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Anomalous Sorption in a Poly(styrene-*b*-isoprene) Diblock Copolymer near the Order−Disorder Transition

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According to the experimental phase diagram reported by Khandpur et al.[1] for poly(styrene-*b*-isoprene) (SI) diblock copolymers, the order−disorder transition (ODT) for lamellar SI copolymers with equal volume fractions of S and I repeat units occurs at a thermodynamic incompatibility (χN) of ≈18, in good agreement with theoretical predictions[2−6] for neat (unmodified) diblock copolymers. Here, χ denotes the Flory−Huggins interaction parameter and N is the number of statistical units along the copolymer backbone. Since χ scales as the reciprocal of temperature,[2] microstructural disorder can generally be induced in an ordered SI copolymer residing in either the weak- or intermediate-segregation regime through an increase in temperature, as verified by, e.g., small-angle scattering[7−14] and rheological[8,10,15,16] and birefringence measurements.[11,17] Recent efforts[18,19] have also demonstrated that the phase behavior of a neat block copolymer at constant N can likewise be systematically influenced through controlled monomer sequencing within the blocks comprising the copolymer. A more convenient alternative by which to reduce the incompatibility of a block copolymer system relies on the addition of a second component, such as a parent homopolymer[20−22] or a (non)preferential solvent,[23−28] to the copolymer.

In conventional order−disorder studies of solvated block copolymers, a predetermined fraction of solvent is added to an ordered block copolymer and the temperature is subsequently elevated in incremental steps to a point above the ODT. The effect of solvent and concentration on the magnitude of χN at the ODT is ascertained from the variation of a system characteristic (e.g., the principal peak scattering intensity or width, or the dynamic storage shear modulus) with temperature. By comparing the ODT conditions for numerous SI copolymers in the presence of a relatively neutral solvent (toluene or dioctyl phthalate), Lodge et al.[28] report that $\chi \mathrm{N} \sim (1 - \phi_s)^{-1.6}$, where ϕ_s is the solvent volume fraction, in agreement with theoretical predictions.[4] In the concentrated polymer regime, attempts[29−34] to elucidate the role of block copolymer microstructure on (non)preferential solvent uptake have relied upon gravimetric sorption, wherein solvent vapor diffuses and dissolves into an ordered (usually intermediately or strongly segregated) block copolymer, and the mass of solvated copolymer is monitored as a function of time. Since each sorption measurement is conducted at a single temperature and since the solvent molecules effectively probe copolymer microstructure (or the lack thereof), this technique is referred to here as isothermal diffusive probe analysis (IDPA). In this work, we employ SAXS and IDPA as independent means by which to examine the solvent-induced disordering of a compositionally symmetric SI diblock copolymer.

The SI diblock copolymer was synthesized via living anionic polymerization in cyclohexane at 60 °C in the presence of *sec*-butyllithium. According to ^{1}H NMR and GPC, the copolymer was 50/50 w/w S/I, and its number-average molecular weight ($\bar{M}_n$) and polydispersity were 13 600 and 1.04, respectively. The upper (styrenic) glass transition temperature (T_g) of the copolymer was 46 °C, as discerned from differential scanning calorimetry. Films of the copolymer were prepared from 4% (w/v) toluene solutions, which were cast into Teflon molds and permitted to dry slowly for 3 weeks. Resultant films were heated for 4 h at 90 °C under vacuum to remove residual solvent. For SAXS analysis, predetermined masses of the neat copolymer and the copolymer with 11.9 wt % toluene were sealed in glass cuvettes and heated at 100 °C for an additional 24 h to promote sample homogeneity. Low-resolution SAXS patterns were collected from each specimen at a sample-to-detector distance of 23.9 cm on a Kratky compact camera (slit collimation) using Cu Kα radiation. (A complete description of the SAXS instrument and data analysis is provided elsewhere.[35]) Scattering data were obtained near ambient temperature and then at 5 °C intervals at elevated temperatures. To ensure thermal equilibration, the dwell time at each temperature was 60 min. The IDPA employed a quartz-spring gravimetric balance housed in a thermally insulated chamber. To avoid sample flow, a small piece of the copolymer film was placed in a solid Al bucket, which was then suspended from the quartz spring. Once the film was degassed for 24 h under vacuum at 70 °C, toluene vapor pressure was introduced in step increments into the chamber. Mass uptake was monitored as a function of exposure time for up to 25 h during each increment.

Shown in Figure 1 are temperature-dependent SAXS profiles obtained from the neat SI diblock copolymer (Figure 1a) and the copolymer with a toluene weight fraction (ω_s) of about 0.12 (Figure 1b). It is apparent from the data in Figure 1a,b that the intensity of the principal scattering peak in each case decreases monotonically with increasing temperature, which is expected from the reciprocal relationship between χ and temperature. Each peak in Figure 1 is centered around a scattering vector (q) of 0.374 nm^{-1} for the neat copolymer and 0.356 nm^{-1} for the solvated copolymer. Corresponding microdomain correlation lengths (periodicities) from Bragg's law are 16.8 and 17.6 nm, respectively,

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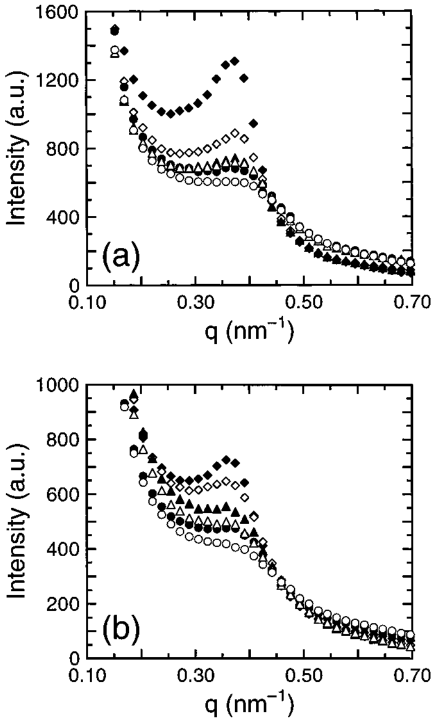

Figure 1. Low-resolution SAXS profiles obtained from (a) the neat SI copolymer and (b) the SI copolymer with 11.9 wt % toluene at several temperatures (in °C): in part a, 25 (◆), 65 (◇), 75 (▲), 85 (△), 95 (●) and 105 (○); in part b, 20 (◆), 40 (◇), 50 (▲), 60 (△), 70 (●), and 80 (○). None of the curves have been shifted.

which can, within experimental uncertainty (estimated to be about ±3%), be considered virtually indistinguishable.

The temperature at which a block copolymer undergoes its ODT can be extracted from a series of temperature-dependent SAXS profiles. The variation in integrated principal peak intensity with temperature, for instance, reveals the ODT as an abrupt step change that is most easily detected by plotting reciprocal peak intensity vs reciprocal absolute temperature. Alternatively, the square of the half-width at half-maximum of the principal peak, rather than the peak intensity, undergoes a similar temperature-induced step change at the ODT. Both methods can be used to analyze high-resolution SAXS data but may fail when applied to low-resolution data in the absence of background correction (as in Figure 1). A less common method of identifying the ODT of a block copolymer from such data has been proposed by Perahia et al.[11] This strategy exploits the observation that, at scattering vectors (q) just beyond the principal scattering peak, the intensity at temperatures below the ODT is lower than that at temperatures above the ODT. Such a demarcation is evident in the profiles shown in Figure 1.

While this signature of the ODT is neither intuitive nor predicted, it has been found[11] to compare well with the identification methods described above. With the apparent validity of this approach in mind, the scattering intensity evaluated at 0.54 nm^{-1} in Figure 1 is displayed as a function of temperature for each copolymer system in Figure 2 and is observed to increase abruptly over a 5 °C temperature range (due to the sampling interval) in each case. For the neat copolymer, this increase occurs between 80 and 85 °C (hereafter listed as 83 ± 3 °C for brevity). According to previously reported experimental data,[12] the ODT temperatures for compositionally symmetric (50/50 w/w S/I) SI diblock copolymers with molecular weights of 13 000 and 14 400 are about 78 ± 1 and 84 ± 1 °C, respectively, which are in very good agreement with the results from Figure 2 for the neat SI copolymer employed here. Figure 2 also reveals that the ODT temperature for the solvated copolymer with $\omega_s \approx 0.12$ is depressed to 68 ± 3 °C. Balsara et al.[25] have measured ODT temperatures (from SAXS) for a compositionally asymmetric SI diblock copolymer (39/61 w/w S/I; $\bar{M}_n = 31\,000$) at several different dioctyl phthalate concentrations and have found a more pronounced dependence of the ODT temperature on solvent content than is observed here.

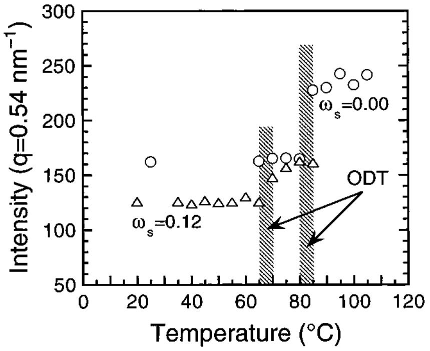

Figure 2. Dependence of scattering intensity (at $q = 0.54$ nm^{-1}) on temperature for the neat SI copolymer at two different solvent weight fractions (ω_s): 0.00 (○) and 0.12 (△). The order–disorder transition (ODT) for each case is shown as the crosshatched region located at the step change in each data set.

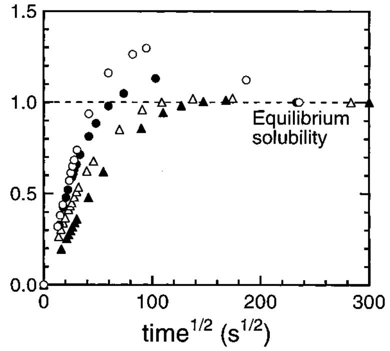

Figure 3. Isothermal mass-uptake curves normalized to the equilibrium solvent uptake (M_t/M_∞) as a function of time$^{1/2}$ at 70 °C for four different toluene vapor pressure intervals (in Torr): 0–29 (▲), 29–93 (△), 74–111 (●) and 111–139 (○). Note that M_t overshoots the equilibrium toluene uptake as M_t/M_∞ exceeds unity in the latter two cases.

Figure 3 shows the dependence of toluene mass uptake (M_t), normalized with respect to the equilibrium mass uptake (M_∞), on time$^{1/2}$ for four toluene vapor pressures at 70 °C (which is above the upper T_g of the copolymer). At low vapor pressures (up to 29 Torr), sorption appears Fickian, as evidenced by (i) an initially linear slope and (ii) a monotonic increase in M_t up to M_∞ after long exposure times. Within the Fickian regime, the linear slope can be used to extract the diffusion coefficient (D) of toluene in the copolymer.[36] From Figure 3, D is found to equal 4.75×10^{-7} cm^2/s. (The uncertainty in D is estimated to be about ±20%.) As the pressure is increased to 93 Torr, Fickian diffusion is retained, in which case D is calculated to be 1.26×10^{-6} cm^2/s. At higher pressures (up to 111 Torr), however, anomalous sorption is observed as M_t/M_∞

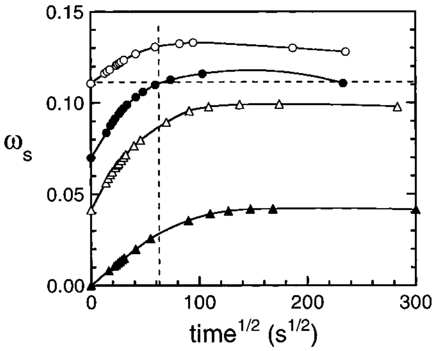

Figure 4. Variation of solvent weight fraction (ω_s) with time$^{1/2}$ for the four isothermal mass-uptake curves presented in Figure 3 (the same symbols are used here). Solid lines connecting the data are guides for the eye, while the dashed lines identify the value of ω_s at which anomalous sorption (equilibrium overshoot) is first observed in Figure 3.

exceeds unity after an exposure time of about 1.1 h and then returns to $M_t/M_\infty = 1.0$ at longer exposure times. Similar, but more pronounced, behavior is likewise seen at the highest pressure used in this study (139 Torr). Under such conditions of equilibrium overshoot, D cannot be evaluated.

The anomalous sorption in Figure 3 is a consequence of solvent expulsion from the copolymer and has been observed in other polymeric systems. For example, equilibrium overshoot has been reported for polymers that undergo a solvent-induced phase transition (e.g., crystallization[37]) or relax at a rate that is significantly slower than the rate of solvent diffusion due to bulky side groups.[38] Since the SI copolymer examined here is molten at 70 °C, the equilibrium overshoot evident in Figure 3 is not attributed to the upper T_g. Thus, it appears that this anomalous sorption reflects relaxation or rearrangement of the block copolymer microstructure. To relate the sorption data in Figure 3 to the SAXS data displayed in Figure 2, we present the mass fraction of toluene (ω_s) as a function of time$^{1/2}$ in Figure 4 and identify the value of ω_s signifying the onset of equilibrium overshoot. At 70 °C, the onset of anomalous sorption is observed to occur at $\omega_s \approx 0.11$. Recall from Figure 2 that the temperature corresponding to the copolymer ODT at $\omega_s \approx 0.12$ is 68 ± 3 °C.

The surprisingly good agreement between these temperature/composition conditions from two independent techniques, one at constant concentration and the other isothermal, strongly suggests that the anomalous sorption reported here is somehow associated with the ODT of the solvated copolymer. Data from other SI diblock copolymers at different temperatures support this conclusion and will be reported in a future publication. While it remains unclear at the present time why the overshoot persists at concentrations beyond that corresponding to the onset of anomalous sorption (see Figure 3),[39] Fickian behavior is regained once the copolymer is completely disordered at, e.g., 110 °C (data not shown). A conclusive physical interpretation of the overshoot cannot be provided at this time, but one consideration is certain: the copolymer chains must undergo a significant solvent-induced change in molecular conformation (due to interfacial dissolution) to induce the level of solvent expulsion evident in Figure 3. The ODT clearly satisfies this requirement.[40] According to Caneba et al.,[41] an ordered triblock copolymer absorbs more solvent than a random copolymer of comparable composition due to the existence of interfacial regions in the triblock copolymer. This observation is consistent with the assignment proposed here; namely, the onset of anomalous sorption constitutes an IDPA signature for solvent-induced microstructural disordering in low-molecular-weight diblock copolymers under isothermal conditions.

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References and Notes

(1) Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(3) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(4) Olvera de la Cruz, M. *J. Chem. Phys.* **1989**, *90*, 1995.
(5) Melenkevitz, J.; Muthukumar, M. *Macromolecules* **1991**, *24*, 4199.
(6) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.
(7) Owens, J. N.; Gancarz, I. S.; Koberstein, J. T.; Russell, T. P. *Macromolecules* **1989**, *22*, 3380.
(8) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.
(9) Wolff, T.; Burger, C.; Ruland, W. *Macromolecules* **1993**, *26*, 1707.
(10) Winey, K. I.; Gobran, D. A.; Xu, Z. D.; Fetters, L. J.; Thomas, E. L. *Macromolecules* **1994**, *27*, 2392.
(11) Perahia, D.; Vacca, G.; Patel, S. S.; Dai, H. J.; Balsara, N. P. *Macromolecules* **1994**, *27*, 7645 and references therein.
(12) Lin, C. C.; Jonnalagadda, S. V.; Kesani, P. K.; Dai, H. J.; Balsara, N. P. *Macromolecules* **1994**, *27*, 7769.
(13) Floudas, G.; Pakula, T.; Fischer, E. W.; Hadjichristidis, N.; Pispas, S. *Acta Polym.* **1994**, *45*, 176.
(14) Sakamoto, N.; Hashimoto, T. *Macromolecules* **1995**, *28*, 6825. Ogawa, T.; Sakamoto, N.; Hashimoto, T.; Han, C. D.; Baek, D. M. *Macromolecules* **1996**, *29*, 2113.
(15) Rosedale, J. H.; Bates, F. S. *Macromolecules* **1990**, *23*, 2329.
(16) Han, C. D.; Baek, D. M.; Kim, J. K.; *Macromolecules* **1995**, *28*, 5886. Baek, D. M.; Han, C. D. *Polymer* **1995**, *36*, 4833.
(17) Amundson, K.; Helfand, E.; Patel, S. S.; Quan, X.; Smith, S. D. *Macromolecules* **1992**, *25*, 1935.
(18) Smith, S. D.; Ashraf, A.; Clarson, S. J. *ACS Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 672; **1994**, *35*, 467.
(19) Laurer, J. H.; Ashraf, A.; Smith, S. D.; Samseth, J.; Spontak, R. J. *Supramol. Sci.* **1997**, *4*, 121. Laurer, J. H.; Ashraf, A.; Smith, S. D.; Spontak, R. J. *Langmuir* **1997**, *13*, 2250.
(20) Tanaka, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 5398.
(21) Floudas, G.; Hadjichristidis, N.; Stamm, M.; Likhtman, A. E.; Semenov, A. N. *J. Chem. Phys.* **1997**, *106*, 3318.
(22) Matsen, M. W. *Phys. Rev. Lett.* **1995**, *74*, 4225; *Macromolecules* **1995**, *28*, 5765.
(23) Hashimoto, T. In *Thermoplastic Elastomers: A Comprehensive Review*; Legge, N. R., Holden, G. Schroeder, H. E., Eds.; Hanser: Munich, 1987 and references therein.
(24) Connell, J. G.; Richards, R. W. *Macromolecules* **1990**, *23*, 1766.
(25) Balsara, N. P.; Perahia, D.; Safinya, C. R.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1992**, *25*, 3896.
(26) Garetz, B. A.; Newstein, M. C.; Dai, H. J.; Jonnalagadda, S. V.; Balsara, N. P. *Macromolecules* **1993**, *26*, 3151.
(27) Jian, T.; Anastasiadis, S. H.; Semenov, A. N.; Fytas, G.; Adachi, K.; Kotaka, T. *Macromolecules* **1994**, *27*, 4762.
(28) Lodge, T. P.; Pan, C.; Jin, X.; Liu, Z.; Zhao, J.; Maurer, W. W.; Bates, F. S. *J. Polym. Sci. B: Polym. Phys.* **1995**, *33*, 2289.
(29) Kinning, D. J.; Thomas, E. L.; Ottino, J. M. *Macromolecules* **1987**, *20*, 1129.
(30) Rein, D. H.; Baddour, R. F.; Cohen, R. E. *J. Appl. Polym. Sci.* **1992**, *45*, 1223.
(31) Lin, H.; Steyerl, A.; Satija, S. K.; Karim, A.; Russell, T. P. *Macromolecules* **1995**, *28*, 1470.

(32) Faridi, N.; Duda, J. L.; Hadjromdhane, I. *Ind. Eng. Chem. Res.* **1995**, *34*, 3556.
(33) Vrentas, J. S.; Vrentas, C. M. *Chem. Eng. Sci.* **1997**, *52*, 985.
(34) Arnold, M. K.; Nagai, K.; Betts, D. E.; Freeman, B. D.; Pinnau, I.; Spontak, R. J.; DeSimone, J. M. *Macromolecules*, to be submitted for publication.
(35) Stölken, S.; Bartsch, E.; Sillescu, H.; Lindner, P. *Prog. Colloid Polym. Sci.* **1995**, *98*, 155.
(36) Hong, S. −U.; Barbari, T. A.; Sloan, J. M. *J. Polym. Sci. B: Polym. Phys.* **1997**, *35*, 1261.
(37) Overbergh, N.; Berghmans, H.; Smets, G. *Polymer* **1975**, *16*, 703.
(38) Vrentas, J. S.; Duda, J. L.; Hou, A.-C. *J. Appl. Polym. Sci.* **1984**, *29*, 399.
(39) Anomalous sorption at concentrations beyond the ODT may reflect solvent-induced composition fluctuations that are analogous to thermal fluctuations at temperatures above the ODT in neat (nonsolvated) block copolymers.
(40) Bartels, V. T.; Stamm, M.; Abetz, V.; Mortensen, K. *Europhys. Lett.* **1995**, *31*, 81.
(41) Caneba, G. T.; Soong, D. S.; Prausnitz, J. M. *J. Macromol. Sci.-Phys.* **1983−84**, *B22*, 693.

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