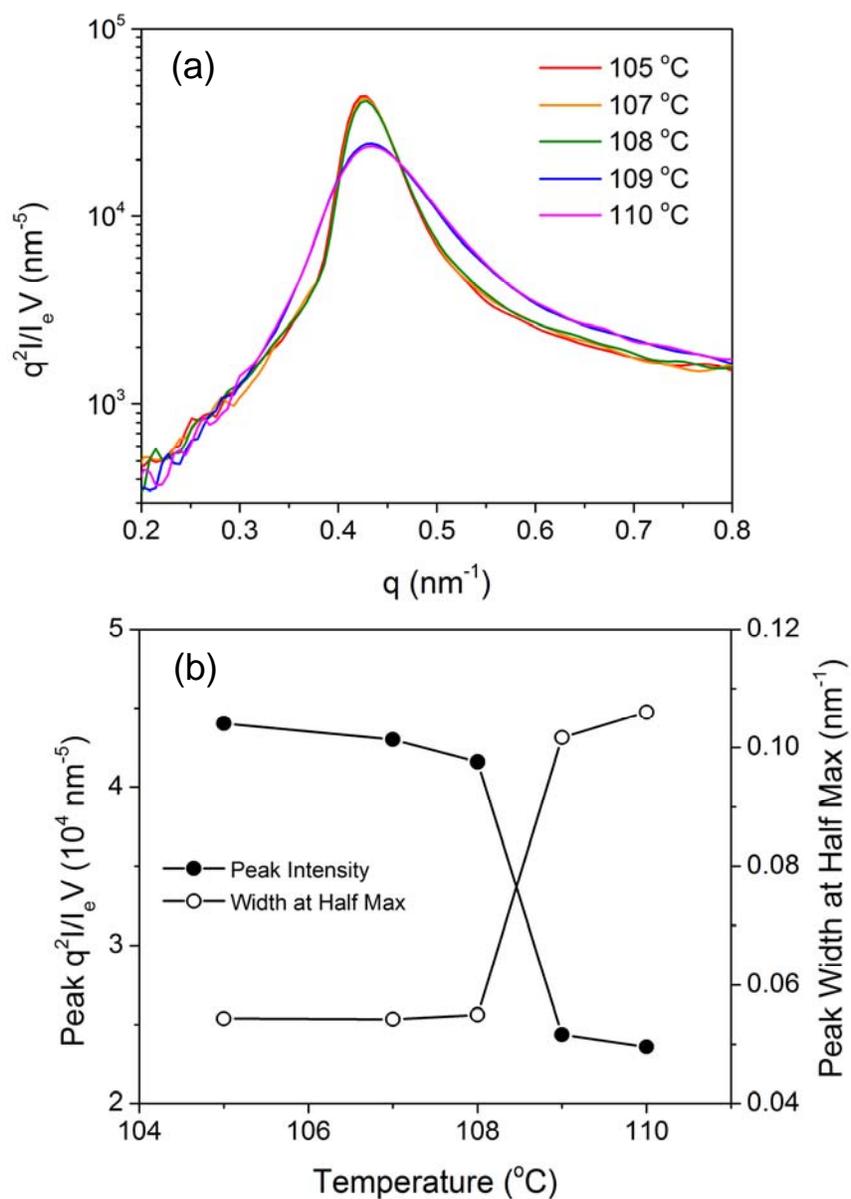


Figure S8. Order-disorder transition determined for a 13.7 kg/mol hPiPrN-PE diblock by SAXS;

$T_{\text{ODT}} = 109 \pm 1 \text{ }^{\circ}\text{C}$. (a) SAXS patterns in the region of the primary peak, on heating through T_{ODT} . (b) SAXS primary peak intensity (left axis) and full width at half maximum (right axis) on heating through T_{ODT} .

DSC Measurements of hPCyN-hPNbN Blends

The interaction energy density for hPCyN-hPNbN was measured by preparing a series of polymer blends and testing for phase separation by DSC. Each blend was composed of hPCyN and hPNbN homopolymers of comparable molecular weights, close to the composition of the critical point, and these were annealed at 150 °C to facilitate phase equilibration. A blend of 122 kg/mol hPCyN and 123 kg/mol hPNbN with $\phi_{\text{hPCyN}} = 0.50$ remained single-phase, while a blend of 122 kg/mol hPCyN and 158 kg/mol hPNbN with $\phi_{\text{hPCyN}} = 0.52$ phase-separated, as illustrated in Figure S10.

The glass transition temperature of the single-phase blend is 103 °C (half-height of the ΔC_p step), very close to the Fox equation⁶ prediction for a blend of this composition, $T_{g,\text{Fox}} = 100$ °C. The two glass transitions of the phase-separated blend occur at 81 °C and 114 °C, also close to the expected glass transition temperatures of the homopolymers (86 °C and 115 °C, respectively).

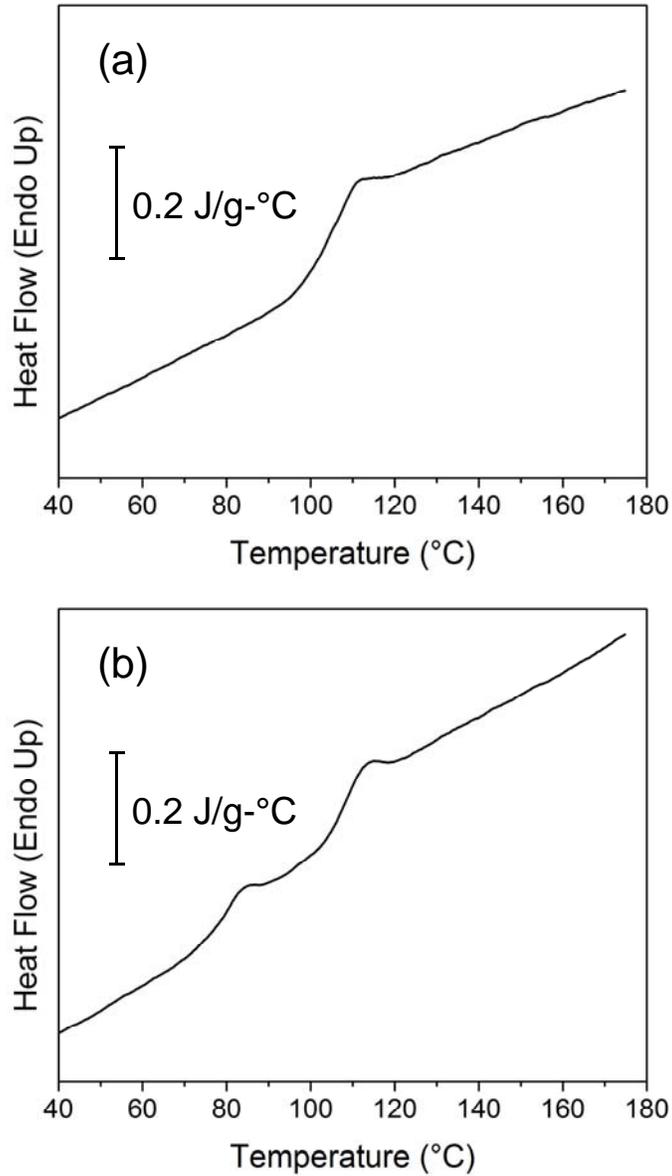


Figure S10. DSC traces of (a) 122 kg/mol hPCyN and 123 kg/mol hPNbN with $\phi_{\text{hPCyN}} = 0.50$ (single-phase), and (b) 122 kg/mol hPCyN and 158 kg/mol hPNbN with $\phi_{\text{hPCyN}} = 0.52$ (phase-separated).

Solubility Parameters and Empirical Mixing Parameters

The family of polymers consisting of polyethylene (PE) and substituted polynorbornenes were compared with the regular solution model, $X = (\delta_1 - \delta_2)^2$; with the regular solution model modified to account for a mismatch in thermal expansion coefficients, $X = (\delta_1 - \delta_2)^2 + \kappa(\alpha_1 - \alpha_2)^2$, where the best agreement with the data occurs when $\kappa = 5.5 \times 10^6 \text{ MPa-K}^2$; and with an empirical power-law mixing rule, $X = (\gamma_1 - \gamma_2)^{1.5}$. The best-fit pure-component parameters, δ and γ , for each species are listed in Table S1. All parameters are assigned relative to a reference, δ_{ref} or γ_{ref} , with PE taken as the reference material in all cases.

Table S1. Pure-component parameters, δ and γ , obtained from the best fit to the regular mixing model, accounting for a thermal expansion coefficient mismatch, $X = (\delta_1 - \delta_2)^2 + \kappa(\alpha_1 - \alpha_2)^2$, or to an empirical power-law mixing rule, $X = (\gamma_1 - \gamma_2)^{1.5}$.

Polymer	$\delta - \delta_{\text{ref}} \text{ (MPa}^{1/2}\text{)}$		$\gamma - \gamma_{\text{ref}} \text{ (MPa}^{0.67}\text{)}$
	$\kappa = 0 \text{ MPa-K}^2$	$\kappa = 5.5 \times 10^6 \text{ MPa-K}^2$	
PE	0	0	0
hPDcN	0.298	0.217	0.399
hPHxN	0.221	0.102	0.320
hPiPrN	0.381	0.267	0.500
hPMeN	0.618	0.225	0.646
hPCyN	0.875	0.736	1.106
hPNbN	1.052	0.887	1.352
hPPhEN	1.871	1.778	2.251
hPPhN	2.313	2.188	2.930

References

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