# The Effect of Hydrostatic Pressure on the Lower Critical Ordering Transition in Diblock Copolymers

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ABSTRACT: The effect of hydrostatic pressure on the lower critical ordering transition (LCOT) was investigated by in situ small angle neutron scattering on symmetric and asymmetric diblock copolymers of perdeuterated polystyrene and poly(*n*-butyl methacrylate). These systems exhibit a transition from the disordered to ordered state upon heating. Similar to the lower critical solution transition (LCST) in polymer mixtures, the LCOT is entropically driven and is accompanied by an increase in volume on demixing of the copolymer blocks. As a consequence, application of hydrostatic pressure markedly increases the temperature at which the transition from the disordered to the ordered state occurs. Small angle neutron scattering studies as a function of temperature and pressure show that the pressure dependence of the LCOT, $\Delta T_{LCOT}/\Delta P$, is up to +147 °C/kbar (1.45 ± 0.07 °C/MPa), roughly 1 order of magnitude greater than that seen at elevated pressures for diblock copolymers exhibiting an upper critical ordering transition (UCOT). Additionally, SANS data obtained at various pressures were superimposed to generate master curves for the peak intensity, peak position, and full width at half-maximum (fwhm). This suggests an equivalence between temperature and pressure of the thermodynamic behavior of systems that exhibit the LCOT.

## Introduction

The ordering or microphase separation transition in block copolymers has been the subject of extensive theoretical and experimental investigation. While most block copolymer systems undergo ordering with decreasing temperature, through an upper critical ordering transition (UCOT), both poly(styrene-*b*-*n*-butyl methacrylate) and more recently poly(styrene-*b*-vinyl methyl ether) have been shown to exhibit ordering with increasing temperature.[1,2] This lower critical ordering transition (LCOT) is analogous to the lower critical solution transition (LCST) observed in polymer blends and solutions. Whereas the UCOT is enthalpically driven, the LCOT results from an increase in available configurations upon volume expansion at elevated temperatures, and is, therefore, entropic in its nature. This entropically driven ordering transition is accompanied by a positive change in volume upon demixing of the copolymer blocks, which should be manifest in the observed pressure dependency of the transition temperature.[3] This notion motivated the present investigation, which aims at quantifying pressure effects on the LCOT in diblock copolymers of styrene and *n*-butyl methacrylate.

The pressure dependence of the UCOT has been carefully investigated by several groups, who reported different trends depending upon the materials and pressure range. Hajduk et al.[4] studied diblock copolymers of polystyrene and polyisoprene and found that the UCOT increased with increasing pressure with a pressure coefficient $\Delta T_{UCOT}/\Delta P$ of 20 °C/kbar (0.20 °C/MPa). Schwann and co-workers[5] reported a coefficient of $\Delta T_{UCOT}/\Delta P$ = 15 °C/kbar (0.15 °C/MPa) for block copolymers of poly(ethylenepropylene) and poly(dimethylsiloxane) for pressures above 1 kbar. At lower pressures (<0.5 kbar), a negative coefficient of similar magnitude was obtained for the same system. Stühn and co-workers[6] saw qualitatively similar trends in the pressure dependency of the UCOT for P(S-b-I). At low pressures (<1 bar), the UCOT dropped precipitously, with a massive coefficient of approximately −3600 °C/kbar (−36 °C/MPa). At higher pressure, the pressure coefficient changed sign and approached the value of 19 °C/kbar (0.188 °C/MPa), consistent with the results of Hajduk et al. Finally, Frielinghaus et al.[7] reported a negative pressure coefficient of −20 °C/kbar (−0.20 °C/MPa) to pressures as high as 1 kbar for poly(ethylenepropylene)-*b*-poly(ethylethylene) block copolymers. The complex dependence of the UCOT on pressure can be ascribed to two competing effects. Predominantly, application of pressure decreases the free volume, thereby increasing the segmental interaction energy and reducing block miscibility. However, if the system exhibits a negative change in volume on mixing, then the application of pressure might first enhance miscibility due to a loss of this "excess volume" associated with the ordered state.

For systems exhibiting LCST behavior, the negative $\Delta V_{mix}$ dictates the pressure dependence of the phase separation, and positive pressure coefficients are always

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**Table 1. Copolymer Characteristics**

| copolymer | $f_{PS}$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| 68K | 0.51 | 68 000 | 1.03 |
| 78K | 0.49 | 78 000 | 1.06 |
| 85K | 0.47 | 85 000 | 1.04 |
| 134K | 0.29 | 134 000 | 1.08 |

observed.[3] Janssen and co-workers[8] reported pressure coefficients of the LCST of ~12 °C/kbar (~0.12 °C/MPa) for mixtures of PS and PVME close to the critical composition, while Hammouda and Bauer[9] observed shifts of ~20–25 °C/kbar (0.20–0.25 °C/MPa) for asymmetric mixtures of the same system. These results are in good qualitative agreement with calculations by Dudowicz and Freed.[10] Hammouda and Bauer also investigated pressure effects on the scattering from mixtures of PS and P(nBMA) but did not report the pressure coefficient of the transition temperature.

The present study reports measurements of the pressure dependence of the lower critical ordering transition in P(S-*b*-nBMA) block copolymers. Small angle neutron scattering studies under hydrostatic pressure reveal a pressure coefficient for the LCOT of 147 ± 7 °C/kbar (1.45 ± 0.07 °C/MPa), nearly 1 order of magnitude higher than the high-pressure values reported for systems exhibiting UCOTs. We additionally find that the SANS data obtained at various pressures can be superimposed to generate master curves for the peak intensity, peak position, and full width at half-maximum (fwhm). This suggests an equivalence between temperature and pressure of the thermodynamic behavior of systems that exhibit the LCOT.

## Experimental Section

Symmetric diblock copolymers of perdeuterated polystyrene and poly(*n*-butyl methacrylate), denoted P(dS-*b*-nBMA), were prepared using high-vacuum anionic polymerization techniques (Table 1). Copolymers having weight average molecular weights of 68 000, 78 000, and 85 000 (denoted 68K, 78K, and 85K, respectively), polydispersities of less than 1.08, and polystyrene volume fractions between 0.47 and 0.51 were used in this study. In addition, an asymmetric P(dS-*b*-nBMA) diblock copolymer with a molecular weight of 134 000 (134K) and a polystyrene volume fraction of 0.29 was investigated. Samples of P(dS-*b*-nBMA) were melt-pressed into 1.2 mm thick, 16 mm diameter disks. High-pressure small-angle neutron scattering (SANS) measurements were performed at the Cold Neutron Research Facility at the National Institute of Standards and Technology on beamline NG-3, using a hydraulic pressure cell that permitted in situ SANS measurements over a pressure range from 1 bar to 1 kbar and over a temperature range from 25 to 200 °C. Silicone oil was used as the pressurizing fluid, with a rubber gasket separating the sample from the fluid. The instrument configuration for all experiments was $\lambda = 6$ Å, $\Delta\lambda/\lambda = 0.15$, sample–detector distance = 9 m. SANS experiments were performed from 152 to 226 °C in 12 °C increments over a pressure range from 0 to 1 kbar in 0.17 kbar increments at each temperature. Reproducibility was verified by repeating several measurements at the conclusion of each temperature sweep, and size exclusion chromatography revealed no changes in the molecular weight distribution as a result of the high temperatures and pressures. The scattering was corrected for background and detector inhomogeneity in the standard manner and was scaled to an absolute level using several standards. Intensities are reported as absolute differential scattering cross sections ($d\Sigma/d\Omega$) in units of $cm^{-1}$. SANS profiles are shown as a function of the scattering vector $Q = (4\pi/\lambda)\sin(\theta)$, where $2\theta$ is the scattering angle.

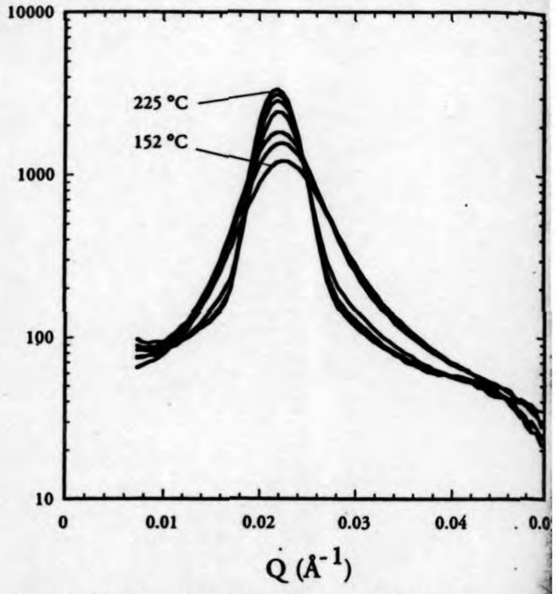

**Figure 1.** Absolute small angle neutron scattering profile for 85K P(dS-*b*-nBMA) at 0.3 kbar of hydrostatic pressure a a function of the scattering vector *Q* at the indicated temper atures.

## Results and Discussion

SANS experiments were performed by first changin the temperature in 12 °C increments from 150 to 22 °C, allowing thermal equilibration and then measurin the scattering at fixed pressures up to 1 kbar. Thi experimental protocol established a 7 × 7 matrix o SANS measurements in temperature *T* and pressure *P* A typical series of SANS results for 85K P(dS-*b*-nBMA as a function of temperature at a fixed pressure of 0.1 kbar is shown in Figure 1. At low temperatures th copolymer exhibits a diffuse scattering maximum characteristic of the disordered state. With increasin temperature the peak intensifies and sharpens, and it position shifts to lower wave vectors as the LCOT i approached.[11,12] At this pressure, the copolymer remains in the disordered state over the entire temperature range investigated.

The effect of pressure on the phase transition behavio of the copolymer is shown in Figure 2. Here SAN profiles are shown for the 85K P(dS-*b*-nBMA) at 17 °C over the pressure range from 0.01 kbar to 1 kbar At lower pressures the copolymer is in the ordere state, as evidenced by a sharp reflection at 0.021 $Å^{-1}$ with a second-order reflection evident at ~0.04 $Å^{-1}$. With increasing pressure the intensity of th reflection decreases dramatically. At pressures abov 0.17 kbar the intense, narrow reflection of the ordere state has changed abruptly to a diffuse peak with n higher order reflections, signifying the transitio from the ordered to disordered state with increasin pressure. This change is quite pronounced and is full reversible.

A convenient means of characterizing the orderin transition in diblock copolymers is by the breadth of th scattering maximum.[13,14] At the transition, the ful width at half-maximum intensity of the peak is expecte to decrease abruptly. Figure 3 shows the temperatur dependence of the fwhm for the 85K copolymer at a series of pressures. At ambient pressure (0.014 kbar) the fwhm decreases from 0.0038 $Å^{-1}$ to 0.0023 $Å^{-1}$ a ~160 °C, which signals the onset of order. At 0.17 kbar

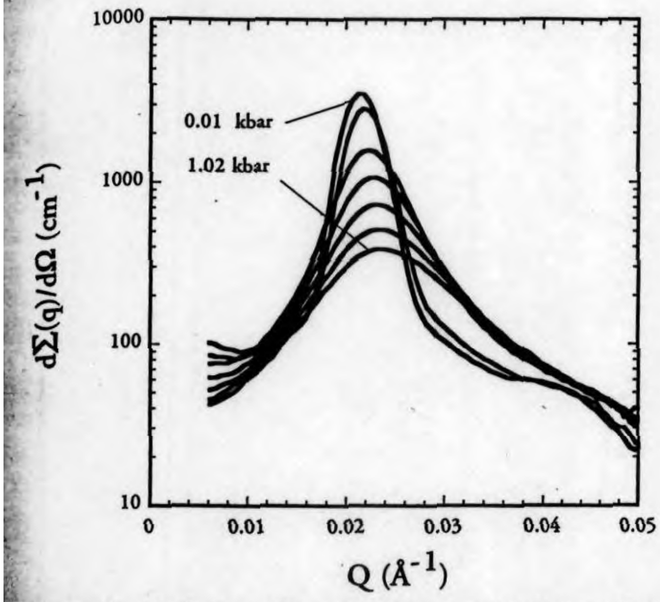

**Figure 2.** Absolute small angle neutron scattering profiles for 85K P(dS-*b*-nBMA) at 170 °C as a function of the scattering vector $Q$ at the indicated pressures.

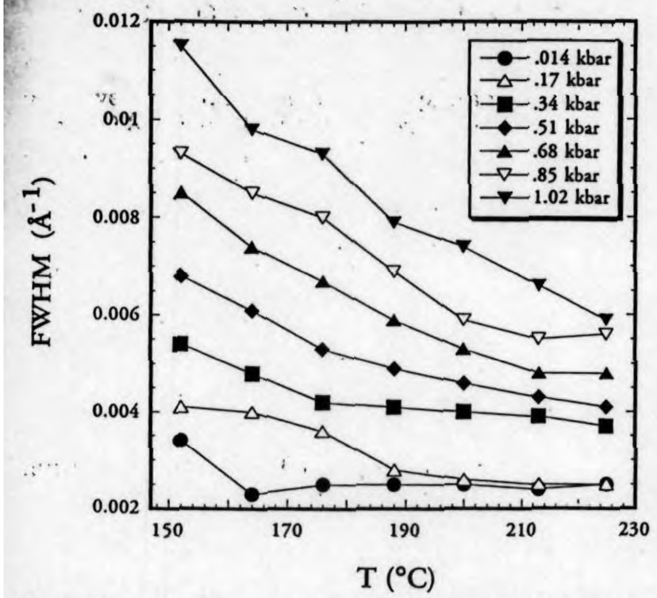

**Figure 3.** Full width at half-maximum intensity (fwhm) for the 85K P(dS-*b*-nBMA) as a function of temperature at the indicated pressures.

the fwhm of the reflection is 0.004 Å$^{-1}$ or greater for temperatures below ~180 °C. At higher temperatures, the fwhm decreases to that characteristic of the ordered state. Hence, the LCOT at 0.17 kbar occurs at ~185 °C, roughly 20 °C higher than that at ambient pressure. At 0.34 kbar, the fwhm is always greater than 0.0034 Å$^{-1}$, indicating that the copolymer remains disordered over the entire temperature range investigated. Consequently, the LCOT at this pressure must exceed 225 °C, an increase of over 60 °C compared to the value at ambient pressure.

Similar observations can be made on considering the data in Figure 3 at constant temperature and varying pressure. At 150 °C, the fwhm is always greater than 0.0034 Å$^{-1}$; i.e., the copolymer is always disordered. At 164 °C, an increase in hydrostatic pressure of 0.156 kbar induces an order-to-disorder transition, as evidenced by the increase of the fwhm from 0.0024 to 0.0034 Å$^{-1}$. At 188 °C and above, the LCOT occurs at pressures between 0.17 and 0.34 kbar. Unfortunately, the pressure increment of 0.17 kbar used in this study was too coarse to locate the transition pressure more precisely in this temperature range. In the disordered state, the continuous broadening of the peak with increasing pressure is consistent with an increase in block compatibility. Notably, this pressure dependence is strongest at low temperatures, where the system is far into the disordered region of the phase diagram.

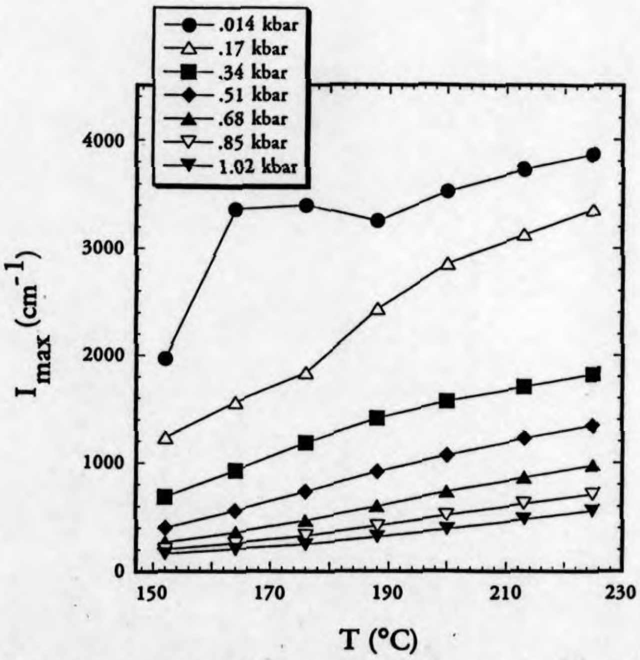

**Figure 4.** Intensity of the maximum $I_{\max}$ as a function of temperature for the 85K P(dS-*b*-nBMA) as a function of temperature.

Another way to identify the ordering transition from the scattering profile is to plot the peak intensity, $I_{\max}$, as a function of temperature for each pressure, as shown in Figure 4. As the LCOT is approached with increasing temperature, a corresponding increase is observed in $I_{\max}$. At 0.014 and 0.17 kbar, $I_{\max}$ displays a sharp rise at ~160 °C and 185 °C, respectively. These temperatures correspond precisely with the LCOT values determined from the fwhm data in Figure 3. For pressures higher than 0.17 kbar, no discontinuity in $I_{\max}$ vs $T$ is observed, as the system remains disordered.

In the disordered state, the increase in peak intensity with temperature is accompanied by a gradual shift of the peak position $Q^*$ toward lower values of $Q$, as illustrated in Figure 5. Similar results have been obtained for block copolymers that undergo ordering upon cooling.[11,12] In the latter case, the shift is associated with a stretching of the copolymer blocks away from their junction point, to reduce the number of unfavorable intrachain segmental contacts. For P(S-*b*-nBMA), which undergoes ordering upon heating, two factors could contribute to the shift in $Q^*$. First, the thermal expansion of the melt will decrease in some measure the value of $Q^*$ due to a corresponding expansion of the coils. Although certain polymers exhibit negative coil expansion coefficients with temperature,[15,16] both PS[15] and PnBMA[17] have positive temperature coefficients for their coil dimensions. To assess the magnitude of this contribution, the predicted shift

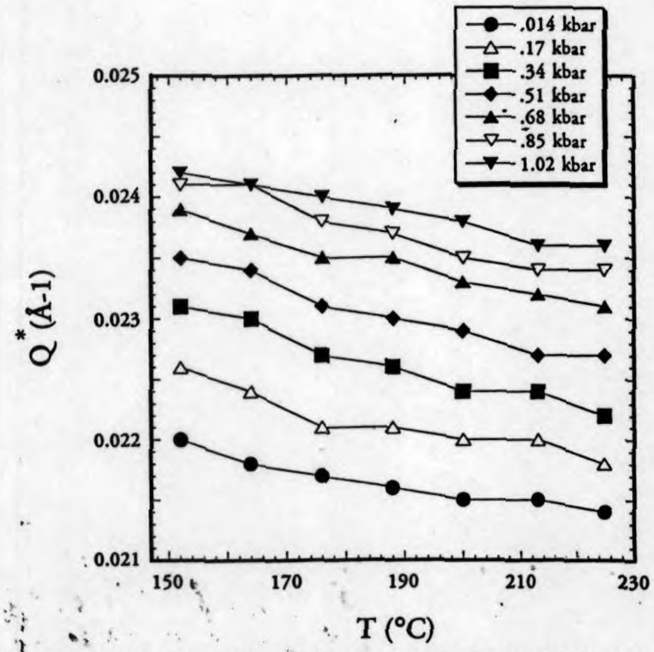

**Figure 5.** Peak position $Q^*$ for the 85K P(dS-*b*-nBMA) as a function of temperature at the indicated pressures.

in $Q^*$ can be estimated from the thermal expansion coefficient according to

$$\langle\alpha\rangle_P = (1/V_{C,i})\,(V_{C,1} - V_{C,2})/(T_2 - T_1)$$

where $\langle\alpha\rangle_P$ is the numerically averaged thermal expansion coefficient for PS and PnBMA at a specified pressure and $V_{C,i} \sim R_{g,i}{}^3$ is the coil volume at temperature $T_i$. At 0.34 kbar, $Q^*$ ($\sim 1/R_g$) decreases from 0.0231 to 0.0226 Å$^{-1}$ as $T$ increases from 130 to 160 °C. This corresponds to an observed coil expansion of ~7%. By comparison, the expected coil expansion due to thermal effects at 0.34 kbar is ~1.7%, using $\langle\alpha\rangle_{0.34} = 5.5 \times 10^{-1}$ °C$^{-1}$. (The value of $\langle\alpha\rangle_P$ was calculated by solving the lattice fluid equation of state model[3] at a pressure of 0.34 kbar.) Hence, the expected value of $Q^*$ at 160 °C based on thermal expansion would be 0.0230 Å$^{-1}$, significantly higher than the observed value.

A second factor responsible for the observed decrease in $Q^*$ is chain stretching, related to local fluctuations in block concentration, as seen for copolymers approaching the UCOT.[4,7,11,12] For the LCOT, thermodynamic considerations and the observed pressure dependence of the transition require an increase in volume upon demixing of the blocks. This increased volume leads to an increased number of available configurations, which is entropically favorable and drives the transition. In the disordered state near the transition, adopting a stretched conformation provides extra configurations due to the resulting local increase in the intrablock concentration. In going from the disordered to the ordered state, the shift in $Q^*$ displays no strong discontinuity, as the coils are considerably stretched prior to the transition.

Examination of the temperature dependence of the $Q^*$, fwhm, and $I_{\max}$ at different pressures indicates that a simple horizontal shift along the temperature axis will generate universal curves. The magnitude of the shift quantifies the equivalence between pressure and temperature in these systems. Shown in Figure 6 are the master curves at atmospheric pressure for $I_{\max}$, fwhm, and $Q^*$, generated by horizontal shifting of the data from Figures 3–5. In all cases temperature–pressur superposition resulted in substantial overlap betwee data taken at successive pressures. At the ambien pressure LCOT (~155 °C), the fwhm and $I_{\max}$ show discontinuous increase (Figure 6b,c). The peak positio in contrast, shows a continuous decrease across th entire range of reduced temperature, as seen in Figur 6a.

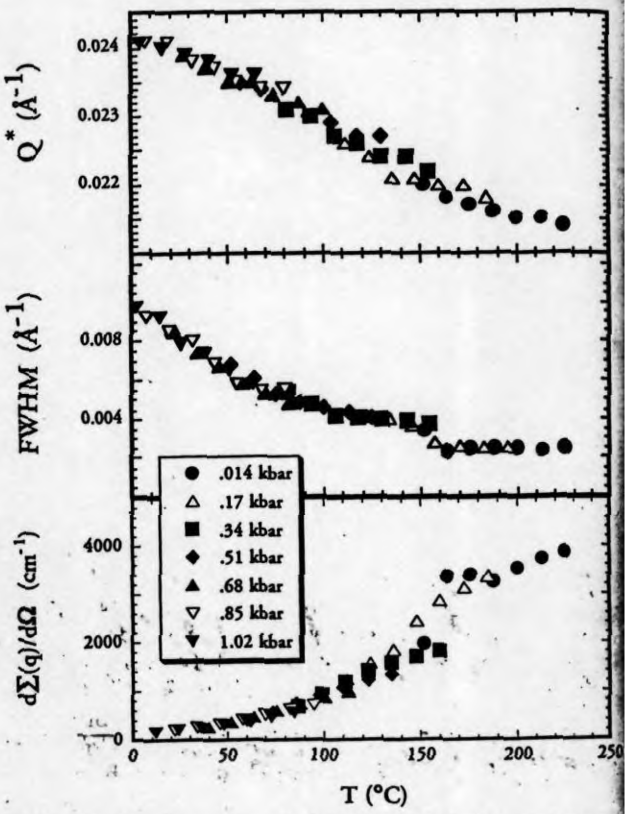

**Figure 6.** Superposition of the (a) $Q^*$, (b) fwhm, and (c) $I_{\mathrm{m}}$ as a function of temperature at the indicated pressures. Th data have been shifted along the temperature axis by a amount corresponding to 147 °C/kbar. Atmospheric pressur was used as the reference pressure.

The extent to which these variables were shifted alon the temperature axis yields $\Delta T$. Figure 7 shows $\Delta T$ a a function of pressure for the 85K P(dS-*b*-nBMA). Th values of $\Delta T$ shifts used for the fwhm, $Q^*$, and $I_{\max}$ ar shown. As seen, good agreement between the shifts fo each characteristic of the scattering is evident. A estimate of the pressure coefficient $\Delta T/\Delta P$ can b obtained from a linear fit to these data, yielding a slop of $\Delta T/\Delta P = 147 \pm 7$ °C/kbar ($1.45 \pm 0.07$°/MPa). Thi pressure coefficient is equivalent to the change in th disorder-to-order temperature with pressure. Com pared to the corresponding values obtained for pressur measurements on different UCOT systems,[4-7] $\Delta T_{\mathrm{LCO}}$ $\Delta P$ for P(S-*b*-nBMA) is roughly 1 order of magnitud greater. This finding is in good agreement with rece predictions by Hino and Prausnitz.[18] Combining th random phase approximation with a perturbed har sphere-chain equation of state model, these autho calculated a pressure coefficient for the LCST/LCOT PS–PnBMA blends and block copolymers of $\Delta T/\Delta P$ 200 °C/kbar (1.97 °C/MPa). A rigorous analysis of th SANS data employing such an equation of state forma ism is planned for future publication.

Similar pressure coefficients were obtained for t other copolymers investigated, regardless of molecul

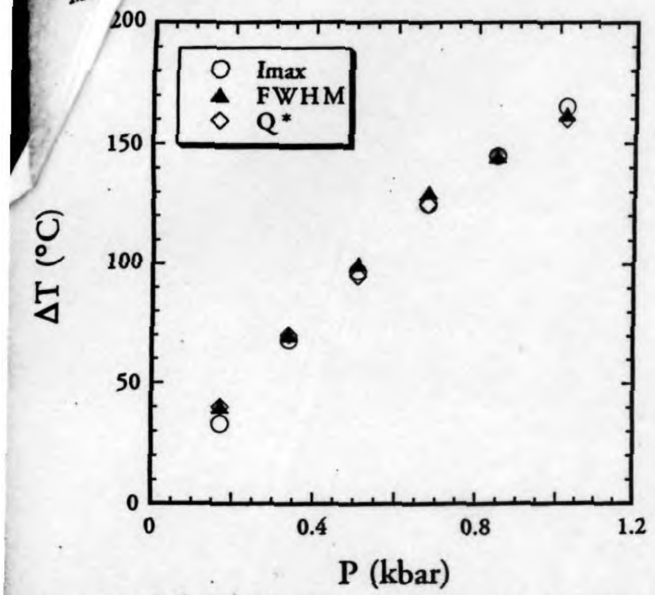

**Figure 7.** Shift along the temperature axis as a function of pressure for the 85K P(dS-*b*-nBMA). These data represent an average of the results obtained from the peak intensity, peak position, and fwhm results. A pressure coefficient of 147 ± 7 °C/kbar (1.45 ± 0.07°/MPa) is obtained.

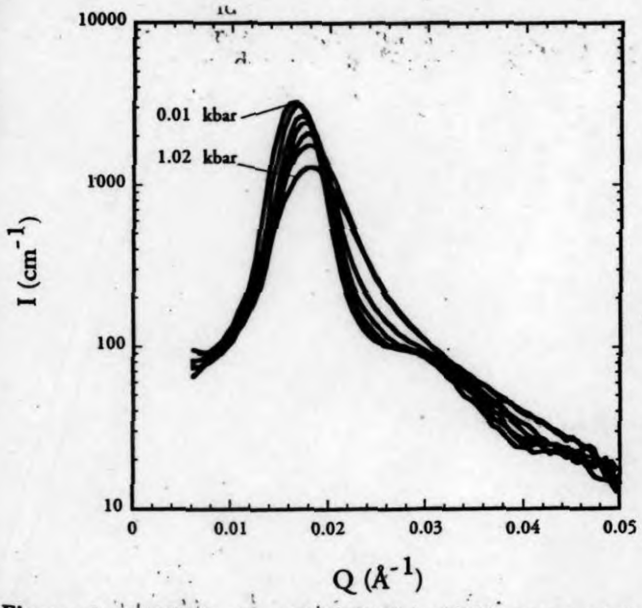

**Figure 8.** SANS for the 134K P(dS-*b*-nBMA) asymmetric diblock copolymer (styrene fraction of 0.29) as a function of the scattering vector $Q$ at the pressures indicated. A dramatic reduction and broadening of the peak with increasing pressure is observed.

weight. The ambient pressure disorder-to-order temperature for the 78K copolymer was roughly 15 °C higher than that for the 85K polymer, at ~170 °C; for the 68K material, the transition was beyond experimental range (>210 °C). For these two molecular weights, the shifting procedure yielded an estimated $\Delta T/\Delta P$ of 127 and 117 °C/kbar, respectively. The strong influence of pressure on the LCOT is beautifully demonstrated in the case of the asymmetric 134K P(dS-*b*-nBMA) copolymer. At atmospheric pressure this copolymer is ordered at all temperatures. However, pressure can be used to drive this system into the disordered state. Shown in Figure 8 are the SANS results for this copolymer at 170 °C as a function of pressure. At atmospheric pressure the scattering exhibits a strong peak at $Q^* = 0.016$ Å$^{-1}$ with a weak second-order reflection at 0.031 Å$^{-1}$. As the pressure is increased, the reflection decreases in intensity, broadens, and shifts to higher $Q$. The SANS at the highest pressure of 1 kbar is characteristic of a diblock copolymer in the disordered state.

## Conclusions

In this study a quantitative examination of the pressure dependence of the LCOT of P(dS-*b*-nBMA) has been presented. The observed pressure dependence is quite strong, with pressure coefficients greater than 147 °C/kbar (1.45 °C/MPa) for three MWs investigated, which is roughly 1 order of magnitude greater than that found for UCOT systems at elevated pressures. With increasing pressure the copolymer is driven into the disordered state; i.e., increased pressure promotes segmental mixing of the blocks. These two features underscore the fact that the driving force for the LCOT is entropic in nature. The qualitative behavior of the scattering profiles is quite similar to that observed for systems that undergo the UCOT. With increasing temperature or decreasing pressure, the position of the peak characterizing the correlation hole scattering shifts to smaller scattering vectors, indicative of the stretching of the copolymer chains as the system approaches the ordered state. A major finding is the equivalence between temperature and pressure, which allows superpositioning of temperature-dependent results at different pressures to generate universal curves with a consistent shift factor.

Hydrostatic pressure has been shown to be a very effective means of driving the system from the ordered to the disordered state. In terms of the rheological properties, pressure at constant temperature can be used to force the material from a solid state where microphase separation impedes flow of the polymer chains to a melt state where the copolymer segments are mixed. If one considers standard processing conditions for polymers, such "baroplastic" behavior could be highly advantageous.

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