High-Pressure Effects on the Order−Disorder Transition in Block Copolymer Melts

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ABSTRACT: We have measured the pressure dependence of the order−disorder transition temperature (T_{ODT}) in two styrene−isoprene diblock copolymers containing 24 and 48 wt % styrene ($M_w = 20\,500$ and 16 500 g mol^{-1}, respectively). Small-angle X-ray scattering measurements indicate that T_{ODT} rises linearly with increasing hydrostatic pressure in both systems at a rate of +20 °C kbar^{-1} (approximately) over the range from 0 to 600 bar; deviations from linearity appear at higher pressures. This increase is approximately twice the value that we have previously estimated from measurements of changes in polymer characteristics with high pressure.[1] We present dilatometric measurements across the ODT which show a volume change ($\Delta V/V$) of order $+5 \times 10^{-4}$ upon disordering. The observation of a change in specific volume at the ODT has implications for experimental and theoretical investigations of polymer phase behavior, which we discuss. Finally, we demonstrate the existence of pressure-induced ("barotropic") phase transitions in these materials and compare their characteristics with those of the analogous temperature-induced ("thermotropic") transitions.

Introduction

The complex mesophase polymorphism exhibited by microphase-separated block copolymers has inspired a number of theoretical attempts to define the characteristics which determine this phase behavior. Early theoretical work suggested that morphology was governed by two parameters, the volume asymmetry of the two blocks (described by f, the minority component volume fraction) and the degree of segregation of the system (described by the product χN, where χ is the Flory−Huggins interaction parameter and N is the total number of statistical segments in the molecule).[2,3] Subsequent theoretical models indicated that additional characteristics of the system, such as the renormalized number of statistical segments $\bar{N} = Nb^6v^{-2}$ (where b is the mean statistical segment length and v is the mean volume per statistical segment)[4,5] or the difference in the degree to which chemically identical blocks interpenetrate,[6−8] might also influence the phase behavior. Although some experimental evidence exists for these propositions,[9] at the present time, the precise role played by these quantities is unclear.

Past experimental assessment of phase behavior[10] relied upon (labor- and time-intensive) synthesis methods to change χ, N, and f. More recent work has exploited the temperature dependence of χ to change the degree of segregation in a sample of fixed composition, thus moving vertically on the conventional (segregation−composition) phase diagram for diblock materials. This approach has resulted in the discovery of several new morphologies[11−13] and led to the identification of thermotropic transitions between different mesophases.[9,11−17] Given the success of this technique, it is surprising that a second thermodynamic parameter, hydrostatic pressure, has received relatively little attention. Recent studies in polymer blends have indicated that the Flory−Huggins interaction parameter increases in magnitude upon pressurization,[18] while the dimensions of the polymer coils decrease to a slightly greater extent than would be predicted by compressibility effects alone.[19] Similar effects in block copolymers would be equivalent to an increase in the degree of segregation, which might produce effects (such as pressure-induced transitions) analogous to those observed by reducing temperature.

Recently, we demonstrated that pressurizing a nearly symmetric polystyrene−polyisoprene (SI) diblock copolymer leads to an increase in the degree of segregation of the system.[1] This induces a substantial *increase* in the radius of gyration (R_g) as the blocks extend away from one another to minimize contact between chemically distinct segments. When the degree of segregation is held constant, R_g *decreases* with increasing pressure at a rate roughly equal to that which would be estimated from the compressibilities of the two blocks. Comparison with measurements of the dimensions of polystyrene chains under pressure by Janssen *et al.*,[19] in which the reduction in R_g exceeded that which would be expected due to compressibility, suggest that the number of statistical segments (N) for polystyrene is an increasing function of pressure; by requiring consistency between our diblock data and that of these authors, R_g for polyisoprene was estimated to be a decreasing function of pressure. The rates of change of these parameters were of such a magnitude that pressure-induced in-

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creases in N for polystyrene were balanced by nearly equal reductions in N for polyisoprene. Thus, in our material, the total number of statistical segments remained roughly constant, and the pressure dependence of R_g for a symmetric SI diblock appeared to result solely from an isotropic reduction in the volume of the system.

A similar rise in the aspect ratio of the disordered state scattering maximum with pressure for a solution of SI diblocks in dioctyl phthalate (DOP) was reported by Hammouda *et al.* [20] while the present paper was in review. In that work, however, the presence of solvent apparently introduced a second scattering maximum in the SANS data which has not been seen in melts of pure diblock copolymers. As the observed behavior might be due to solvent effects such as pressure-induced changes in the quality of the solvent for one or both blocks of the molecule, the authors refrained from interpreting their data in terms of changes in the structural characteristics of the solution.

If the phase behavior of block copolymers is determined solely by a limited set of structural characteristics (as is postulated by current theory), comparison of the temperature and pressure dependence of these characteristics should suffice to determine the pressure dependence of thermotropic phase transition temperatures in these materials. Agreement between the experimentally measured temperature dependence and that predicted from measurements of these structural parameters strongly suggests that models based on a limited number of such parameters are sufficient to describe the phase behavior of these molecules; departures from this prediction will reflect the degree to which the assumptions used in constructing models of block copolymer phase behavior reflect the actual behavior of the system. Our earlier results[1] predict a pressure dependence of 10 ± 2 °C kbar^{-1} for the order−disorder transition (ODT) in a symmetric SI diblock.

While the present paper was in review, Kasten and Stühn[21] published a study indicating a fractional reduction in volume at the ODT of $\Delta V/V = (3 \pm 1) \times 10^{-3}$ in a symmetric SI diblock with composition and molecular weight similar to that studied here. In combination with new calorimetric data which indicated a change in enthalpy at the transition of order 0.1 J/g, this implied a *decrease* in the ODT temperature with increasing pressure of 30 °C kbar^{-1}, in contrast to the increase predicted by the aforementioned structural study.

We have measured the pressure dependence of the order−disorder transition temperature (T_{ODT}) using small-angle X-ray scattering (SAXS) in two weakly segregated SI diblock copolymers. We find a linear relationship between T_{ODT} and the applied pressure which persists up to pressures of 600 bar; contrary to the predictions of Kasten and Stühn,[21] we find that T_{ODT} *increases* with applied pressure. Deviations from linearity appear at higher pressures, with the experimentally observed transition temperature falling below the value predicted by the linear model. Such a dependence of transition temperature on pressure for a (presumably) first-order transition[4] with a nonzero enthalpy[21,22] indicates a change in the volume of the system upon moving from the ordered to the disordered state. We present dilatometric measurements which confirm the existence of this volume change. Regardless of the source of this discontinuity, these results demonstrate the importance of such volume changes in a proper treatment of the order−disorder transition.

Table 1. Polymer Characteristics at 100 °C and 1 bar[a]

block	M_w (g mol−1)	ρ (g cm^{-3})	f
	SI 8/8 ($M_w/M_n = 1.05$)		
S	8000	1.00[25]	0.44
I	8500	0.84[26]	0.56
	SI 5/15 ($M_w/M_n = 1.05$)		
S	5100	1.00[25]	0.22
I	15 400	0.84[26]	0.78

[a] M_w = weight-average molecular weight of each block. M_w/M_n = polydispersity index. ρ = homopolymer density. f = volume fraction of the appropriate component in the copolymer.

Materials and Methods

The SI diblock copolymers used in this study were synthesized using previously described anionic polymerization techniques. The materials are denoted "SI *A*/*B*", where *A* and *B* are the polystyrene and polyisoprene weight-average molecular weights (M_w) in kg mol^{-1}. The synthesis and characterization of SI 8/8 has been described elsewhere;[1] the polymer has a total molecular weight of 16 500 g mol^{-1}, a styrene block volume fraction of 0.44 at 100 °C and 1 bar, and a polydispersity index (M_w/M_n) of 1.05. Note that this polymer is similar to the SI diblock examined by Kasten and Stühn[21] (M_w 17 700 g mol^{-1}; $M_w/M_n = 1.04$; $f = 0.44$). SI 5/15 was synthesized using high-vacuum techniques previously described by Morton and Fetters.[23] The molecular weight distribution was measured by size exclusion chromatography (SEC) with toluene as the solvent; in addition to the primary peak, the chromatogram revealed the presence of a small quantity of homopolystyrene (approximately 1 wt %) arising from premature termination of the styrene chains upon addition of the isoprene monomer. The polydispersity of the diblock material was estimated to be 1.05. Using 400 MHz ^{1}H NMR spectroscopy, the polyisoprene microstucture was measured to be 94% 1,4 addition and 6% 3,4 addition.[24] From the known densities of polystyrene[25] and polyisoprene[26] at 100 °C and 1 bar, the minority component volume fraction (f) was calculated; this may be regarded as pressure-independent over the range of interest (0−1000 bar) due to the compressibilities of polyisoprene[27] (−0.075 kbar^{-1}) and polystyrene[28] (−0.043 kbar^{-1}). These values are summarized in Table 1.

The glass transition temperatures (T_g) of the polystyrene blocks at 1 bar are estimated to be of order 60 °C, based on previous measurements[14] in a polystyrene-poly(ethene-*co*-butene) diblock with a polystyrene block molecular weight of 7 500 g mol^{-1}. Measurements in commercial polystyrenes indicate that T_g increases by 7.5 °C (approximately) per 100 bar of applied pressure over the range from 0 to 2000 bar,[28,29] suggesting that kinetic effects might influence system behavior under conditions of high pressure and low temperature.

X-ray diffraction was used to determine the sample morphology as a function of annealing temperature and pressure. Cu K_α X-rays were generated from a Rigaku RU-200BH rotating-anode X-ray machine equipped with a 0.2 × 2 mm microfocus cathode and Franks mirror optics. Samples were placed inside a high pressure cell[1] or 1.5 mm unsealed quartz capillary, mounted inside an evacuated sample chamber, and maintained at the temperature of interest by a set of thermoelectric devices (temperature range 0−185 °C, stability about setpoint ±0.050 °C). SEC performed on selected samples after prolonged annealing at high temperatures and pressures (at least 48 h at temperatures between 90 and 110 °C and pressures from 0 to 900 bar) matched traces obtained prior to the runs, demonstrating that the experimental protocols did not produce measurable degradation of the material. Two-dimensional diffraction images were collected with an image-intensified area detector designed around a Thomson CCD chip;[30] at the specimen-to-detector distance employed for this experiment, each pixel of this detector corresponds to a square of edge length 0.00036 $\mathrm{Å}^{-1}$ in reciprocal space. The sensitivity of the detector and the intensity of the beamline permitted collection of sufficient signal to identify the sample morphology after only 10 min of integration. After collection, images were digitized, corrected for detector response characteristics, and

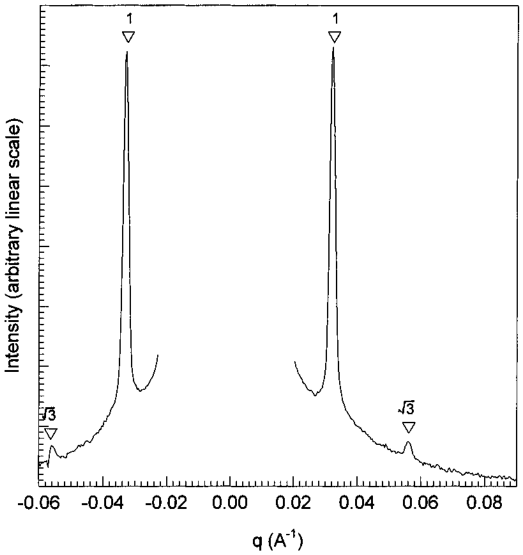

Figure 1. Diffraction recorded from SI 5/15 after 1 h of annealing at 90 °C and 1 bar. Two diffraction reflections (indicated by inverted triangles) appear at position ratios of 1:√3, indicating the presence of a hexagonally packed array of cylinders, in agreement with previous studies of this material.[24,32]

written to magnetic tape. Images were collapsed into a one-dimensional format by integrating azimuthally along an arc ±15° from the horizontal axis.

X-ray diffraction from the hexagonally packed cylindrical morphology was characterized by sharp Bragg reflections at reciprocal space position ratios of 1 and √3; the √4 reflection is not observed due to a minimum in the structure factor for scattering from cylinders of the appropriate minority component volume fraction. Diffraction from the lamellar morphology was characterized by a single, relatively sharp scattering maximum with a Gaussian line shape; the absence of higher order reflections after prolonged annealing at temperatures above T_g but below T_{ODT} is attributed to a nearly sinusoidal electron density profile in this symmetric, weakly segregated material. Diffraction from the disordered phase was characterized by a single broad scattering maximum with a Lorentzian line shape.

Phase boundaries were identified either by holding temperature constant and changing pressure in 50 bar increments or by holding pressure constant and changing temperature in 1 °C steps. Samples were permitted to equilibrate for 1 h following a temperature or pressure change; the equilibration time was chosen by requiring that peak maxima and widths recorded after twice that time differ from those recorded after the equilibration time by at most 10% of the mean value. Studies of thermally induced ordering behavior in samples of SI 5/15 at 0 bar reveal that the characteristic time over which the transition occurs decreases as the depth of the temperature jump—the difference between the final temperature and the ODT—increases. These experiments suggest that the equilibration time used in the present study is sufficient to resolve ordering and disordering temperatures to within 1 °C at constant pressure. In typical constant-pressure scans, the highest temperature at which the ordered phase persisted upon heating and the lowest temperature at which it appeared upon cooling differed by 1 °C; the corresponding value for constant temperature scans was 100 bar. Although we define a "transition temperature and pressure" as the midpoint of the range of values over which heating and cooling scans (or pressurizing and depressurizing scans) produce different phase states, this value does not necessarily represent the actual boundary separating the ordered and disordered phases. Preliminary kinetic data suggest that the phase boundaries may be determined to higher resolutions by employing significantly longer equilibration times; a detailed discussion of the kinetics of the ODT under high pressure will be deferred to a future publication.

Pressure–volume–temperature measurements were conducted using a high-pressure dilatometer previously employed for investigations of phospholipid–water phase behavior by So *et al.*[31] For investigations of block copolymer behavior, the thermoelectrics used in the original device were replaced by a pair of flexible Kapton heaters (Omega Engineering, Stamford, CT), and the original lock-in amplifier was replaced by a more sophisticated dual-phase unit (EG&G model 5210; EG&G Princeton Applied Research, Princeton, NJ). Briefly, samples containing 0.5 wt % antioxidant (Irganox 1010; Ciba-Geigy) are enclosed in a thin-walled steel tube which rests in a mercury-filled high-pressure valve. A piece of Teflon tape stretched across the mouth of the tube transmits pressure to the sample and prevents mixing of the polymer and mercury. A sample volume of *ca.* 450 μL was used in these experiments. The pressure inside the cell is monitored by a commercial pressure sensor (UHP/1269-06 and 450D; Sensotec; Columbus, OH); volume reductions in *ca.* 8 nL steps are produced by a computer-controlled stepper motor attached to the cell piston through a reducing gearbox. The position of the piston, and thus the cell volume, is determined by a linear variable differential transducer (LVDT), resulting in a sensitivity to volume changes of order 3 parts in 10^5. A platinum resistance thermometer (RTD) mounted in the loading plug for the dilatometer measures the temperature of the sample, which is controlled to within 0.020 °C over 20–200 °C by adjusting the duty cycle of a 120 V, 1 Hz square wave signal applied to the Kapton heaters. Readers are referred to So *et al.*[31] for additional information on the design and operation of the dilatometer.

Results

Diffraction obtained from SI 5/15 after 1 h of annealing at 90 °C and 0 bar indicates the presence of a hexagonally packed cylindrical morphology, in agreement with previous studies of this material.[24,32] Two sharp Bragg reflections appear at reciprocal space position ratios of 1 and √3; see Figure 1. Diffraction obtained from SI 8/8 after 1 h of annealing at 70 °C and 0 bar shows only one sharp reflection, as would be expected for a weakly segregated, nearly symmetric material. Such relatively narrow peaks with temperature-independent full-widths at half maximum (fwhm) of order 0.002 Å^{-1} characterize ordered-phase diffraction from both materials at temperatures up to within 1 °C of the ODT at 0 bar. Diffraction from diblocks heated into the disordered region of the phase diagram exhibits only a single, relatively broad scattering maximum with a Lorentzian line shape. fwhm for such peaks range from 0.004 to 0.006 Å^{-1} at temperatures at least 1 °C above the ODT at 0 bar. Thus, when large steps in temperature (2 °C or more) are employed, detection of the order–disorder transition is straightforward owing to the discontinuous change in peak width as the sample moves from one phase to another. This behavior has been exploited in previous studies of weakly segregated SI diblock materials.[24,32–34]

Unfortunately, when a finer step size is employed, the apparent magnitude of this discontinuity becomes less pronounced, and differentiation of the ordered and disordered morphologies becomes more difficult. Figure 2a presents diffraction profiles for a temperature scan of SI 5/15 from 105 to 107 to 104 °C at a constant pressure of 350 bar. Comparison of the peak widths observed upon heating to 105 and 107 °C reveals that the ODT lies between these two temperatures. Although the non-Gaussian shape of the profile recorded at 106 °C suggests a disordered morphology (note the broad "wings" at the base of the peak) and a discontinuous jump in the peak width of nearly 200% is recorded upon heating from 105 to 106 °C, the transformation

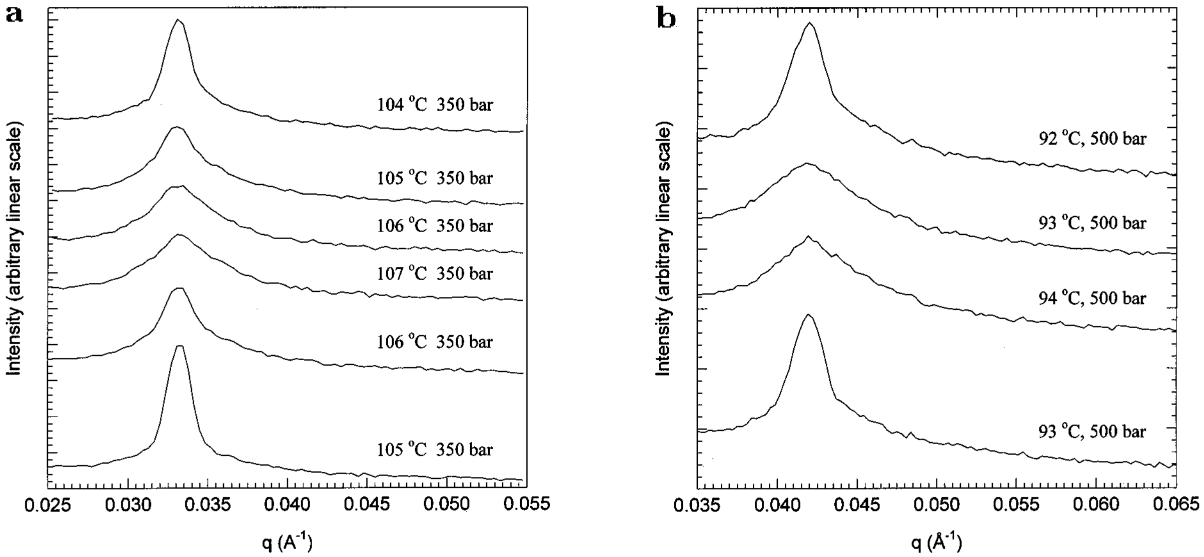

Figure 2. (a) Typical one-dimensional diffraction profiles recorded in a scan through the ODT at constant pressure in SI 5/15. The data shown were recorded at 350 bar during a sweep from 105 to 107 to 104 °C (bottom to top) in steps of 1 °C. Initially, the sample is in an ordered morphology, as evidenced by the relatively sharp Bragg reflection with a Gaussian line shape centered at 0.033 Å^{-1}; the corresponding intercylinder spacing is 220 Å. Upon heating to 106 °C, the peak width nearly doubles, and the peak intensity falls dramatically; this indicates the formation of the disordered state. Unlike the profile recorded for the ordered morphology, the disordered state scattering is not well described by a Gaussian line shape; note the broad wings at the base of the disordered peak. Subsequent heating does not produce further dramatic changes in peak characteristics. Cooling the material to 104 °C returns the polymer to the original ordered morphology, as demonstrated by the return of the original narrow (Gaussian) line shape. 1 °C of hysteresis separates the phase transition temperatures observed upon heating and cooling. (b) Typical one-dimensional diffraction profiles recorded in a scan through the ODT at constant pressure in SI 8/8. The data shown were recorded at 500 bar during a sweep from 93 to 94 to 92 °C (bottom to top) in steps of 1 °C. As in SI 5/15 (see (a)), the low-temperature ordered morphology produces a single narrow reflection with a Gaussian line shape. Heating the sample results in a transformation to the disordered morphology, as evidenced by the appearance of a much broader peak with a Lorentzian line shape; subsequent cooling returns the sample to the original (ordered) morphology. As in SI 5/15, 1 °C of hysteresis separates the phase transition temperatures observed upon heating and cooling.

from the ordered to the disordered state is not as obvious as it would be if the larger step size of 2 °C was used; the observed peak width at 106 °C, 0.0036 Å^{-1}, is somewhat less than the widths of 0.004−0.006 Å^{-1} usually associated with disordered state diffraction from both materials. To circumvent this difficulty, such profiles were fitted to the Gaussian and Lorentzian line shapes which characterize diffraction from the ordered and disordered states (respectively) in order to determine the profile which best represents the observed signal. Application of this criterion to the data in Figure 2a indicates that the ODT occurs between 105 and 106 °C upon heating and between 105 and 104 °C upon cooling. Typically, 1 °C of hysteresis is observed in scans at constant pressure. Unfortunately, the peak-fitting approach is not unambiguous, as a microphase-separated structure with a considerable amount of type II disorder also produces reflections with apparently Lorentzian line shapes;[35] thus, in the absence of higher diffraction orders, it is possible to mistake a poorly ordered but microphase-separated morphology for a disordered-phase material.

Figure 2b presents a similar constant-pressure scan for SI 8/8; in this case, the polymer is heated from 93 to 94 to 92 °C at a constant pressure of 500 bar. As in SI 5/15, the increase in peak width and change in peak line shape observed upon heating from 93 to 94 °C, or upon cooling from 93 to 92 °C, indicates the ODT.

Pressurizing the disordered state leads to the formation of the ordered morphology, in agreement with earlier results[1] that indicate that the degree of segregation increases with pressure in SI 8/8. Figure 3 presents a series of profiles recorded at 104 °C in SI 5/15. As the pressure applied to the sample increases from 200 to 300 bar, the peak fwhm declines dramatically, indicating a transformation to the ordered morphology. Subsequent depressurization returns the polymer to the initial disordered state. As in the case of the temperature-driven (thermotropic) ODTs examined above, some hysteresis is observed: the highest pressure at which the disordered state persists upon pressurization frequently differs from the highest pressure at which it appears upon depressurization by approximately 50 bar.

Figure 4a summarizes the results of constant-pressure and constant-temperature scans conducted on three samples of SI 5/15; similar results for SI 8/8 appear in Figure 4b. Conditions under which the ordered state was observed on heating and cooling (or depressurization and pressurization) are indicated by filled circles; the corresponding conditions for the disordered state are marked by hollow circles. Half-filled circles denote hysteresis points where the ordered state was observed upon heating (depressurization) but the disordered state was recorded upon cooling (pressurization). Data from different samples are offset horizontally for clarity. No significant changes in disordering kinetics were observed at the highest pressures examined. Since the aforementioned pressure dependence of T_g in polystyrene[28,29] suggests that the ordered state of SI 8/8 should be glassy for pressures above 450 bar, dT_g/dp for such low molecular weight polystyrenes may differ from the value reported for commercial materials. Alternatively, the interpenetration of polystyrene and polyisoprene blocks which occurs in the vicinity of the ODT may reduce the glass transition temperature of the polystyrene domains.

Figure 5a plots the ODT temperatures extracted from the data shown in figure 4a. Over 50−600 bar, a linear

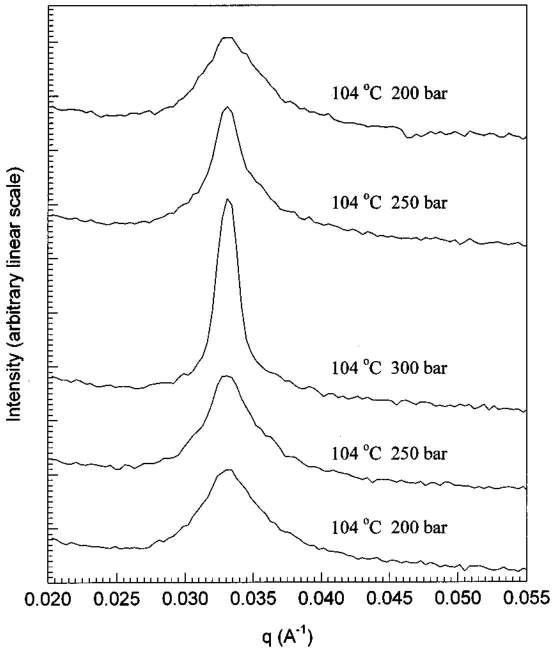

Figure 3. A pressure-induced ("barotropic") ODT in SI 5/15. The scans shown were recorded at 104 °C during a sweep from 200 to 300 to 200 bar (bottom to top) in 50 bar increments. As in the case of the temperature-induced ("thermotropic") ODTs discussed in Figures 2, differentiation of the ordered and disordered state is accomplished through examination of the peak widths and comparison of the scattering line shape with the Gaussian profile expected for an ordered microstructure. Pressurization of the initial disordered morphology leads to the formation of the ordered phase; reducing the applied pressure returns the sample to the original disordered state. Although the peak width observed upon depressurization to 250 bar appears to lie in between the values expected for the ordered and disordered phases, the non-Gaussian shape of the scattering profile indicates the disordered morphology.

fit to the data yields an ODT temperature of 99.2 ± 0.5 °C at 0 bar for SI 5/15. This agrees reasonably well with previously reported values of 101 ± 1 °C (via rheological measurements)[24] and 102.5 ± 2.5 °C (via SAXS using a Kratky camera).[24] Figure 5b shows the measured ODT temperatures as a function of pressure for SI 8/8. A linear fit to this data yields an ODT temperature of 83.9 ± 0.4 °C at 0 bar in this material. The difference between our result and that of Kasten and Stühn[21] (108 °C) arises from the difference in the molecular weights of the systems (16 500 *vs.* 17 700 weight-average g/mol); correcting for this difference leads to an estimate for the transition temperature of their material of (17.7/16.5)(357 K) = 383 K, in excellent agreement with their reported value of 381 K.

Unfortunately, direct measurement of T_{ODT} at very low pressures (less than 25 bar) proved difficult: at such low pressures, upon heating into the disordered phase, the sample flowed out of the space between the beryllium windows and into the steel tubing joining the cell to the pressurizing cylinder. The resulting drop in scattered intensity made determination of sample morphology extremely difficult. After cooling the cell and returning the polymer in the tubing to the ordered morphology, the resulting plug of material proved able to withstand a pressure difference of at least 150 bar between the pressure generator and the sample cell before failing; thus, the pressure inside the sample cell was uncontrolled after migration of the polymer out of the sample space.

In both materials, the ODT temperature increases linearly with applied pressure at rates of 22 ± 2 °C (SI 5/15) and 19 ± 1 °C kbar^{-1} (SI 8/8), with departures from linearity appearing at higher pressures. This is approximately twice the value of 10 ± 2 °C kbar^{-1} predicted from measurements of the degree of segregation of SI 8/8.[1] There are several possible explanations for this discrepancy. First, our earlier evaluation of the change in segregation with pressure[1] did not contain a sufficient density of points in the vicinity of the ODT to permit an accurate measurement of the change in apparent segregation with temperature; as a result, our estimate for $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$ was based in part on a linear extrapolation of the high-temperature measurements to the ODT temperature at 100 bar. This approach excludes fluctuation effects, which have been shown to cause deviations from linearity as the ODT is approached.[4,36] A proper incorporation of these effects would lead to an increase in the predicted $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$. Second, this discrepancy might result from our neglect of barotropic shifts in a third (undetermined) structural characteristic which, in combination with the degree of segregation and the minority component volume fraction, would determine the location of the ODT. Third, this difference might be attributable to compressibility effects which are (by definition) excluded from the incompressible models used to determine the parameters responsible for determining the location of the ODT.

One source of compressibility phenomena might be a difference in the specific volumes of the microphase-separated and the disordered morphologies. For a first-order transition, the Clausius–Clapeyron equation relates the slope of the phase boundary in the $p-T$ plane ($\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$) to the changes in volume (ΔV) and enthalpy (ΔH) at the transition:

$$\frac{\mathrm{d}p}{\mathrm{d}T_{\mathrm{ODT}}} = \frac{\Delta H}{T\Delta V} \tag{1}$$

Using differential scanning calorimetry, Stühn[22] has measured this change in enthalpy for a symmetric SI diblock ($M_{\mathrm{n}} = 10\,500$ g mol^{-1}) to be 1.1 ± 0.2 J g^{-1} (this includes the uncertainty induced by including the glass transition in the DSC baseline). If the ODT is assumed to be a first-order transition (as is expected for a molecule of finite length), insertion of the appropriate values for SI 8/8 into eq 1 yields a fractional volume change ($\Delta V/V$) of $(6 \pm 2) \times 10^{-4}$ at the ODT. A similar calculation using calorimetric data for an asymmetric SI diblock (in ref 19, 25 vol % polystyrene, $M_{\mathrm{w}} = 14\,600$ g mol^{-1}, $\Delta H = 0.7 \pm 0.1$ J g^{-1}) yields a fractional volume change of $(3 \pm 1) \times 10^{-4}$ in SI 5/15.

More recent work by Kasten and Stühn[21] (published while the present paper was in review) has provided a second estimate for the change in enthalpy of 0.11 J/g, a full order of magnitude less than that reported previously. The authors note that this is only a lower bound on the latent heat due to the slow kinetics associated with the disordering transition and the rapid scan rate (20 K/min) used in the DSC measurements (for comparison, the effective scan rate for both the SAXS and dilatometric measurements presented here was ~0.01 K/min). A second estimate of ΔH may be obtained from the incompressible, fluctuation-corrected theory of Fredrickson and Helfand;[4] we have opted for a theoretical prediction as experimental measurements rarely incorporate fluctuation corrections in the vicinity of the ODT and hence tend to understate the actual

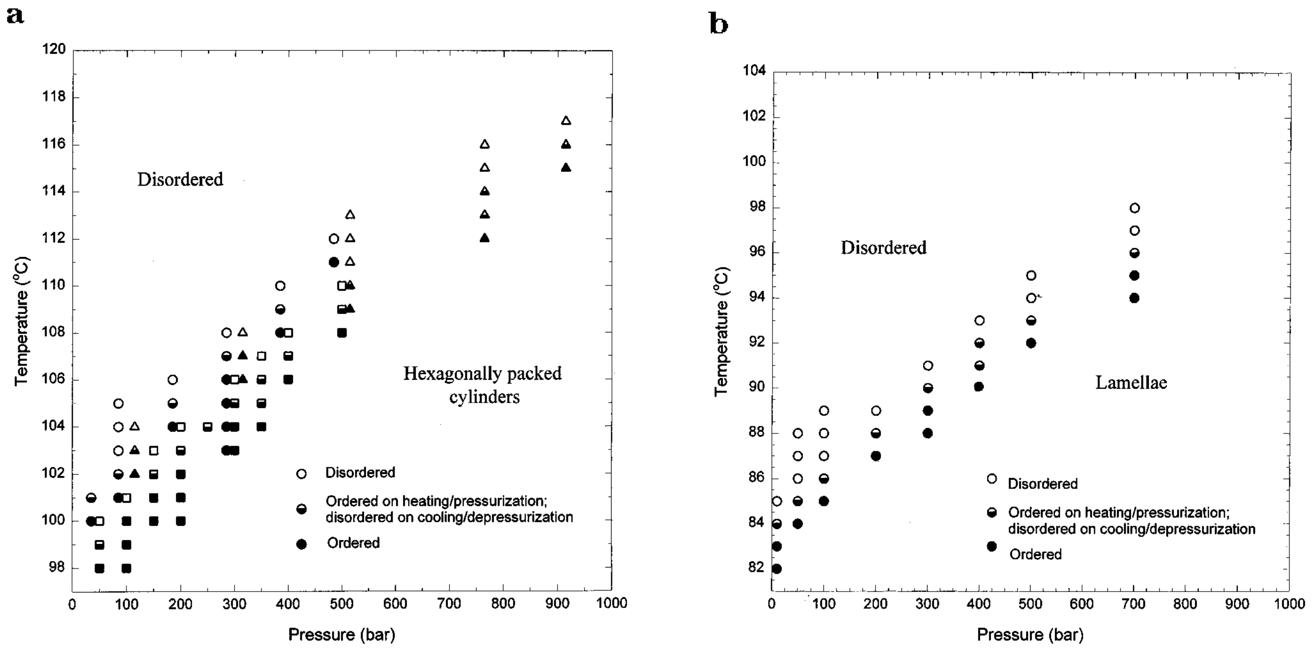

Figure 4. (a) SI 5/15 morphology as a function of annealing temperature and pressure. Data are spaced in increments of 50 bar (in pressure) and 1 °C (in temperature). Different symbol shapes indicate different samples, which are offset horizontally in 15 bar increments for clarity: data appearing between 285 and 315 bar, for example, were recorded at a pressure of 300 bar. Solid black symbols denote the ordered phase of this material (hexagonally packed cylinders), while open symbols represent the disordered phase. Half-filled symbols indicate that different morphologies were obtained upon heating and cooling (or pressurization and depressurization). (b) SI 8/8 morphology as a function of annealing temperature and pressure. Solid black symbols denote the ordered (lamellar) morphology; open symbols represent the disordered phase; and half-filled symbols indicate that different morphologies were obtained upon heating and cooling (or pressurization and depressurization) through the ODT.

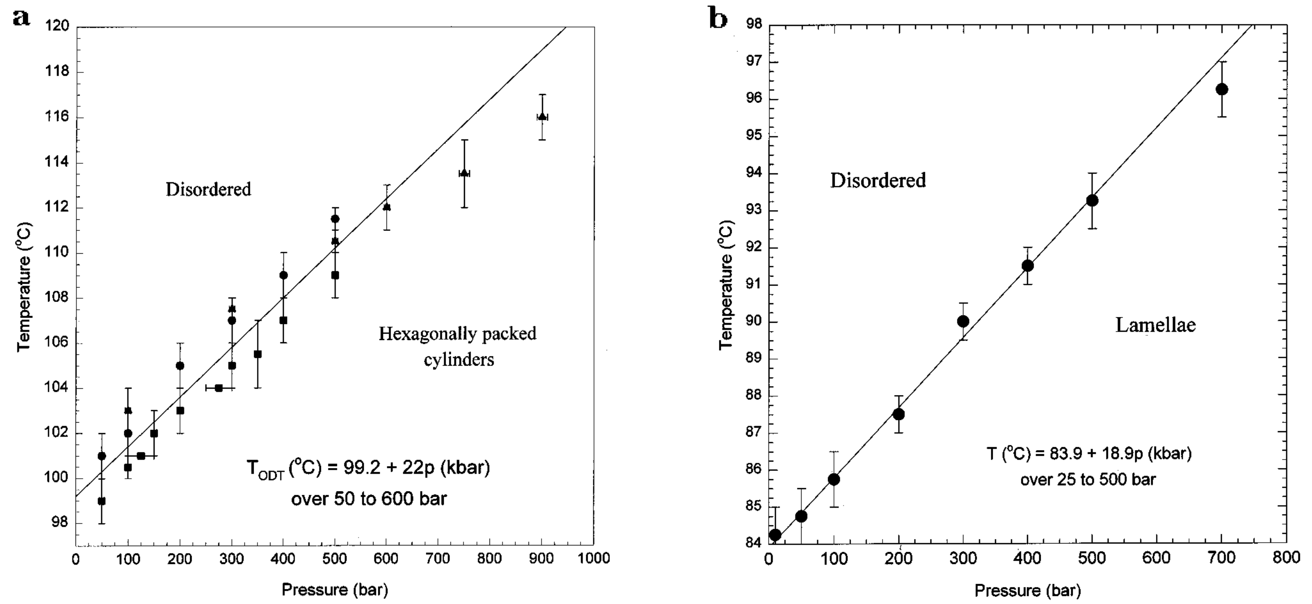

Figure 5. (a) Order-disorder transition temperatures for SI 5/15, determined from the data shown in Figure 4a by taking the midpoint of the region in which different morphologies were observed upon heating (depressurization) and cooling (pressurization); the error bars indicate the width of the hysteresis region. The error in the perpendicular direction (in temperature for scans at constant temperature, or in pressure for scans at constant pressure) is too small (±0.05 °C in temperature, ± the greater of 5 bar or 1% in pressure) to appear on this plot except at the highest pressures shown. Different symbols represent different samples. A linear fit to the data over pressures from 50 to 600 bar yields a value for T_{ODT} at 0 bar of 99 °C, in agreement with previous studies of this material,[24,32] and a rate of increase of T_{ODT} with pressure of 22 ± 2 °C kbar^{-1}. (b) Order-disorder transition temperatures for SI 8/8, determined from the data shown in Figure 4b as described in the text and in the caption to that figure. The error in the perpendicular direction (in temperature for scans at constant temperature, or in pressure for scans at constant pressure) is too small (±0.05 °C in temperature, ± the greater of 5 bar or 1% in pressure) to appear on this plot except at the highest pressures shown. Different symbols represent different samples. A linear fit to the data over pressures from 25 to 600 bar yields a value for T_{ODT} at 0 bar of 84 °C and a rate of increase of T_{ODT} with pressure of 19 ± 1 °C kbar^{-1}.

interaction energy between the blocks. For a diblock[37] with $\bar{N} = Nb^6v^{-2} = (R_0^2/M)^3(N_A\rho)^2M_n$ ~700 and $f = 0.45$, the theory predicts that $(\chi N)_{\text{mean field, ODT}} = 10.70 + 43.16\bar{N}^{-1/3}$ ~15.5.[38] (Recent measurements at 1 bar[39] in a SI diblock of comparable molecular weight and volume fraction yield $(\chi N)_{\text{mean field, ODT}}$ ~10.6; incorporation of fluctuation corrections suggest $(\chi N)_{\mathrm{ODT}}$ ~17, in reasonable agreement with this prediction.) Then, to

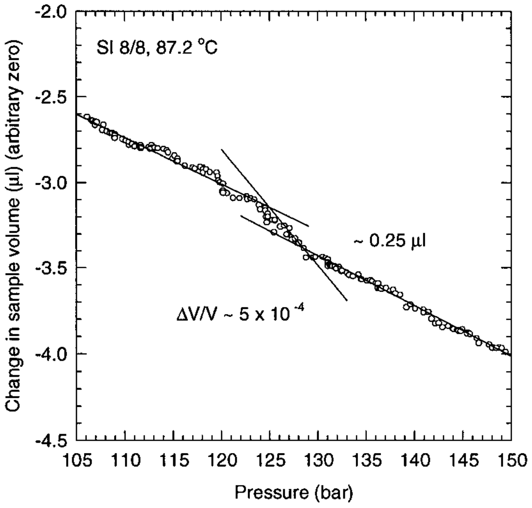

Figure 6. A typical dilatometric scan through the ODT in SI 8/8. The sample was maintained at a constant temperature of 87.2 ± 0.1 °C throughout this scan. The discontinuity at a pressure of 127 bar denotes the transition; the associated volume change is estimated from the data by the geometrical construction shown. The fractional change in volume under these conditions ($\Delta V/V$) is approximately 5×10^{-4}, in good agreement with the value of $(6 \pm 2) \times 10^{-4}$ predicted from the phase diagram in Figure 5b, the calorimetric data of Stühn,[22] and the Clausius−Clapeyron equation.

lowest order, $\Delta H \sim RT_{\mathrm{ODT}}\, f(1-f)(\chi N)_{\mathrm{ODT}}/M_{\mathrm{n}} \sim 0.8$ J/g for SI 8/8. The corresponding change in volume ($\Delta V/V$) is 4×10^{-4}. Thus, it appears likely that the more recent measurement of ΔH is an underestimate.

Confirmation of the volume change at the ODT was obtained through dilatometric methods. A typical dilatometric scan of SI 8/8 at a constant temperature of 87.2 °C appears in Figure 6. Although the figure displays specific volume as a function of pressure, the dilatometer actually measures sample pressure as a function of specific volume. The change in volume at the transition is estimated from the dilatometric data using the geometrical construction shown on the figure. Repeated measurements revealed a slight, but measurable (± 10 bar), variation in the location of this discontinuity across multiple scans at constant temperatures.

Figure 7 compares values for T_{ODT} obtained from SAXS and dilatometric measurements; the linear fit to the SAXS data of Figure 5b appears here as a solid line, while different symbols represent different dilatometric samples. To correct for a systematic difference in temperatures of *ca.* 1.4 °C between the two instruments, temperature values are shown relative to the value for T_{ODT} at 100 bar. Linear fits to each dilatometric data set indicate that T_{ODT} increases at a rate of 16 ± 2 °C kbar^{-1}, in reasonable agreement with the rate of 19 ± 1 °C kbar^{-1} measured via SAXS. This reinforces our claim that the observed dilatometric discontinuity represents the ODT. The fractional change in sample volume at the ODT, $\Delta V/V = (4.5 \pm 1.5) \times 10^{-4}$, was measured to be independent of transition pressure to within experimental resolution. Reinsertion of the experimentally measured values for ΔV and $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$ into eq 1 produces a value of the change in enthalpy at the transition of 0.9 ± 0.3 J g^{-1}. To within experimental error, this value agrees with the previously published value[22] of 1.1 ± 0.2 J g^{-1} and is in surprisingly good agreement with the value of 0.8 J g^{-1} estimated from the incompressible, fluctuation-corrected theory. In contrast to these findings, Kasten and Stühn[21] have measured a volume *decrease* $\Delta V/V = -(30 \pm 4) \times 10^{-4}$ in their material using a capillary dilatometer. Given a positive change in enthalpy upon disordering, this would imply a *decrease* in T_{ODT} with pressure, contrary to the SAXS results reported here.

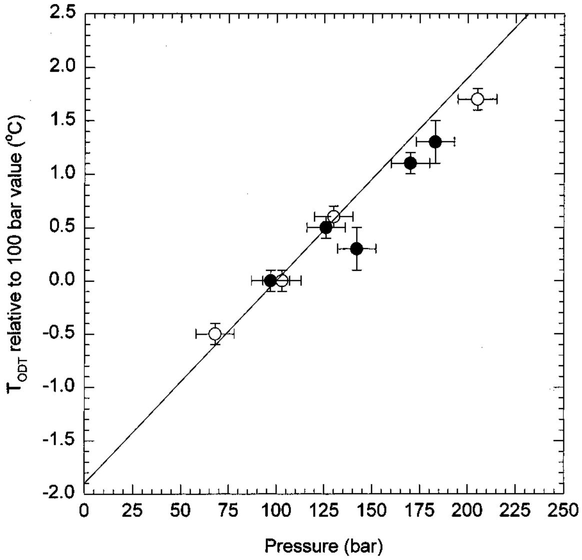

Figure 7. Comparison of ODT temperatures for SI 8/8 measured through dilatometric and scattering techniques. Different symbols indicate different dilatometric samples; the line shows the linear fit to the scattering data in Figure 5b. Direct comparison of transition temperatures measured with the two techniques reveals a systematic shift of about 1.4 °C between the dilatometric and scattering measurements; the data are therefore reported relative to the ODT temperatures measured for each sample at 100 bar. Linear fits to the data produce values for $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$ of 19 ± 1 °C (SAXS) and 16 ± 2 °C kbar^{-1} (dilatometry); the agreement between these two values suggest that discontinuities of the sort shown in Figure 6 do in fact represent the ODT in this material.

Discussion

Most theories of block copolymer phase behavior assume that the specific volume of a block copolymer is given by the sum of the volumes of the individual blocks. This assumption of additivity implies that the volume of an assembly of such molecules does not depend on the state of microphase separation. The data presented here indicate that this is incorrect; a slight but definite increase in volume accompanies the change from the microphase-separated to the disordered state. As the ODT is believed to be a first-order phase transition,[4] this change in volume can be related to the slope of the order−disorder phase boundary in the pressure−temperature plane and the measured enthalpy of the transition at 1 bar via the Clausius−Clapeyron equation. The consistency observed between independent measurements of these three quantities provides additional evidence for this first-order nature.

Of course, experimental confirmation of a well-known relation from elementary thermodynamics is of little interest by itself. Of greater significance are the implications of this volume discontinuity for theories of block copolymer phase behavior. Traditionally, descriptions which include the possibility of volume changes have been labeled “compressible”, in order to distinguish them from “incompressible” treatments which assume that the melt possesses a constant density regardless of the phase state of the material. Unfortunately, inappropriate use of these terms can lead to a misunderstanding regarding the mechanism by which pressure affects a block copolymer melt. The nomenclature suggests a connection between the isothermal bulk compressibility of a block copolymer and the phase behavior exhibited by that material. Since the compressibility is influenced by intermolecular steric interactions, this suggests that pressure alters phase behavior by inducing changes in molecular-level structural characteristics thought to govern the morphology of the system. While our earlier work[1] indicates that pressure influences many structural characteristics such as the radius of gyration and the degree of segregation, we find that the barotropic shifts in such quantities are insufficient to account for the measured change in the location of the ODT. Instead, the changes in phase behavior arise from the presence of the aforementioned volume discontinuity. In block copolymers at the ODT, then, pressure has its greatest effect in coupling to extremely small volume changes associated with phase transitions; pressure-induced shifts in other structural characteristics such as R_g and N are of comparatively minor importance. Such effects are compressibility phenomena only in the sense that the system exhibits an anomalously large compressibility as the sample passes through the ODT; see Figure 6. Indeed, analysis of disordered state scattering data indicates that compressibility corrections are not necessary for identification of these structural changes. This should not be interpreted as evidence that "compressible" theories do not provide a proper description of the ODT, however. A proper description must incorporate the change in volume at the transition, which is not possible in an "incompressible" context.

There are at least two possible interpretations of this volume discontinuity on the statistical segment length scale. Within the context of theories developed by Freed and co-workers,[40−42] it would be interpreted as a discontinuous increase in the amount of free volume present in the melt. Although our previous measurements of the disordered state scattering from SI 8/8 do not indicate a role for a nonzero "free volume fraction" as postulated by these authors,[40] experimental detection of such subtle corrections to the incompressible RPA form for the disordered state scattering[2,4] is expected to be extremely difficult. Alternatively, any volume change might be distributed uniformly throughout the sample instead of being confined to individual "voids" within the melt. Since χ describes an interaction energy which is defined with reference to a certain characteristic separation between segments, this implies that χ would change discontinuously at the transition as well. The magnitude of this discontinuity can be estimated from structural data,[1] which indicates that 1000 bar of applied pressure reduces the volume of the system by about 5% and increases the degree of segregation by 1% at low temperatures. If this change in segregation arises solely from an increase in χ which in turn results from a reduction in system volume, then our observation of a fractional change in volume of $\Delta V/V \sim 5 \times 10^{-4}$ would imply a corresponding fractional shift in χ of $\Delta\chi/\chi \sim 1 \times 10^{-4}$ at the ODT. Direct measurement of this discontinuity would require an extremely sensitive experimental method for self-consistently measuring the degree of segregation in both the ordered and disordered morphologies. Verification of the existence of this discontinuity would invalidate a common assumption in block copolymer theory, that the segregation product χN is continuous across phase boundaries. Unfortunately, at the present time, we are unaware of any such technique; thus, we are unable to determine which of these two interpretations better describes the behavior of the system.

It is tempting to describe this change in volume as solely a mixing phenomenon. Such a description is at least partially correct in that the degree to which the blocks interpenetrate differs in the two phases. However, simple characterization of the ordered phase as "unmixed" and the disordered phase as "mixed" overlooks the fact that in weakly segregated but ordered morphologies, considerable mixing of dissimilar chains occurs throughout an interfacial volume which may occupy a significant fraction of the unit cell. Perhaps some fraction of the observed behavior results from the appearance or disappearance of the ordered, spatially varying concentration profile which differentiates the ordered and disordered morphologies. The mechanism by which the creation or dissolution of this profile would produce this volume change in the absence of any change in the degree of mixing is unclear, however.

This "mixing interpretation" implies that high pressure might also influence order−order transitions (OOTs) in block copolymers. Studies of such phenomena have indicated that such transitions may be accompanied by sizable changes in the interfacial area per block junction.[14] For an interfacial region of constant thickness measured normal to the (nominal) interface, this implies a corresponding change in the fraction of the polymer volume throughout which the blocks mix. This might, in turn, produce a difference in the system volume on either side of the OOT which could be explored using high-pressure techniques similar to those described in this work. Experimental investigations of high-pressure effects in OOTs are expected to be much more challenging than the corresponding studies of ODTs, however. First, the considerable hysteresis often associated with OOTs[11,14−17,43] will increase the required equilibration times in typical experiments and restrict the precision to which the location of the transition can be specified. Second, differentiation of initial and final ordered morphologies will probably require high-quality diffraction data containing one or more higher order reflections. This will increase the minimum integration times necessary in experiments. Third, the rapid rise in the glass transition temperature with pressure[28,29] may produce a rapid increase in the degree of hysteresis associated with a particular transition upon pressurization, severely restricting the maximum pressure employable at low temperatures in certain block copolymer systems (*e.g.*, those containing polystyrene or poly(2-vinylpyridine)).

Conclusions

High-pressure studies on the order−disorder transition of weakly segregated SI diblock copolymers reveal a pressure dependence of the ODT temperature, dT_{ODT}/dp, roughly twice that expected from previous evaluation of pressure-induced changes in structural characteristics. The discrepancy results from a slight increase in the volume of the system upon disordering; pressure couples to this volume change to produce the shift in T_{ODT} as predicted by measurements of the transition enthalpy[21,22] and the Clausius−Clapeyron equation. Changes in other structural parameters such as f, N, R_g, and χ appear to be of comparatively minor importance.

From the data, we are unable to determine if the change in volume at the transition is distributed isotropically throughout the melt volume, or if it localized in "voids" as implied by certain theoretical descriptions.[40−42] The former interpretation suggests that χ changes discontinuously at the ODT, a possibility which (to the best of our knowledge) has not been explicitly considered in treatments of block copolymer phase behavior.

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