High-Pressure Effects on the Disordered Phase of Block Copolymer Melts

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ABSTRACT: We have measured the effect of high pressure on the scattering from the disordered state of a styrene–isoprene diblock copolymer containing 48 wt % styrene ($M_w \sim 16\,500$). Small-angle X-ray scattering measurements performed at the Cornell High Energy Synchrotron Source (CHESS) show an increase in the aspect ratio of the scattering maximum and a decrease in the angle at which the maximum occurs with increasing pressure. Within the context of the mean-field theory of block copolymer phase behavior originally developed by Leibler,[1] this behavior is due to an *increase* in both the radius of gyration of the molecule (R_g) and the degree of segregation of the system (χN). Examination of the data using the theory of Tang and Freed[2] reveals an identical quantitative dependence of R_g and χN on pressure without indicating a role for the free volume fraction used by these authors to treat compressibility effects. We therefore propose that the observed behavior arises primarily from shifts in the structural characteristics of the blocks, rather than from a reduction in free volume. From comparison of the pressure-induced changes in the structural characteristics of the system with the corresponding temperature-induced ones, we predict the pressure dependence of the order–disorder transition temperature in this material, provided that the phase state of this polymer is determined solely by the structural characteristics examined in this experiment.

Introduction

Though many aspects of block copolymer phase behavior as a function of temperature have been studied in detail,[3-12] the effect of pressure has remained relatively unexplored. Theoretical treatments of block copolymer phase behavior usually assume an incompressible system, in which the local density of the melt remains constant regardless of the microstructure of the material. In particular, theories developed using the incompressible random phase approximation (RPA)[13,14] have been used to interpret the scattering from disordered diblock copolymer melts[1] and binary polymer blends[14,15] in terms of the structural characteristics of the system. This approach is one of the most common methods for experimental determination of the Flory–Huggins interaction parameter (χ), a quantity which is difficult to measure with other techniques. However, real polymer melts are compressible, and the assumption of incompressibility might produce inaccurate results, especially as pressure is varied. Experimental observation of pressure effects are therefore expected to be important in assessing the range of validity of these theories.

Pressure may be expected to influence polymer melts because of two rather different effects. The first is that hydrostatic pressure reduces the overall free volume in the system, causing an isotropic reduction in sample dimensions. All other things being equal, this compressibility effect is expected to result in a decrease in R_g as pressure is applied. A second (quite distinct) effect is that, if a volume difference exists between *gauche* and *trans* rotamers in the polymer backbone, pressure might alter the statistical segment length (b) and thereby affect both the total number of statistical segments (N) and the radius of gyration (R_g). Prior work in phospholipid–water suspensions has indicated that effects of the latter sort dominate the response of such materials to applied pressure.[16]

Several authors have examined the implications of nonzero compressibility. Tang and Freed[2] applied the McMullen–Freed[17] compressible RPA formulation to diblocks and presented scattering curves for disordered diblocks as a function of void fraction (which is inversely related to applied pressure). The effect of pressure was expected to be small far from the order–disorder transition (ODT), but large close to the transition. Their work implied that analyzing data with the incompressible RPA could produce χ values which are functions of pressure, even when the actual interactions between segments are assumed to be pressure-independent. Recently, Bidkar and Sanchez[18] have used the lattice fluid theory to develop expressions for the scattering from single-phase compressible polymer blends. An interesting result of this theory is that the presence of voids (holes) in the lattice leads to an increase in the apparent R_g of the chains, if data are analyzed using

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the incompressible RPA. Since the void fraction decreases with applied pressure, this suggests that R_g would appear to be a decreasing function of pressure; for diblocks, the equivalent statement would be that the position of the correlation hole peak in the disordered state scattering (q^*) would increase with applied pressure.

More recently, Dudowicz and Freed[19] extended their lattice cluster theory (which incorporates compressibility) to diblocks and explicitly calculated phase diagrams for selected block types and lengths. An increase in pressure was predicted to either raise or lower the ODT temperature, depending on the monomer structure and monomer–monomer interactions. For a model polystyrene–poly(ethylene-*co*-propylene) diblock, assuming representative monomer–monomer interactions equivalent to those in the polystyrene–poly(methyl methacrylate) system, the ODT temperature for a diblock with the critical composition was predicted to increase by roughly 30 K on pressurizing to 1000 bar. These calculations suggest that pressure effects on the ODT may be substantial. Furthermore, they provide insight into the energetics of monomer–monomer interactions which complement similar measurements of disordered state characteristics as a function of temperature.

Recent neutron scattering experiments have provided structural data which can be used to address effects of the second type outlined above. Hammouda and Bauer[20] have investigated high-pressure effects in binary polymer blends using small-angle neutron scattering (SANS). Their analysis (conducted using the incompressible RPA) revealed a strong linear dependence of χ on applied pressure in a poly(deuterated styrene)–poly(*n*-butyl methacrylate) blend over the range from 0 to 800 bar; for their system, $\chi = -5 \times 10^{-5}$ and $(1/\chi)(\mathrm{d}\chi/\mathrm{d}p) \sim 2.25$ kbar^{-1} at 95 °C and 0 bar. The slopes of the Zimm plots, related to R_g but not interpreted as such due to fluctuation effects encountered near the spinodal, were observed to decrease with increasing pressure, suggesting that $\mathrm{d}R_g/\mathrm{d}p < 0$ in this system. Similar effects ($\mathrm{d}\chi/\mathrm{d}p < 0$, $\mathrm{d}R_g/\mathrm{d}p < 0$) were also observed by these authors in blends of poly(deuterated styrene) and poly(vinyl methyl ether). Janssen et al.[21] examined blends of hydrogenated and deuterated polystyrenes in order to assess changes in the structural dimensions of polystyrene with pressure. A fractional decrease in R_g of order 0.02 kbar^{-1} was observed at 97 °C, comparable in magnitude to the size of the effect observed by Hammouda and Bauer,[20] with the size of the effect decreasing with increasing temperature. Comparison with pressure–volume–temperature measurements on the same blend revealed that the decrease in R_g was greater than that expected due to the reduction in sample volume.

In this work, we present disordered state scattering curves from a symmetric polystyrene–polyisoprene diblock copolymer as a function of temperature and pressure. Pressurizing this system produces readily detectable changes in scattering characteristics such as the height of the scattering maximum above the background and the position of this maximum in reciprocal space, suggesting that pressure influences the radius of gyration of the copolymers as well as the degree of segregation of the system. We analyze these changes within the context of the incompressible mean-field theory developed by Leibler[1] and compare the results of that analysis with those obtained from the compressible theory of Tang and Freed.[2] Finally, we use the results of this study to test a fundamental assumption in block copolymer theory, that the behavior of these melts can be understood simply from a few gross structural parameters without reference to the microscopic details of the molecular interactions. We introduce a generalized Clausius–Clapeyron relation and compare pressure-dependent ("barotropic") changes in structural parameters to the corresponding temperature-induced ("thermotropic") ones in order to predict the pressure dependence of thermotropic transitions in this material. Experimental measurement of this predicted dependence[22,23] will therefore assess the degree to which the phase behavior of this system is determined solely by these structural characteristics.

Table 1. Characteristics of SI 8/8 at 100 °C and 1 bar

block	M_w[a]	ϱ[b] (g cm^{-3})	$(1/\varrho)\,\mathrm{d}\varrho/\mathrm{dp}$[c] (kbar^{-1} × 10^{-2})	f[d]	$\langle R_0^2\rangle/M_w$[e] (Å^2 g^{-1} mol)	$\langle R_g^2\rangle^{1/2}$[f] (Å)
S	8000	1.00[24]	−4.3[46]	0.44	0.434[38]	24
I	8500	0.84[25]	−7.5[47]	0.56	0.616[39]	29

[a] M_w, weight-average molecular weight of each block. [b] ϱ, homopolymer density. [c] $(1/\varrho)\,\mathrm{d}\varrho/\mathrm{dp}$, homopolymer bulk compressibility. For polystyrene, the value given was estimated from curves of specific volume vs temperature by extrapolating the results of high-pressure measurements above the glass transition temperature to 100 °C. [d] *f*, volume fraction of the appropriate component in the copolymer. [e] R_0, root-mean-square end-to-end distance of the appropriate homopolymer with the same weight-average molecular weight. [f] R_g, radius of gyration of the appropriate homopolymer with the same weight-average molecular weight.

Materials and Methods

The SI diblock copolymer used in this study (denoted SI 8/8) was synthesized in cyclohexane under a nitrogen blanket. Polymerization of the first (styrene) block was initiated with *sec*-butyllithium and took place at 60 °C; subsequent polymerization of the second (isoprene) block was performed at 35 °C. A small quantity of homopolystyrene (terminated first block) was removed from the resulting material by toluene/methanol fractionation. The sample composition and the polyisoprene microstructure were determined by ^{1}H NMR (48 wt % S, 5.2% 3,4 addition). Molecular weights were determined by size exclusion chromatography (SEC) in toluene, using a 60 cm PLGel column (Polymer Laboratories) calibrated with narrow-distribution polystyrene standards. The molecular weight of the first block ($M_w = 8000$, $M_w/M_n = 1.06$) was determined from an aliquot taken from the reactor prior to the addition of the isoprene monomer; the resulting weight-average molecular weight for the entire diblock was 16 500. The polymer has an apparent polydispersity of 1.05; an approximate correction for column broadening yields an estimate of 1.04 as the true polydispersity. From the known densities of high molecular weight polystyrene[24] and polyisoprene[25] at 100 °C and 1 bar, the minority component volume fraction (*f*) is calculated to be 0.44. These values are summarized in Table 1.

X-ray scattering measurements were conducted on beamline F1 of the Cornell High Energy Synchrotron Source (CHESS). White radiation was generated by a 24-pole, 1.2 T wiggler magnet. A horizontally bent Si(111) monochromator was used to select an energy of 13.6 keV ($\lambda = 0.91$ Å) from this white radiation and focus the beam in the horizontal direction; a Rh-coated silicon mirror located downstream from the monochromator was used to remove higher energy harmonics and focus the beam in the vertical direction. A pair of remotely-controlled slits mounted on the hutch wall defined the beam, while a second set of manually operated slits located approximately 3 m from the hutch wall eliminated parasitic scattering from the first set. Samples were placed inside a high-pressure cell (described in detail below), 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 ±0.05 deg). Remote temperature sensing was provided by a platinum resistance thermometer (RTD) attached to the brass block enclosing the pressure cell. Two-dimensional diffraction im-

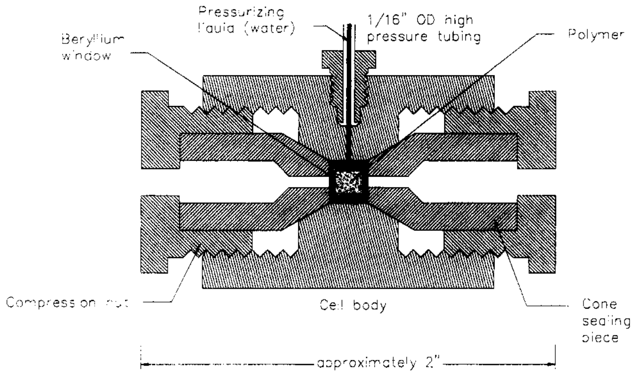

Figure 1. Side view schematic of the high-pressure cell (not to scale). The cell and cone seal pieces are machined from high-pressure steel; beryllium disks mounted on the cone seals permit the passage of X-rays through the cell. The sample is enclosed within a stainless steel tube contained within the cylindrical volume at the center of the cell. The entire assembly rests within a brass block which is maintained at a temperature between 0 and 185 °C by a set of thermoelectric units attached to the face of the block.

ages were collected with an area detector designed around a CCD chip with 2048 × 2048 pixels.[26] Due to the degree of collimation required to reach the extremely small scattering angles desired, collection of sufficient signal to identify the structural characteristics of the disordered state required between 20 and 30 s of integration, depending on the temperature of the sample and the flux then being generated by the synchrotron (measured with an ionization chamber located immediately after the parasitic slit assembly to be of order 10^{11} photons s^{-1}). After collection, images were digitized, corrected for detector response characteristics, and written to magnetic tape. Images were collapsed into a one-dimensional format by integrating azimuthally along an arc ±30° from the vertical axis.

Views of the high-pressure SAXS cell appear in Figure 1. The cell consists of a hollow cylinder of tempered high-pressure stainless steel (Vascomax 300; Teledyne Allvac/Vasco, Agawam, MA) surrounding a stainless steel tube which in turn encloses the polymer. (The inner sleeve merely facilitates removal of the polymer from the cell at the completion of the experiment). Compression pieces threaded onto the ends of the cell press two cones of high-pressure steel against the cell body to create a line seal. Holes drilled into the center of each cone admit X-rays into the cell interior. The ends of these holes are capped by 0.040 in. thick beryllium disks 0.125 in. in diameter. These disks deform slightly under high pressure to create a metal-to-metal seal between the disk and the cone face. At low pressures, the disks are sealed against the cone faces by a thin film of epoxy (Epoxi-Patch 1C White; Dexter Corp., Seabrook, NH). Deionized water is used as a pressurizing medium. Since the boiling point of water rises rapidly as a function of pressure,[27] use of water does not significantly limit the temperatures at which the cell can be operated. High pressure (up to 3000 bar) is generated hydrostatically with a commercial hydraulic cylinder (model 37-5.75-60; High Pressure Equipment Co., Erie, PA) and is transmitted into the cell interior by a line of 0.0625 in. diameter high-pressure tubing which attaches to the top of the cell as shown. Since the beryllium disks do not seal the ends of the steel sleeve containing the polymer, the pressurizing fluid comes into direct contact with the sample material. Pressure sensing is accomplished through a commercial piezoresistive pressure sensor attached to the pressure line (Sensotec models UHP/1269-06 and 450D; Columbus, OH); the accuracy and resolution of the sensor are of order 0.5%.

At the start of each scan at constant temperature, samples were first pressurized to 100 bar, set to the desired temperature, and permitted to equilibrate for 30 min. After scattering from this initial state was recorded, pressure was stepped upward in 100 bar increments. Once the maximum pressure of 700 bar was achieved, pressure was reduced in 100 bar increments until the system returned to the initial pressure. Samples were permitted to equilibrate for 3 min at each pressure before taking data.

The observed scattering consisted of three components: parasitic scattering due to glancing reflection of the main X-ray beam off of one or more components of the optical system; incoherent scattering arising primarily from the beryllium windows of the high-pressure cell as well as the large-scale characteristics of the polymer sample; and a signal produced by monomer–monomer correlations in the disordered state of the material. When present, parasitic scattering was usually of sufficient intensity to obscure the signal from the disordered state, and images containing significant parasitic scattering could not be analyzed. The scattering produced by the cell in the absence of the polymer was found to be well represented by a function of the form

$$I_{\text{background}}(q) = \frac{b_0}{q^n} + b_1 \tag{1}$$

Accordingly, the incoherent background present in each one-dimensional profile was determined by fitting the data to this form over $q = 0.015-0.03$ Å^{-1} and $0.12-0.20$ Å^{-1}. As expected, b_0 was a linear function of the main beam intensity, while n was nearly constant for all scattering curves ($n = 2.56 \pm 0.03$). After removal of this background, the resulting scattering curve was fit over $q = 0.03-0.15$ Å^{-1} to the appropriate functional form for the scattered intensity from a disordered diblock copolymer melt. In order to analyze the data, the system was initially assumed to be incompressible,[1] and the intensity $I(q)$ was represented as

$$I(q) = \frac{I_0}{F(f,q,R_g) - B} \tag{2}$$

where the fit parameters I_0, R_g, and B represent an arbitrary scale factor, the radius of gyration of the entire molecule, and the degree of segregation in the system, respectively. f is the minority component *volume* fraction at 0 bar, which has been shown to be the appropriate parameter for describing the symmetry of diblock copolymers in the Leibler theory.[28] The analytic form of the function $F(f,q,R_g)$ in an incompressible and monodisperse system has been defined elsewhere.[1] Polydispersity corrections were incorporated by integrating each term in the expression for $F(f,q,R_g)$ over the expected Zimm–Schulz distribution of lengths for each block in the system;[29] the more conservative value for M_w/M_n of 1.05 was used in these calculations.

In the absence of fluctuations, $B = 2\chi N$, where χ is the Flory–Huggins interaction parameter and N is the number of statistical segments in the entire molecule. The low molecular weight of the polymer and the proximity of the experimental temperature range (97–141 °C) to the order–disorder transition (measured to be 84 °C at 0 bar[23]) implies that the contribution of fluctuation effects to the disordered state scattering may be significant; [30] neglecting this contribution and assuming that $B = 2\chi N$ leads to an overestimation of the segregation product. Although the fluctuation-corrected theory has not been extended to the extremely low number of statistical segments expected in experimental systems, recent experimental results have confirmed its prediction for the nonlinear temperature dependence of B at temperatures approaching the order–disorder transition temperature.[3] Unfortunately, due to the limited temperature range examined in this experiment, an assessment of the effect of high pressure on this nonlinear temperature dependence is beyond the scope of the present work.

Compressibility corrections to the mean-field result were incorporated by following Tang and Freed,[2] in which the preceding expression for the disordered state scattering is modified to

$$I(q) = \frac{I_0[1 + \phi C_2(f,q,R_g)]}{F(f,q,R_g) - B + \phi C_1(f,q,R_g)} \tag{3}$$

where the additional fit parameter f represents the free volume

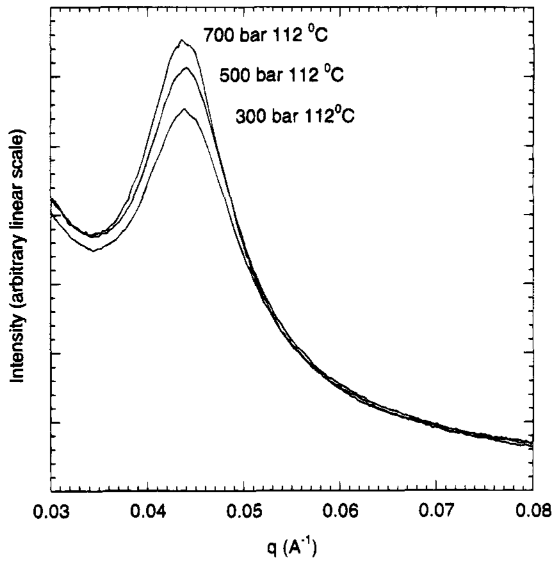

Figure 2. One-dimensional scattering profiles for the disordered state at 112 °C, prepared from the corresponding two-dimensional images by integrating the counts within 20° of the vertical axis at each radial distance from the center of the image. Each profile shown has been corrected for detector response characteristics and variation in main beam intensity (as measured by an ionization gauge located immediately after the second set of slits). The increase in the peak height upon pressurization suggests an increase in the degree of segregation of the system.

fraction in the system, and $C_1(f,q,R_g)$ and $C_2(f,q,R_g)$ are correction factors defined by Tang and Freed.[2] For a polydisperse system, these functions may be calculated using an approach analogous to that used to determine $F(f,q,R_g)$, and the disordered state scattering may be fit to eq 3 with I_0, f, B, and R_g as free parameters.

Results

The application of high pressure produces observable effects on the disordered state scattering which may be demonstrated in a model-independent manner. Figure 2 presents raw scattering data (corrected only for detector response characteristics and variation in main beam intensity) collected at a sample temperature of 112 °C. As the sample is pressurized from 300 to 700 bar, the height of the scattering maximum rises, suggesting an increase in segregation with increasing pressure. Figure 3 displays the locations of the scattering maxima observed in the raw scattering data as a function of pressure for two of the four temperatures examined. At all four measurement temperatures, the location of the scattering maximum (denoted q^*) moves inward as pressure is applied, suggesting that the radius of gyration of the copolymer *increases* upon pressurization. Values obtained upon pressurization match those obtained upon depressurization to within experimental error, indicating that any pressure-induced increases in the glass transition temperature of the disordered melt did not appreciably retard the equilibration of the system.

Typical results for the fitting procedure described in the previous section are shown in Figure 4a,b. The raw scattering data, together with the background determined by fitting the raw data to eq 1, appear in Figure 4a. Figure 4b shows the background-subtracted curve and the fit to this curve using the polydispersity-corrected, incompressible RPA model for the disordered state scattering.

Figure 5 shows the effect of high pressure on the value of the radius of gyration (R_g) extracted using the fitting procedure described above. Values obtained upon pressurization match those obtained upon depressurization to within the experimental error up to 126 °C, indicating that any degradation of the material under these conditions is insufficient to affect the location or shape of the scattering maximum. The hysteresis observed at 141 °C is probably due to degradation of the material; SEC performed after annealing at 155 °C revealed a slight amount of branching and chain scission (approximately 10 wt %). Over a pressure range of 100–700 bar, R_g *increases* linearly with increasing pressure at a rate of 1 Å kbar^{-1}, in contrast to the *decrease* in R_g with pressure expected due to bulk compressibility effects (-1 Å kbar^{-1}; see Table 1). Decreases in R_g have also been predicted by the theory of Bidkar and Sanchez[18] and observed *via* SANS in a variety of blends.[20,21] Linear fits to the data appear on the figure; the fitted parameters appear in Table 2. The statistical error bars shown for each point arise primarily from uncertainty in the location of the center of each one-dimensional scattering profile. An additional systematic error of 0.8 Å due to the uncertainty of 0.01 in the sample polydispersity index (M_w/M_n) affects all data points equally and thus may be neglected in subsequent discussions of dR_g/dp.

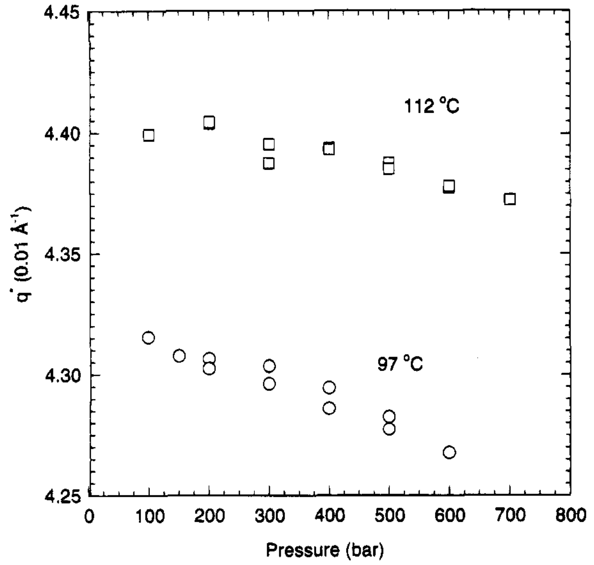

Figure 3. Change in the location of the disordered state scattering maximum (q^*) with pressure at 97 and 112 °C, determined from the raw scattering profiles by fitting the observed intensity in the region immediately surrounding the maximum to a parabola. The shift of the maximum to smaller values of q^* with increasing pressure suggests an increase in the radius of gyration of the molecule.

Plots of the fit parameter B (equal to $2\chi N$ in the mean-field limit) as a function of pressure and temperature appear in Figure 6. As was the case for the fitted values of R_g, values of B obtained upon pressurization match those obtained upon depressurization to within statistical error limits for the three lower measurement temperatures. The linear fits to the data shown in Figure 6 indicate that B increases linearly with increasing pressure over the range from 100 to 700 bar; the fit parameters appear in Table 3. The statistical error associated with each point due to the fitting procedure is less than 0.01; however, there is a significant systematic error of 0.16 across all data due to the uncertainty of 0.01 in the minority component volume fraction (f). Although the difference in compressibility between the two blocks (see Table 1) implies that the difference in block electron densities depends on the applied pressure, this contrast factor affects only the overall

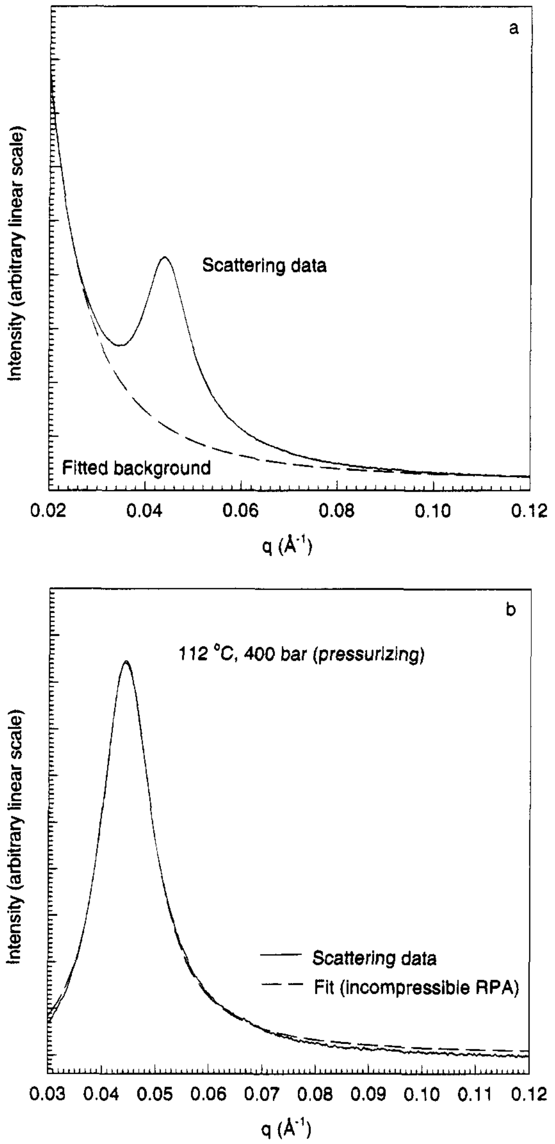

Figure 4. (a) Typical raw scattering curve, and the background fit to that curve, by following the procedure described by the text. The data shown were recorded after 3 min of annealing at 112 °C following pressurization of the sample to 400 bar. The solid line represents the raw scattering data; the dashed line represents the fit to the background determined using the procedure described in the text. (b) Background-subtracted curve from figure 4a, shown as a solid line, and the fit to this data using the incompressible form for the disordered state scattering. The fit parameters are $R_g = 43.6$ Å and $B = 21.06$ at 112 °C, 400 bar.

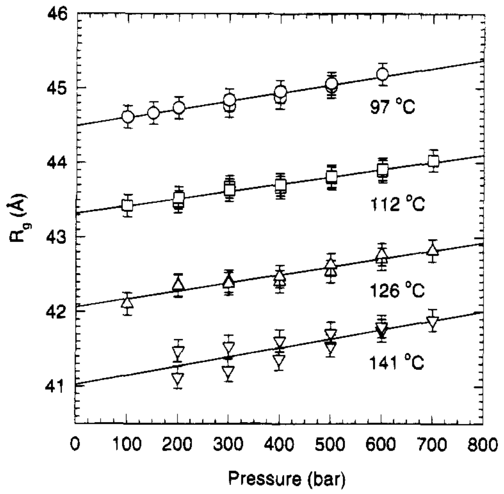

Figure 5. Variation in R_g with pressure, determined by fitting the background-subtracted scattering profiles to the incompressible RPA form. The uncertainty in R_g of 0.15 Å arises primarily from uncertainty in the determination of the center of each image; this is considerably less than the error due to uncertainty in the fit to the scattering profile, which is of order 0.03 Å. R_g increases linearly with increasing pressure at all temperatures.

Table 2. Linear Fit Parameters for R_g as a Function of Pressure[a]

temp (°C)	R_g (p = 0) (Å)	dR_g/dp (Å kbar^{-1})
97	44.5 ± 0.02	1.10 ± 0.07
112	43.3 ± 0.02	0.98 ± 0.05
126	42.1 ± 0.04	1.10 ± 0.09
141	41.0 ± 0.12	1.22 ± 0.26

[a] The error listed for each parameter is that calculated by the fitting procedure. As described in the text, the statistical uncertainty associated with each experimental value of R_g is ±0.15 Å; the systematic uncertainty is ±0.8 Å.

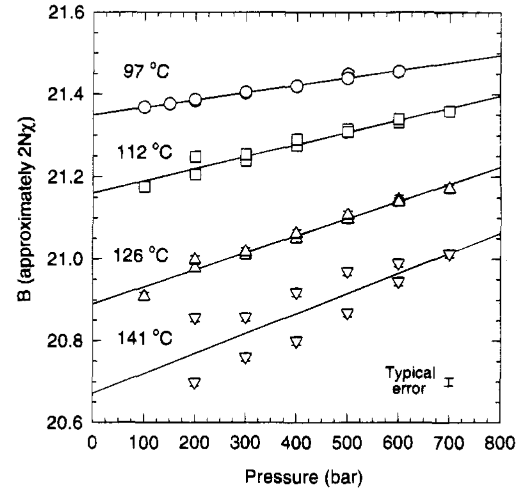

Figure 6. Variation in the fit parameter B, which describes the degree of segregation of the system, with applied pressure. B is expected to equal $2\chi N$ in the absence of fluctuations, a situation which is achieved only for an infinitely long chain; for a polymer of finite length, assuming that $B = 2\chi N$ leads to an overestimation of the segregation product. The error bars (which are partially obscured by the symbols) show the statistical uncertainty in B of 0.01 obtained from the fitting procedure; a typical error bar appears at the lower right. At all temperatures, B increases linearly with increasing pressure.

intensity of the disordered state scattering, which is captured in the fit parameter I_0; the fit parameter B, which depends on the shape of the scattering curve, is unaffected by this behavior.

Compressibility corrections to the disordered state scattering[2] suggest a strong dependence of the apparent degree of segregation in the system (i.e. the aspect ratio of the scattering maximum) on the free volume present in the system. It is therefore possible that the observed pressure dependence of B results from a decrease in the free volume with increasing pressure, rather than from pressure-induced changes in χ and N. Such a decrease in free volume is believed to account for the experimentally observed dependence of the glass transition temperature (T_g) on applied pressure.[31,32] However, fits to the scattering data using the compressible RPA formulation for the scattered intensity (eq 3) produced values for dB/dp and dR_g/dp that were identical to those obtained using the incompressible RPA form of $I(q)$ (to within experimental error). The resulting values for the void volume fraction (ϕ) were always less than zero and displayed no systematic variation with applied pressure; a slight decrease (toward more negative values of ϕ) was apparent with increasing temperature. Due to the

Table 3. Linear Fit Parameters for B as a Function of Pressure[a]

temp (°C)	$1/T$ (1/K × 1000)	B ($p = 0$)	dB/dp (kbar^{-1})
97	2.72	21.35 ± 0.01	0.18 ± 0.01
112	2.61	21.16 ± 0.01	0.29 ± 0.02
126	2.51	20.89 ± 0.01	0.42 ± 0.02
141	2.42	20.67 ± 0.05	0.5 ± 0.1

[a] The error listed for each parameter is that calculated by the fitting procedure. As described in the text, the statistical uncertainty associated with each experimental value of B is ±0.01; the systematic uncertainty is ±0.16.

unphysical nature of these results, we conclude that the proposed compressibility corrections[2] do not account for the pressure-induced changes in the disordered state scattering observed in this experiment; it is possible, however, that our inability to separate the disordered state scattering from the background for $q \ll q^*$ biases our analysis against identification of such compressibility effects. This result does not rule out the possibility of detecting changes consistent with this theory at higher pressures and/or temperatures. However, given the mathematical complexity of the correction factors and the (presumably) small value of ϕ which precedes them in the expression for the disordered state scattering, it will be difficult to perform experiments that succeed in distinguishing changes attributable to variations in free volume from those resulting from shifts in the other parameters characterizing the scattering curve.

Discussion

Interpretation of high-pressure effects in block copolymers is complicated by the variety of ways in which pressure can affect the structural parameters believed to govern phase behavior. Such interpretation is necessary, however, if experimental results are to influence subsequent theoretical developments. Pressure effects can be separated into two categories: those which affect general characteristics of polymer chains, such as the radius of gyration (R_g) and the statistical segment length (b) and those which influence characteristics which arise from the presence of two chemically distinct types of polymer in the experimental system, such as the Flory–Huggins interaction parameter (χ) and the segmental asymmetry parameter (ϵ). We shall examine each of these effects in turn.

The observed shift in the location of the disordered state scattering maximum (q^*) upon pressurization might be the result of changes in both the total number of statistical segments (N) and the statistical segment length (b). Such changes would probably arise from differences in the volumes of the different conformational states (*trans* vs *gauche* rotamers) of the carbon–carbon bonds forming the main chain of the polymer. To lowest order, if the volumes of two states differ by an amount δv, pressure will further separate these states in energy by an amount $p\ \delta v$, thereby changing the distribution of conformations and altering the statistical segment length. Such effects have already been observed in phospholipid–water suspensions.[16] A crude estimate of the magnitude of this effect can be made by assuming ideal (Gaussian) chains in which the contour length L of the entire molecule remains constant upon pressurization. In this case, $R_g^2 \sim L^2/N$; and for the system examined here, Figure 5 would imply that the total number of statistical segments at 97 °C is reduced by 5% from its value in vacuum upon pressurization to 1000 bar. If an affine pressure-induced reduction of L is estimated from published compressibility data (see Table 1), the fractional change in N, $(1/N)(\mathrm{d}N/\mathrm{d}p)$, rises to -0.09 kbar^{-1} at 97 °C. The corresponding temperature-induced fractional change in R_g is -0.002 K^{-1} at 97 °C and 0 bar; thus, an increase in sample temperature of 12.5 deg (for constant L) or 23 deg (for pressure-dependent L) will reverse the change in R_g observed upon pressurizing from 0 to 1000 bar. Note that this is not consistent with the data of Figure 5.

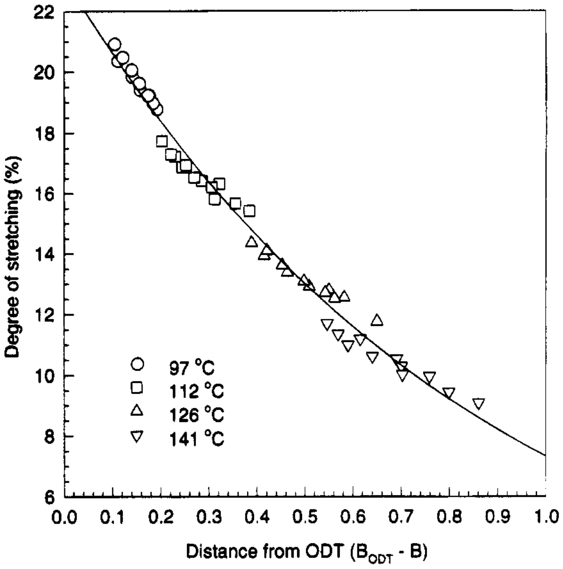

Figure 7. Degree of stretching of the copolymer coils as a function of the distance from the ODT in units of B (B is roughly equal to twice the segregation product, or $2\chi N$). The degree of stretching was defined as the percentage increase in the experimentally measured value for R_g over the value calculated from the dimensions of polystyrene and polyisoprene homopolymers of the appropriate molecular weight and the known dependence of these homopolymer dimensions on pressure and temperature. (As no published data on the pressure dependence of polyisoprene chain dimensions was found, dR_g/dp was assumed to be zero for this block). The value for B_{ODT} of 21.58 at 0 bar was estimated by linear extrapolation of the fitted values for $B(T)$ at 0 bar (see Table 3) to the measured ODT temperature of 84 °C at 0 bar. The degree of stretching appears to depend primarily on the distance from the ODT, suggesting that departure of the polymer coils from their ideal conformations may account for a significant fraction of the observed pressure dependence of R_g. The solid line shows a simple exponential fit to the data as described in the text; departures from this curve presumably represent pressure-induced reductions in the overall dimensions of the system as well as changes in the number of statistical segments.

The assumption of ideal chain behavior is only valid for a block copolymer at extremely high temperatures ($T \gg T_{ODT}$), which is not the case for the temperatures encountered in this experiment. At lower temperatures ($T \rightarrow T_{ODT}$), Owens *et al.*[33] and Almdal *et al.*[34] have suggested that the polymer coils are distorted from their Gaussian conformations, with a corresponding increase in the apparent radius of gyration. Theoretical support for this proposition has been provided by Barrat and Fredrickson;[35] computer simulations which show similar behavior have also been reported.[36,37] The unperturbed R_g of the diblock at each of the experimental temperatures can be estimated from known results for polystyrene and polyisoprene homopolymers;[38,39] pressure corrections may be incorporated by using published data for polystyrene[21] and assuming that polyisoprene chain dimensions are insensitive to applied pressure. Figure 7 shows the "degree of stretching" of the diblock (defined as the percentage by which the experimentally determined radius of gyration exceeds the predicted (presum-

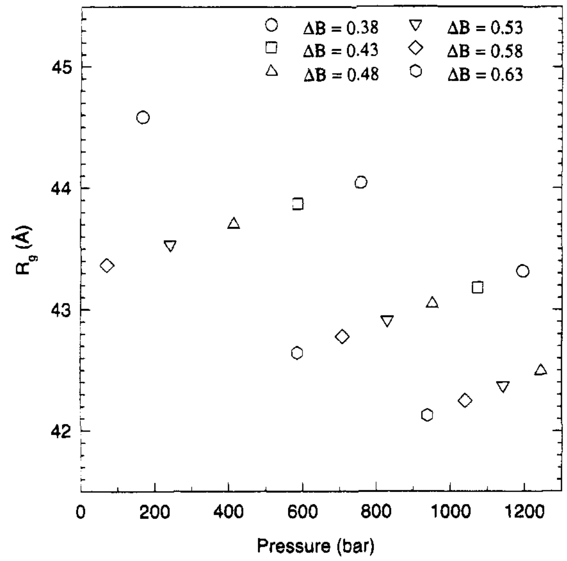

Figure 8. Radius of gyration of SI 8/8, as a function of pressure at a constant distance ΔB from the ODT. By fixing the degree of segregation, the effect of chain stretching in the vicinity of the ODT (see Figure 7) is held constant. Each point shown was estimated from the data shown in Figures 5 and 6 using the linear fits to the data listed in Tables 2 and 3; although the results of such a procedure are expected to remain valid only over the experimental pressure range of 100–700 bar, the results have been extended outside of this range to illustrate the effect of pressure on R_g in the absence of stretching effects. R_g appears to decline with increasing pressure at an approximate rate of 2% per kilobar. This finding is consistent with the reduction in this parameter expected due to compressibility effects (see Table 1).

ably unperturbed) value at that temperature and pressure) as a function of the distance from the ODT in units of the segregation product (χN). Prior measurement[23] has indicated that the ODT occurs at 84 °C (0 bar) in this material; a linear fit to the values shown in Table 3 (which therefore neglects fluctuation effects in the vicinity of the ODT) yields $B = 21.58$ at this temperature. The data suggest that the degree of stretching depends in part on the distance from the ODT. A simple exponential fit to the data yields

$$\text{Stretch (\%)} = (23.1 \pm 0.2)\exp\left[-\left(\frac{B_{\text{ODT}} - B}{0.87 \pm 0.02}\right)\right] \tag{4}$$

This is a phenomenological relation only; other functional forms might represent the data equally well. The maximum observed coil elongation (20%) agrees reasonably well with that observed by Almdal *et al.* (13%)[34] and predicted by Barrat and Fredrickson (of order 20% for a diblock of low molecular weight).[35] It is therefore likely that this "Gaussian-to-stretched coil" transition accounts for a significant fraction of the observed pressure dependence of R_g.

This transition does not account for all of the observed pressure dependence, however. Since R_g and B depend linearly on applied pressure (see Figures 5 and 6), linear fits to the data may be used to determine R_g as a function of pressure at a fixed distance from the ODT; see Figure 8. Although such calculations are strictly valid only over the pressure range examined in this experiment (100–700 bar), we have extended them downwards to 0 bar and upward to 1200 bar in order to illustrate the response of R_g to applied pressure in the absence of stretching effects. (This assumption of a linear barotropic response beyond 700 bar is not a very good one, as $\mathrm{d}R_g/\mathrm{d}p$ and $\mathrm{d}B/\mathrm{d}p$ probably decrease at very high pressures.) At a fixed distance from the ODT, R_g appears to *decrease* with increasing pressure at an approximate rate of $(1/R_g)(\mathrm{d}R_g/\mathrm{d}p) = -0.02\ \text{kbar}^{-1}$. (Recall that at fixed temperature, R_g *increases* with increasing pressure; see Figure 5). This is roughly equal to the fractional reduction in R_g expected due to compressibility effects in this diblock (see Table 1); it is also consistent with previously observed measurements in polystyrene,[22] if a pressure-dependent fractional shift in R_g for polyisoprene of $-0.02\ \text{kbar}^{-1}$ is assumed as well.

It is reasonable to assume that the blocks comprising the molecule differ in their response to applied pressure. Since homopolystyrene and homopolyisoprene are nearly incompressible (see Table 1), we expect little change in f with pressure. However, the pressure-induced fractional shift of R_g in polystyrene[21] ($-0.02\ \text{kbar}^{-1}$) exceeds the value predicted due to compressibility effects in that material (see Table 1) ($-0.014\ \text{kbar}^{-1}$), suggesting that the number of statistical segments in the chain (N) increases upon pressurization by about 1% per kilobar. A similar estimate for polyisoprene yields a fractional *decrease* in N for that system of 1% per kilobar, if R_g for polyisoprene decreases at 2% per kilobar (as is required for agreement between our results and those of Janssen *et al.*[21]). This asymmetric response suggests that pressure might alter the segmental asymmetry parameter (ϵ), recently proposed by several authors[40-42] to explain certain features in experimentally measured phase diagrams for diblock copolymer melts. Since

$$\epsilon = \frac{f_A {R_{gB}}^2}{f_B {R_{gA}}^2} \tag{5}$$

where f_A and f_B are the volume fractions of the minority and majority component materials, respectively, and R_{gA} and R_{gB} are the corresponding radii of gyration,

$$\frac{1}{\epsilon}\frac{\partial \epsilon}{\partial p}\bigg|_T = \left[\frac{1}{\varrho_B}\left(\frac{\partial \varrho_B}{\partial p}\right)_T - \frac{1}{\varrho_A}\left(\frac{\partial \varrho_A}{\partial p}\right)_T\right] + 2\left[\frac{1}{R_{gB}}\left(\frac{\partial R_{gB}}{\partial p}\right)_T - \frac{1}{R_{gA}}\left(\frac{\partial R_{gA}}{\partial p}\right)_T\right] \tag{6}$$

where ϱ_A and ϱ_B are the mass densities of the two blocks. Estimates of ϵ for polystyrene–polyisoprene diblock copolymers[41] range from 1.0 to 1.3; our estimate for SI 8/8 is 1.15, based on the values in Table 1. Depending on the barotropic (pressure-dependent) response of the constituents of a particular melt, significant *continuous* variation in ϵ might be achieved with relatively modest pressures. This possibility represents one of the more promising approaches for experimentally measuring the importance of ϵ in block copolymer phase behavior. Current technique[6] involves only *discrete* changes in ϵ, achieved by changing the chemical composition of the experimental system and attempting to compensate for all of the attendant changes in other system parameters such as N, χ, and b. From the bulk compressibilities of homopolystyrene and homopolyisoprene (see Table 1), and by assuming a pressure-dependent shift in polyisoprene dimensions as described above, we estimate that the fractional change in ϵ with pressure is $-0.032\ \text{kbar}^{-1}$ in this material. Incorporation of this segmental asymmetry into the calculation of $F(f,q,R_g)$ yields an approximate pressure dependence for B, $\mathrm{d}B/\mathrm{d}p$, of $+0.05\ \text{kbar}^{-1}$ at all temperatures. This is significantly less than the observed dependence of this parameter (see Figure 6 and Table 3), but it does imply that the actual pressure-induced shift in the degree of segregation may be slightly less than that reported here. Repeated calculation indicates that $F(f,q,R_g)$ is relatively insensitive to changes in ϵ, suggesting that the considerable uncertainty present in our crude estimate of $d\epsilon/dp$ should not affect these conclusions.

An additional possibility for the pressure dependence of B arises from shifts in the quantities which describe the relative importance of fluctuations in determining the characteristics of the disordered state (such as the composite parameter $c^3\,d\lambda$ described by Fredrickson and Helfand[30] and measured by Wolff *et al.*[3]). As was discussed earlier, the limited temperature range employed in this experiment prevents us from directly measuring these fluctuation effects and assessing their pressure dependence. A further complication arises from the increasingly nonideal conformations adopted by the polymer chains as the system nears the ODT (see Figure 7). Since most theoretical predictions for the disordered state scattering assume Gaussian chain conformations,[1,30] use of such models to analyze the observed shift in peak aspect ratio with increasing pressure is suspect. Unfortunately, the only theoretical treatment of this behavior of which we are aware[35] requires extensive calculation in order to determine the appropriate corrections to the fluctuation-corrected theory[30] and is not expected to remain valid at the small values of N characteristic of experimental materials. We therefore neglect such effects and assume $B = 2\chi N$, which permits us to estimate the sensitivity of χ to applied pressure. Since χ is not a directly measurable quantity (unless assumptions are made concerning the number of statistical segments in the system), we quote only its fractional pressure dependence. From the analysis in the preceding paragraph, the *total* number of statistical segments is unaffected by pressure in a symmetric SI diblock, and so $(1/\chi)(d\chi/dp) = +0.01$ kbar^{-1} at 97 °C, rising to $+0.025$ kbar^{-1} at 141 °C. Again, this is an approximate value only; future measurements may produce different results for the pressure dependence of polystyrene and polyisoprene chain dimensions, which would imply different fractional shifts in the number of statistical segments for these polymers and thereby require substantial revision of this estimate.

The preceding discussion illustrates the variety of ways in which the experimental data may be interpreted to yield information on the structural parameters believed to govern diblock copolymer phase behavior. Such analysis naturally requires reference to one of several theoretical models, and the shortcomings of these models—for example, assumption of incompressible melts with ideal chain conformations near the ODT and neglect of fluctuation effects—will affect the validity of the results deduced from the experimental data. Yet some conclusions may be reached without reference to a particular model. If we assume that the shape of the disordered state scattering curve, which is governed by the fit parameter B, describes the degree of segregation between the two blocks in SI 8/8 and we further assume that it is this degree of segregation alone which determines the location of the ODT in SI 8/8, then

$$\frac{\Delta T_{\mathrm{ODT}}}{\Delta p} = -\left.\frac{\partial T}{\partial B}\right|_p \left.\frac{\partial B}{\partial p}\right|_T \qquad (7)$$

For SI 8/8 at 87 °C and 100 bar, we extrapolate the observed temperature dependence of B at 100 bar and combine it with data from Table 3 to predict a pressure dependence of the ODT temperature of 10 ± 2 °C kbar^{-1}. Departures of the experimentally observed pressure dependence from this prediction will reflect a variety of factors, including the degree to which the assumptions used to construct this estimate reflect the actual thermodynamics of the system. For example, revision of this estimate to include fluctuation effects[30] (which is not possible for our data due to the limited number of temperatures studied) might produce a larger pressure dependence of T_{ODT} than is predicted above. The essential point is that the left-hand side of eq 7 represents a purely thermodynamic quantity, the Clausius–Clapeyron coefficient, which may be obtained from calorimetric, dilatometric, or structural studies. The factors on the right-hand side may be determined purely from structural X-ray diffraction studies. Agreement between these two experimentally measured quantities is a strong argument that models based on a limited number of gross structural parameters alone are sufficient to describe the phase behavior, without having to take into account the details of the underlying molecular interactions. Preliminary experiments[22] indicate that T_{ODT} does, in fact, rise with increasing pressure in SI diblocks at a rate roughly equal to that predicted here. More precise measurements will be reported in a separate publication.[23]

Although our results suggest that the compressible RPA formalism[2,17] is not required to understand our data, this does not mean that compressibility effects are not relevant to descriptions of pressure-dependent behaviors in polymer melts. The question addressed in this paper has to do with whether the observed changes can be accounted for by a reduction in free volume or whether shifts in the structural characteristics of the blocks themselves are more important. Our results suggest the latter.

Conclusions

High pressure provides a new tool for understanding the phase behavior of macromolecular systems. Like temperature, pressure affects many of the characteristics which govern system behavior. When used for continuous modulation of parameters such as segmental asymmetry, it offers an alternative to traditional chemical synthesis methods. Because the modulation can be done *in situ* in the same sample, combining high-pressure studies with synchrotron radiation provides a means of rapid systematic studies of the phase behavior of copolymer systems.

We have found that application of high pressure increases the degree of segregation of this symmetric SI diblock. The radius of gyration of the entire chain (R_g) also rises, contrary to previous expectations. This increase in R_g is interpretable within the context of incompressible RPA models; although a small fraction of this change is believed to result from a pressure-induced reduction in the length of the entire molecule (as predicted by measurements of the bulk compressibility), most of this increase represents the adoption by the chains of stretched conformations (relative to the ideal, or Gaussian, conformation) in the vicinity of the ODT. We find that close to the ODT, the degree of stretching may be characterized by a simple exponential (see Figure 7). Although compressibility must play a role in understanding pressure effects, we find that models incorporating void volumes are not required in understanding the simplest effects of hydrostatic pressure. Anisotropic effects (such as chain stretching) appear to play a much more important role than isotropic bulk compressibility effects, again contrary to existing models. Our work suggests that models incorporating nonideal chain statistics are required in order to understand not only pressure effects but also the overall phase behavior.

The pressure–temperature equivalence measured for the degree of segregation of the system has been used to predict the pressure dependence of the ODT temperature. Should this prediction be confirmed, it will provide proof for an important assumption in block copolymer theory, viz. that the phase behavior of copolymer systems can be understood using only some gross structural parameters without reference to molecular level details. Attempts at building such models for incorporating nonideal chain statistics should therefore be encouraged.

Perhaps the most exciting aspect of high-pressure studies is the potential for novel experiments. For example, since pressure jumps can be conducted in much less time than equivalent temperature jumps,[43] experiments combining synchrotron radiation and high-pressure techniques might be used to study a variety of rapid processes in polymer systems, such as the dynamics of microphase separation and subsequent lattice ordering.[44,45] Hammouda and Bauer have already demonstrated the utility of such an approach for observing the spinodal ring in binary polymer blends.[20] The relationship described in eq 7 between pressure- and temperature-induced changes in system segregation implies that precise but rapidly adjustable implementation of very small changes in this parameter might be accomplished by controlling the pressure of the system. We anticipate that such experiments will be particularly useful in studying fluctuation-induced behaviors near the ODT. They might also find application in examining phenomena expected to occur within a very narrow range of temperatures at 0 bar, such as phase coexistence in a material of narrow molecular weight distribution between two different microphases in the immediate vicinity of a phase boundary.

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