Effect of Saturation on Thermodynamics of Polystyrene–Polyisoprene Block Copolymers

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Received September 28, 1993; Revised Manuscript Received November 24, 1993®

ABSTRACT: The effect of saturation on thermodynamic interactions in polystyrene–polyisoprene (SI) diblock copolymers is examined by small-angle neutron scattering (SANS) and birefringence. Experiments were conducted on an SI sample in which both blocks had molecular weights of 7.5×10^3 and its saturated product—a poly(vinylcyclohexane)–poly(methylbutylene) block copolymer (HSHI). The SANS data show a reversal in miscibility in the vicinity of 96 °C. Above this temperature, the Flory–Huggins interaction parameter, χ, is higher in the HSHI polymer than in the SI polymer, while the reverse is true at temperatures below 96 °C. The high-temperature result is consistent with published data of Gehlsen and Bates, while the low-temperature result is confirmed by birefringence measurements presented here.

Introduction

There have been several experimental investigations of thermodynamic interactions in blends and block copolymers of chemically distinct polyolefins.[1-4] The large body of information available on mixtures of saturated hydrocarbons is due, in part, to the pioneering work of Rachapudy et al.,[5] who devised a simple method for synthesizing nearly monodisperse model polyolefins. The method consists of saturation of the double bonds in anionically polymerized polydienes using palladium catalysts and has successfully yielded model polypropylene as well as ethylene–propylene and ethylene–butene copolymers. Recently, Gehlsen and Bates have studied the effect of changing the supporting material and have shown that $Pd/BaSO_4$ catalysts can be used to hydrogenate the double bonds in polystyrene to give model poly(vinylcyclohexane) polymers.[6] They also examined the rheological properties of a polystyrene–polyisoprene block copolymer (SI) and a hydrogenated polymer derived from it—a poly(vinylcyclohexane)–poly(methylbutylene) block copolymer (HSHI). The molecular weights of the polystyrene and polyisoprene blocks were 9×10^3. Gehlsen and Bates found that the order–disorder transition (ODT) in the HSHI block copolymer occurred at a *higher* temperature than that of the parent SI.

We examined the phase behavior of a lower molecular weight SI (with block molecular weights = 7.5×10^3) and its hydrogenated counterpart and found the opposite effect, namely, that the ODT temperature of the HSHI polymer was *lower* than that of the parent SI. The difference between our result and that of Gehlsen and Bates was resolved by small-angle neutron scattering (SANS) experiments. These data, when recast in terms of Flory–Huggins interaction parameters, χ, show a reversal in miscibility at ca. 96 °C. Above this temperature we find that χ_{HSHI} is larger than χ_{SI}, while the opposite is true at lower temperatures.

Synthesis and Characterization of Polymers

A polystyrene–polyisoprene diblock copolymer was synthesized by anionic polymerization under high vacuum in a benzene/cyclohexane mixture, using *sec*-butyllithium as the initiator and methanol as the terminator. The polystyrene block was synthesized first, followed by the polymerization of the polyisoprene block. An aliquot of the reaction mixture containing the poly(styryllithium) anions (precursors) was isolated and terminated with methanol before the addition of the isoprene. The molecular weight and polydispersity of the polystyrene block was obtained from GPC measurements on the polystyrene precursor. The GPC was calibrated using polystyrene standards. The composition of the block copolymer was obtained by ^1H NMR spectroscopy. The polydispersity of the block copolymer was estimated from GPC measurements using the polystyrene calibration curve. The polydispersities of the polystyrene precursor as well as the block copolymer were less than 1.07. The reaction conditions used here give a predominantly (93%) 1,4-polyisoprene block. A small amount (<0.5%) of 2,6-di-*tert*-butyl-4-methylphenol was added to the block copolymer to prevent degradation of the polyisoprene block.

Table 1. Characteristics of Polymers Used in This Study

sample desig	mol wt of S or HS block	mol wt of I or HI block	polydispersity[a]	glass transition onset (°C)	glass transition end point (°C)
SI(7.5–7.5)	7500	7500	1.07	61	71
HSHI(7.9–7.7)	7900	7700	1.08	68	90

[a] Uncorrected for column dispersion.

A portion of the block copolymer was subjected to catalytic hydrogenation in cyclohexane using a $Pd/BaSO_4$ catalyst at 250 psi and 100 °C. The GPC traces of both polymers were essentially superposable, indicating that no large-scale alteration of the structure had occurred during hydrogenation. The lack of a C=C signal in the ^1H NMR spectra confirmed complete saturation (>99.9%). The polymers were precipitated in methanol/acetone mixtures, redissolved in benzene, filtered through 0.2-μm filters, and isolated by freeze-drying. Both samples are expected to have lamellar microphases in the ordered state owing to their symmetric structure.

DSC scans on a Perkin-Elmer Series 7 instrument at 10 °C/min from both polymers in the temperature range 0–180 °C revealed a single glass transition. For the SI polymer, the onset of the glass transition occurred at 61 °C and the end point occurred at 71 °C. A much broader glass transition was observed in the HSHI polymer with an onset point at 68 °C and an end point at 90 °C. The observed transitions were independent of thermal history.

The characteristics of the SI and HSHI polymers are summarized in Table 1.

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® Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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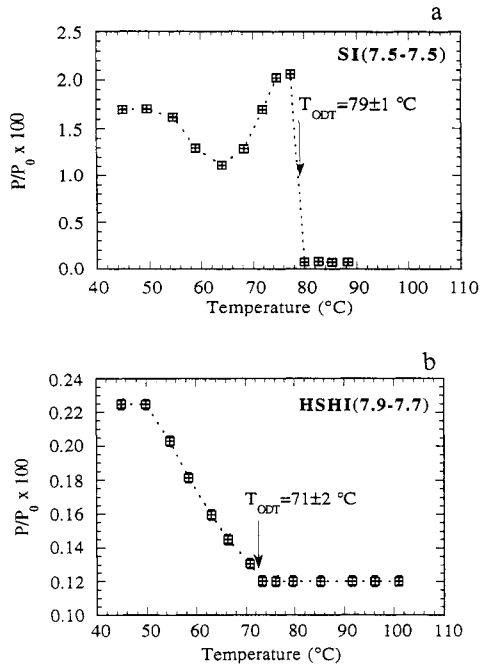

Figure 1. Dependence of birefringence (P/P_0) on temperature for (a) SI(7.5–7.5) and (b) HSHI(7.9–7.7). The error bars in (b) represent typical fluctuations after the signal has reached "steady state".

Birefringence Detection of the Order–Disorder Transition

The relationship between birefringence and the granular organization in ordered block copolymer materials has been established both experimentally[7–10] and theoretically.[7,10,11] Balsara and co-workers have shown if an ordered sample consisting of randomly oriented lamellar grains is illuminated with plane polarized light, then the fraction of incident power transmitted through a crossed polarizer, P/P_0 (P is the transmitted power and P_0 is the incident power), is given by[7,10]

$$\frac{P}{P_0} = \frac{4\pi^2}{15}(\Delta n)^2 \frac{L l_{av}}{\lambda^2} \qquad (1)$$

where Δn is the difference in refractive index for light polarized parallel and perpendicular to the optical axis of a single grain, L is the sample thickness (path length of the beam), l_{av} is the characteristic size of the grains, and λ is the wavelength of the light. Equation 1 is restricted to samples with small birefringence ($P/P_0 \ll 1$).[7,10] Milner has recently extended this result and derived an expression for samples with arbitrarily large birefringence.[11] The birefringence of disordered materials must be zero (or nearly so).[8–10] Thus the ODT can be unambiguously identified as the temperature at which P/P_0 decreases to zero.

The freeze-dried polymer samples were placed in glass cuvettes (0.74-cm inner diameter) and annealed in a vacuum oven at 100 °C. This caused the polymers to flow to the bottom of the cuvette and form bubble-free, transparent "plugs". The cuvettes were heat sealed and the birefringence of the encased samples were measured on an instrument described elsewhere.[7] The experiment consisted of illuminating the samples with plane polarized light (λ = 632.8 nm), and the fraction of incident of power transmitted through a crossed polarizer was recorded. The samples, initially at room temperature, were subjected to a series of temperature jumps, and the steady-state values of P/P_0 obtained at different temperatures are shown in Figure 1. The time required to reach steady state after each temperature jump was ca. 1 h. The response of SI(7.5–7.5) shows an initial decrease in birefringence with increasing temperature (see Figure 1a). At temperatures well below the glass transition, the grain structure is probably locked in (i.e., l_{av} is independent of temperature) and the decrease in the birefringence is attributed to increased mixing between the isoprene and styrene monomers in regions of the sample that have mobility (i.e., a decrease in Δn). As the glass transition is approached, the birefringence increases with increasing temperature, indicating an increase in the average grain size, which may be due to the elimination of high free energy defects, before it abruptly drops to a value close to zero between 78 and 80 °C. We thus conclude that the ODT of SI(7.5–7.5) is 79 ± 1 °C.

The relationship between average grain size and thermal history has been discussed in previous publications.[7,9,10] Since the birefringence depends on grain structure (i.e., l_{av}), different P/P_0 versus T trajectories can be obtained from the same sample if it is subjected to different thermal histories. Note that both Δn and l_{av} can change in response to a temperature increase. Several different thermal histories were imposed on SI(7.5–7.5). However, all of the P/P_0 versus temperature data converged to zero at temperatures between 78 and 80 °C, indicating that the lamellar structure is destroyed at the same temperature, regardless of the granular organization. This is expected because the ODT is predicted by theory to be a weakly first-order transition[12,13] and should not depend on grain size. The trajectory shown in Figure 1a was obtained from a sample that was first disordered, then annealed at 75 °C for 30 min (a temperature which is in the ordered region of the phase diagram but above the glass transition, to facilitate the formation of well-defined lamellae), and then quenched to room temperature.

In Figure 1b we show the result of birefringence measurements on the HSHI sample. It is evident that the birefringence from HSHI(7.9–7.7) decreases to a value close to zero between 69 and 73 °C, and thus the ODT of HSHI(7.9–7.7) is 71 ± 2 °C. However, this point is very close to the onset of the glass transition. Due to decreased mobility at this temperature, the defect density in the ordered HSHI sample is expected to be large. Also, the refractive index difference between the two polyolefinic blocks is expected to be lower than that between polystyrene and polyisoprene. This implies that both Δn and l_{av} in this sample are expected to be small, and thus it is not surprising that the birefringence of ordered HSHI(7.9–7.7) is an order of magnitude lower than that of ordered SI(7.5–7.5) (see eq 1). Consequently, the ODT in HSHI is not accompanied by as sharp a drop in the signal as was observed in SI. Similar, nondiscontinuous changes in the sample birefringence at the ODT have been reported in the literature.[8,9,14] As was the case with the SI sample, different thermal histories led to different P/P_0 versus T trajectories. However, all of them converged to zero birefringence between 69 and 73 °C. The trajectory shown in Figure 1b was obtained from a sample that was first heated to 95 °C (above the ODT and the glass transition) and then quenched to room temperature.

These experiments indicate that the ODT temperature of HSHI(7.9–7.7) is lower than that of SI(7.5–7.5). This result of greater miscibility in HSHI relative to SI is opposite to that of Gehlsen and Bates.[6]

Small-Angle Neutron Scattering

We also performed small-angle neutron scattering experiments on SI(7.5–7.5) and HSHI(7.9–7.7) over a range

of temperatures (83–167 °C) to gain further information on the thermodynamics. Two-dimensional SANS patterns were obtained from 1-mm-thick samples held within quartz windows on the 8-m SANS machine (on the NG5 beam line) at the National Institute of Standards and Technology at Gaithersburg, MD. Neutrons with a wavelength λ = 9.0 Å ($\Delta\lambda/\lambda$ = 0.25) were used. The scattering data were corrected for background, empty cell scattering, and detector sensitivity, converted to an absolute scale using secondary standards provided by NIST, and azimuthally averaged. The absolute intensity calibration was verified using secondary standards developed by the Exxon/Princeton group[15] as well as standards developed by the Polytechnic group.[16] The incoherent scattering, I_{inc}, for each of the block copolymers was estimated from SANS measurements on a pure poly(methylbutylene) homopolymer, assuming that it is proportional to the concentration of H atoms in the copolymer, and substracted from the azimuthally averaged scattering profiles to give the coherent scattering intensity, $I(q)$ ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle). Measurements on many hydrocarbon polymers demonstrate that, within this class of polymers, I_{inc} does scale with H atom concentration.[15] The coherent intensity was thus obtained from the raw data without resorting to any adjustable parameters.

Flory–Huggins interaction parameters were estimated from SANS measurements, using the random phase approximation (RPA) due to Leibler.[12] In this approximation, the coherent scattered intensity from a block copolymer melt is given by

$$I(q) = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \left\{\frac{S_{11}^\circ + S_{22}^\circ + 2S_{12}^\circ}{S_{11}^\circ S_{22}^\circ - (S_{12}^\circ)^2} - \frac{2\chi}{v}\right\}^{-1} \quad (2)$$

where the subscripts 1 and 2 refer to the two blocks, b_i and v_i are the scattering lengths and volumes of the monomers in each block, χ is the Flory–Huggins interaction parameter based on a reference volume, v, and S_{ij}° are well-known ideal correlations between blocks i and j in the absence of interactions.

$$S_{ii}^\circ = \phi_i N_i v_i P_i(q) \qquad (i = 1,2) \quad (3a)$$

$$S_{12}^\circ = (\phi_1 N_1 v_1 \phi_2 N_2 v_2)^{1/2} F_1(q)\, F_2(q) \quad (3b)$$

N_i is the number of monomers in block i, ϕ_i is its volume fraction, and the functions $P_i(q)$ and $F_i(q)$ describe the intrablock and interblock correlations, respectively. Assuming Gaussian chains, we use the Debye function for $P_i(q)$ and the Leibler function[12] for $F_i(q)$.

$$P_i(q) = 2\frac{\exp(-x_i) - 1 + x_i}{x_i^2} \qquad (i = 1,2) \quad (4a)$$

$$F_i(q) = \frac{1 - \exp(-x_i)}{x_i} \qquad (i = 1,2) \quad (4b)$$

where $x_i = q^2 N_i l_i^2/6$ and l_i is the statistical segment length of species i.

Typical results for $I(q)$ obtained from SI(7.5–7.5) are shown in Figure 2, while those obtained from HSHI(7.9–7.7) are shown in Figure 3. The measured SANS profiles were fit to eq 2, using χ as the adjustable parameter. All other parameters in eqs 2–4 were estimated independently and are summarized in Table 2. The procedures used to obtain these parameters are given in the Appendix. $I(q)$ from the SI sample is an order of magnitude larger than that from the HSHI sample, due primarily to differences in scattering contrast. The neutron contrast between poly(vinylcyclohexane) and poly(methylbutylene) arises from

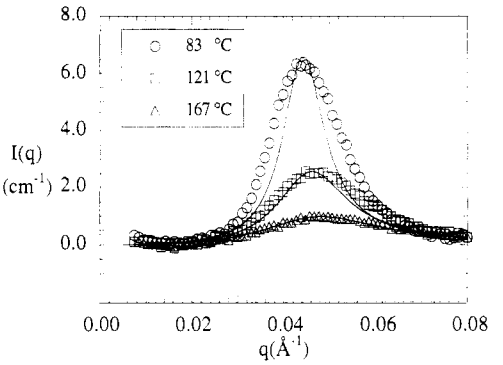

Figure 2. Coherent SANS intensity, $I(q)$, from SI(7.5–7.5) versus scattering vector, q, at selected temperatures. The solid curves through the data are best RPA fits from which χ parameters were obtained.

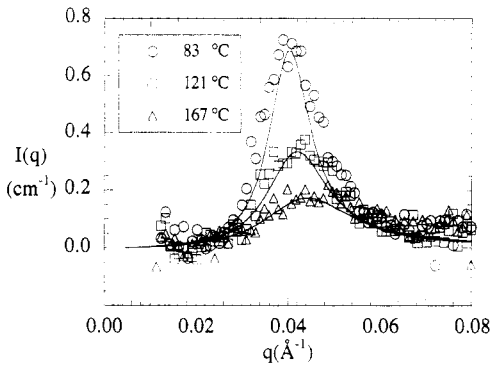

Figure 3. Coherent SANS intensity, $I(q)$, from HSHI(7.9–7.7) versus scattering vector, q, at selected temperatures. The solid curves through the data are best RPA fits from which χ parameters were obtained.

density differences, while that between polystyrene and polyisoprene blocks is augmented by differences in level of saturation (number of C=C bonds per unit volume). The solid curves through the data in Figures 2 and 3 represent the best theoretical fits. The theoretical curves at the lower temperatures are somewhat narrower than the experimental data, probably due to instrumental smearing.[17] The results of the fitting procedure for both polymers are given in Table 3. The geometric means of the monomer volumes at 83 °C were used as reference volumes. For comparison, χ_s, the Flory–Huggins interaction parameters at the spinodal point (i.e., the value of χ at which the theoretical $I(q)$ diverges), are also included in Table 3. One advantage of using the present definitions of N_i and v is that the χ_s values for both molecules are nearly identical ($\chi_s = 5.94 \times 10^{-2}$ for SI(7.5–7.5) and $\chi_s = 5.92 \times 10^{-2}$ for HSHI(7.9–7.7)).

The temperature dependence of χ/χ_s for the two polymers is shown in Figure 4. It is evident from Figure 4 that the χ parameters are approximately linear functions of $1/T$ (T is the absolute temperature). The following equations represent least squares fits through the SANS data and are represented by dashed lines in Figure 4.

$$\chi = 0.012 + 16.7/T \quad \text{for SI(7.5–7.5)} \quad (5a)$$

$$\chi = 0.024 + 12.2/T \quad \text{for HSHI(7.9–7.7)} \quad (5b)$$

Extrapolating these temperature dependences to $\chi/\chi_s = 1$ gives the following estimates for the spinodal points, i.e., the ODT temperatures:

$$T_{ODT,SANS} = 77\ °C \quad \text{for SI(7.5–7.5)}$$

$$T_{ODT,SANS} = 70\ °C \quad \text{for HSHI(7.9–7.7)}$$

These estimates are consistent with the ODT temperatures measured by birefringence which are represented

Table 2. List of Parameters Used To Obtain χ from SANS[a]

	I_{inc}[b] (cm^{-1})	N_1	N_2	v_1[b] (Å^3)	v_2[b] (Å^3)	b_1 (Å)	b_2 (Å)	α_1 (°C^{-1})	α_2 (°C^{-1})	l_1[b] (Å)	l_2[b] (Å)
SI(7.5–7.5)	1.07	72	110	179.7	125.7	2.32×10^{-4}	0.33×10^{-4}	5.5×10^{-4}	6.5×10^{-4}	7.8	8.1
HSHI(7.7–7.9)	1.32	72	110	196.9	136.4	0.08×10^{-4}	-0.42×10^{-4}	6.0×10^{-4}	6.0×10^{-4}	9.8	8.0

[a] Subscript 1 implies S or HS block; subscript 2 implies I or HI block. [b] At 83 °C. See text for estimation of these parameters at higher temperatures.

Table 3. χ Parameters for SI and HSHI Block Copolymers from SANS

temp (°C)	χ for SI(7.5–7.5)[a,c]	χ for HSHI(7.9–7.7)[b,c]
83	0.057_9	0.057_6
104	0.056_4	0.056_3
123	0.054_8	0.054_9
147	0.051_6	0.052_9
167	0.048_8	0.051_0
spinodal point	0.0594[d]	0.0592[d]

[a] Based on a reference volume, $v = 150.3$ Å^3. [b] Based on a reference volume, $v = 163.9$ Å^3. [c] Errors in χ are ±0.003, due to a ±5% uncertainty in molecular weight and a ±7% uncertainty in absolute calibration. However, the relative values of χ obtained from the SI and the HSHI polymers are not affected by these errors due to the synthesis protocol and the fact that the measurements were made back to back on the same instrument. [d] Calculated values based on the random phase approximation (see text).

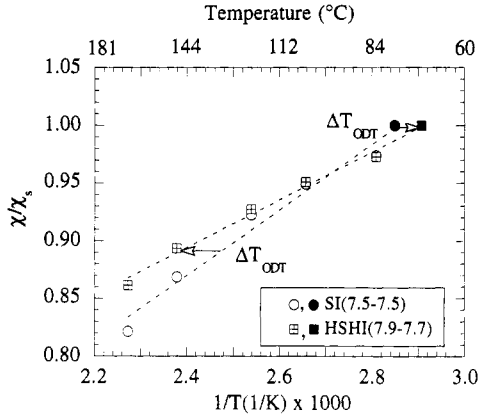

Figure 4. Dependence of χ/χ_s, the ratio of the SANS-determined Flory–Huggins interaction parameter at a given temperature to its value at the spinodal, on temperature, T, for the S/I and HS/HI systems. The dashed lines represent least squares linear fits through the data. The shift in the order–disorder transition temperature upon saturation, ΔT_{ODT}, of symmetric SI block copolymers can be estimated from the horizontal distance between the two lines. The solid symbols represent the spinodal points for SI (circles) and HSHI (squares) measured by the birefringence method.

by solid symbols in Figure 4. This implies that the mean field theory of Leibler is adequate for describing the thermodynamics of these block copolymers. This is surprising because for the short chains employed in this study fluctuation effects are expected to be important.[13] Perhaps the χ parameters in the SI and HSHI systems change rapidly enough with temperature that mean field theories are applicable relatively close to the spinodal temperature.

It is evident from Figure 4 that the use of birefringence to locate ODTs in block copolymers is analogous to the use of cloud point (light scattering) measurements to locate the onset of macrophase separation in binary mixtures. The consistency of optically determined cloud points and χ parameters determined from SANS in binary polymer blends was first demonstrated by Shibayama et al.[18]

The data in Figure 4 can be used to predict the change in the ODT of SI block copolymers upon hydrogenation (ΔT_{ODT}). The horizontal "difference" between the two lines is equal to the shift in the ODT upon saturation for symmetric SI block copolymers. Similar predictions, based on the random phase approximation can be made for asymmetric block copolymers, if χ is independent of composition. Note that ΔT_{ODT} changes sign in the vicinity of 96 °C. For an SI block copolymer with an ODT at 124 °C, a 11° *increase* is predicted upon hydrogenation; Gehlsen and Bates observed a 16 ± 4 °C increase.[6] Considering the fact that the polymers were synthesized in different laboratories and that there are uncertainties in the SANS measurements and polymer characterization, the agreement is reasonable. On the other hand, we predict a 10 °C *decrease* in the ODT for an SI polymer with an ODT at 78 °C. Our birefringence experiments show an 8 ± 3 °C decrease. The agreement is better because the above-mentioned uncertainties do not apply.

Concluding Remarks

We conclude by pointing out that the effect of saturation on the thermodynamic interactions between polystyrene and polyisoprene is surprisingly small, considering the large changes in monomer architecture and density that are caused by the saturation process. Our data indicate that the shift in the phase transition points in polystyrene/polyisoprene systems (ODTs in block copolymers and single-phase to two-phase transitions in homopolymer blends) is at most 22 °C in the temperature window between 70 and 167 °C. In contrast, over the same temperature range, phase transition points in polyolefin blends were shifted by as much as 70 °C when deuterium labels were simply switched from one polymer to another.[19,20] It is perhaps significant that the data from the HSHI block copolymer represent the first SANS estimates of χ parameters between chemically distinct polyolefins without deuterium substitution.

Acknowledgment. We acknowledge Bill Graessley for making the saturation apparatus at Princeton University available to us and NIST for providing us with instrument time on the SANS machine. We also thank John Barker, Charlie Glinka, and Charles Han of NIST for discussions and help during the SANS experiments. Financial support by grants from the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Education Foundation, and the National Science Foundation (Grant CTS-9308164) to Polytechnic University and a grant by the National Science Foundation (Grant DMR89-05187) to Princeton University is gratefully acknowledged.

Appendix: Parameter Estimation for SANS Data Analysis

The procedures employed here are similar to those of Balsara et al.[16] We have chosen to define the monomers as the chemical repeat units, i.e., C_8 units for the polystyrene and the poly(vinylcyclohexane) blocks and C_5 units for the polyisoprene and poly(methylbutylene) blocks. The quantities N_i and b_i were obtained directly from the chemical structure of the polymers, which, in turn, were obtained from GPC and NMR experiments. The monomer volumes (v_i) were calculated from room temperature densities of the homopolymers and thermal

expansion coefficients, $\alpha_i = d \ln v_i / dT$ (for materials in the rubbery state), given in Table 2.[21,22] The block copolymer composition ϕ_1 is equal to $N_1 v_1/(N_1 v_1 + N_2 v_2)$. The value of q at the maximum in the SANS intensity, q_m, was used to estimate the statistical segment lengths, l_i. The values obtained at 83 °C are given in Table 3. At higher temperatures, these values were changed at the same rate, so that the calculated and experimental q_m were in agreement. In the temperature range between 83 and 167 °C this amounts to a 10% decrease in l_i for both polymers. The statistical segment lengths obtained by this procedure are larger than those obtained from binary polymer blends.[6] Bates et al. have found similarly large l_i in their investigation of other hydrocarbon block copolymers near the order–disorder transition.[3] At this stage one can only speculate about the origin of this effect. Due to this uncertainty, the estimation procedures for χ were repeated with several different combinations of statistical segment lengths. The values of χ/χ_s were insensitive to the choice of statistical segment lengths.

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