

Pressure Effects on the Phase Behavior of Styrene/*n*-Alkyl Methacrylate Block Copolymers

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ABSTRACT: Earlier experimental investigations performed on a family of block copolymers formed from styrene and a homologous series of *n*-alkyl methacrylates revealed a strong dependence of thermodynamic compatibility between the two blocks on the length of the alkyl side chain of the methacrylate. Here we report the effect of hydrostatic pressure on the phase behavior of the same series of block copolymers, as determined by in situ small-angle neutron scattering. We find that hydrostatic pressure is a very effective means of driving styrene/*n*-alkyl methacrylate block copolymers with intermediate side chains from the highly viscous ordered state to the fluid disordered state of the copolymer. Hence, for *n* ranging from 2 to 6 (ethyl to hexyl methacrylate), pressure induces mixing with an absolute value of the pressure coefficient of the order/disorder transition, dT_{ODT}/dP , of up to 1.5° C/MPa (150° C/kbar). Similar results are obtained when the methacrylate block consists of a random sequence of short and long alkyl side chains with carefully chosen and predictable composition. In contrast, pressure suppresses mixing when the methacrylate block is composed of either very short (*n* = 1) or very long (*n* > 8) side chains. In terms of rheological properties, these results indicate that pressure applied at a constant temperature can be used to induce flow in some copolymers of this series. The ability to design such “baroplastic” behavior into commercially relevant thermoplastic elastomers would be highly advantageous from a processing standpoint.

Introduction

The self-assembly of block copolymers comprising two or more distinct polymer blocks into periodic nanostructures has been exploited in the development of engineering materials such as thermoplastic elastomers, pressure-sensitive adhesives, and impact resistant thermoplastics.^{1,2} Over the past decade it has further been recognized that, besides their interesting mechanical properties, these nanostructured polymers provide attractive avenues for the development of nanotechnologies,³ optically active materials,^{4,5} biomaterials,^{6–8} and battery electrolytes.^{9,10} The recent development of versatile and industrially amenable synthetic routes for the preparation of block copolymers has unveiled unprecedented opportunities for optimizing the properties of these molecules for a given application through the judicious choice of both chemistry and molecular architecture.^{11–13}

Upon considering the potential uses of such molecularly designed materials, a significant limitation arises from the difficulty to control the bulk thermodynamics of block copolymers, particularly the appearance of order/disorder. Indeed, from an applications standpoint,

the strong thermodynamic incompatibility typically found for block copolymers is highly advantageous, as it results in remarkably stable solidlike microphase-separated morphologies. However for processing, where flow is essential, the ability to access the more fluid, segmentally mixed (disordered) state is clearly desirable.¹ In current practice, this is achieved by either heating the material to a sufficiently high temperature in the presence of antioxidants or by adding a common solvent for the different polymer blocks constituting the copolymer. The former approach is generally viable only for rather low molecular weight systems of limited commercial application, unless more complex copolymer architectures such as multiblock are used.¹⁴ The latter is disadvantageous from the standpoint of cost and environmental considerations.

One potential approach to enhanced processability in block copolymer melts might be to exploit the phenomenon of pressure-induced miscibility previously observed for a limited number of polymer pairs. In earlier work, we demonstrated by small-angle neutron scattering that both polystyrene-*block*-poly(*n*-butyl methacrylate), PS-*b*-PBMA, and PS-*b*-poly(hexyl methacrylate), PS-*b*-PHMA, exhibit pressure-induced miscibility,^{15,16} although the former undergoes ordering upon heating through a lower disorder–order transition (LDOT),^{17,18} while the latter exhibits an upper disorder–order transition (UDOT).¹⁹ For PS-*b*-PBMA, applying 100

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Table 1. Molecular Characteristics of Diblock Copolymers Investigated

copolymer	M_n (kg/mol)	M_w/M_n	PS mass fraction (%)	remarks ^b
19K PS ₄₈ - <i>b</i> -PLMA	19	1.01	50 (theor)	
23K PS- <i>b</i> -POMA	23	1.06	55.8	
43K PS- <i>b</i> -POMA	43	1.03	50.7	
27K PS- <i>b</i> -POMA	27		54.3	30/70 mixture of 43K and 23K
28.6K PS- <i>b</i> -PHMA	28.6	1.01	49.0	
41K PS- <i>b</i> -PHMA	41	1.01	49.0	
34.3K PS- <i>b</i> -PHMA	34.3		49.0	45/55 mixture of 41K and 28.6K
136K PS- <i>b</i> -PPMA	136	1.01	49.8	<5% homopolymer
70K PS- <i>b</i> -PEMA	70	1.02	49.1	~5% homopolymer
110K PS- <i>b</i> -PEMA	110	1.01	48.7	<5% homopolymer
79K PS- <i>b</i> -PEMA	79		49.0	70/30 mixture of 70K and 110K
27.6K PS ₄₈ - <i>b</i> -PMMA ^a	27.6	1.01	50	
80K ps- <i>b</i> -P(MMA- <i>r</i> -LMA)	80	1.01	50	26.5% MMA, 23.5% LMA

^a Purchased from Polymer Laboratories. ^b All percentages are mass fractions.

MPa of hydrostatic pressure raised the LDOT by 150 °C,¹⁵ while experiments on PS-*b*-PHMA gave a negative pressure coefficient for the UDOT of $-0.6^\circ\text{C}/\text{MPa}$ ($-60^\circ\text{C}/\text{kbar}$).¹⁶ A qualitatively similar enhancement in miscibility with pressure has been observed for the UDOT-exhibiting block copolymers poly(ethylene propylene)-*b*-poly(dimethylsiloxane) (PEP-*b*-PDMS) and PEP-*b*-poly(ethylene),^{20,21} although the reported pressure coefficients are smaller in magnitude ($dT_{\text{UDOT}}/dP \approx -0.1$ to $-0.2^\circ\text{C}/\text{MPa}$) than those found for the styrene/methacrylate systems mentioned above. More commonly, pressure is known to decrease the miscibility of block copolymers and polymer blends that exhibit UDOT/UCST behavior.^{22–27}

In this paper, we extend our pressure studies on the styrene/*n*-alkyl methacrylate family of block copolymers to further explore how molecular structure relates to the thermodynamic behavior of polymer pairs under pressure. Temperature studies on this family of materials reported earlier¹⁹ revealed a strong dependence of the phase behavior of these block copolymers on the side chain length of the methacrylate block. For intermediate side chain lengths ($2 \leq n \leq 4$), the styrene and methacrylate blocks are compatible and microphase separate upon heating through an LDOT. By contrast, for very short²⁸ ($n = 1$) and long¹⁹ ($n \geq 6$) alkyl side chains, the classical UDOT-type phase behavior is found. The systematic changes observed in the T -dependent phase behavior of this family of materials was shown to be correlated with trends in the solubility parameter and mass density of the block components. A more quantitative description of the phase behavior for these systems was later achieved using a revised Flory–Huggins regular solution model for polymer mixtures that accounts for the pure component compressibilities.^{16,29} Here we demonstrate experimentally a similar systematic dependence in how pressure influences the thermodynamics of this series of materials.

Experimental Section

The anionic synthesis of the compositionally symmetric diblock copolymers of styrene and various *n*-alkyl methacrylates, namely, ethyl (EMA), propyl (PMA), hexyl (HMA), octyl (OMA), and lauryl methacrylate (LMA), used in this study is described elsewhere.¹⁹ The characteristics of these block copolymers are repeated in Table 1. The absolute molecular weights listed are based on the measured weight fraction and molecular weight of the styrene block. For some materials, a small fraction of PS homopolymer was present, as noted in the table. In some cases, mixtures of two different molecular weights of the same material were prepared in order to access the order–disorder transition without requiring further synthesis. Mixtures were prepared as described in ref 18.

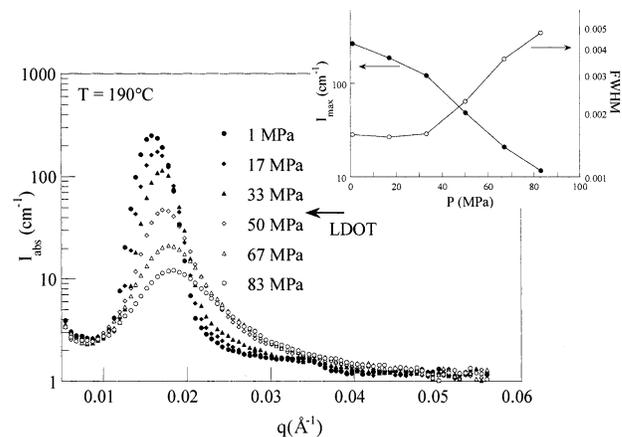


Figure 1. Scattering intensity profile for 136K PS-*b*-PPMA at 190 °C and indicated pressures.

Small-angle neutron scattering (SANS) measurements under hydrostatic pressure were performed at the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST) on beamline NG-3, using a hydraulic pressure cell that permits in situ measurements over a pressure range from 1 to 100 MPa and over a T range spanning 25–190 °C. The instrument configuration was $\lambda = 6.00 \text{ \AA}$, $\Delta\lambda/\lambda = 15\%$, and sample-to-detector distance = 6 m, resulting in a q range spanning 0.008–0.08 \AA^{-1} . Block copolymer samples were melt-pressed into 1.2 mm thick, 16 mm diameter disks. Silicone oil was used as the pressurizing fluid, with an encapsulated O-ring gasket separating the sample disk from the fluid. The scattered intensity was corrected for background and detector inhomogeneity in the standard manner and scaled to absolute units (cm^{-1}) using a silica standard. To extract pressure coefficients of the order–disorder transitions, dT_{ODT}/dP , pressure was varied isothermally from 1 to 100 MPa in 17 MPa increments, at various temperatures ranging from 100 to 190 °C. Thermodynamic reproducibility of the measurements was verified by cycling both T and P .

Results and Discussion

It has already been predicted^{30–33} and shown experimentally^{15,34–37} that LDOT/LCST-type block copolymers and homopolymer blends display an increase in thermodynamic compatibility with increasing pressure. This results from the denser nature of the segmentally mixed state in these materials ($\Delta V_{\text{dis}} \text{ or } \Delta V_{\text{mix}} < 0$) compared to the (micro)phase-separated state. The magnitude of this pressure effect on the LDOT of 136K PS-*b*-PPMA is illustrated in Figure 1, where the scattering intensity profile is shown for a fixed temperature of 190 °C and as a function of pressure. At this temperature and 1 MPa pressure, the block copolymer is fully microphase separated, as evidenced by the sharp first-order reflec-

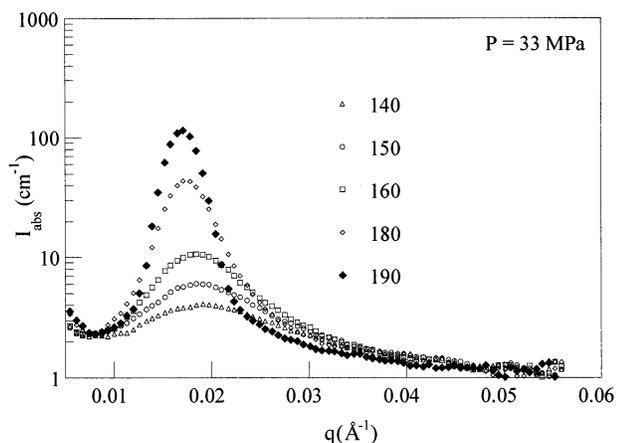


Figure 2. Scattering intensity profile for 136K PS-*b*-PPMA at 33 MPa and indicated temperatures.

tion at a wave vector $q^* = 0.0158 \text{ \AA}^{-1}$ as well as the second-order reflection at $2q^*$, consistent with the expected lamellar morphology for this nearly symmetric block copolymer.³⁸ Upon increasing pressure, the intensity of the first-order reflection decreases dramatically while the peak becomes broader. At the same time, the small reflection at $2q^*$ vanishes. In fact, at pressures exceeding 33 MPa, the higher-order reflection is no longer visible, and more importantly, the intense, narrow first-order reflection changes abruptly to a broad maximum, signifying the onset of segmental mixing upon the application of pressure. Hence, at a fixed temperature of 190 °C, an order–disorder transition pressure can be identified which lies somewhere between 33 and 50 MPa. This is also seen by plotting I_{max} , the first-order scattering peak intensity, or fwhm, the peak width, as a function of pressure, as shown in the inset of Figure 1. Both quantities show a distinct increase in slope above 33 MPa, signifying the onset of disorder.^{15,39} Likewise, at a fixed pressure of 33 MPa, an order–disorder transition temperature is observed at around 190 °C, as shown in Figure 2. At atmospheric pressure, on the other hand, the transition temperature was approximately 155 °C.¹⁹ This indicates that the LDOT roughly increased by 35 °C upon the application of 33 MPa of hydrostatic pressure, yielding an estimate of the pressure coefficient dT_{LDOT}/dP for this material of about 1.06 °C/MPa (106 °C/kbar).

As suggested previously,¹⁵ a much more precise estimate of the pressure coefficient of the order–disorder transition can be obtained by constructing master curves for the peak intensity I_{max} and its fwhm as a function of temperature by pressure–temperature superposition. At each pressure, the fwhm decreases and I_{max} increases with increasing temperature, as expected for this LDOT-exhibiting block copolymer (Figure 3a). Examination of the temperature dependence of I_{max} and fwhm at different pressures indicates that a simple horizontal shift along the temperature axis will generate universal curves for these two parameters. Shown in Figure 3b are the master curves at 1 MPa for I_{max} and fwhm, generated by horizontal shifting of data obtained at six different pressures ranging from 1 to 83 MPa. The shift factor for each pressure was calculated, assuming the following linear relationship between temperature and pressure:

$$\Delta T = -\frac{dT}{dP}(P - P_0) \quad (1)$$

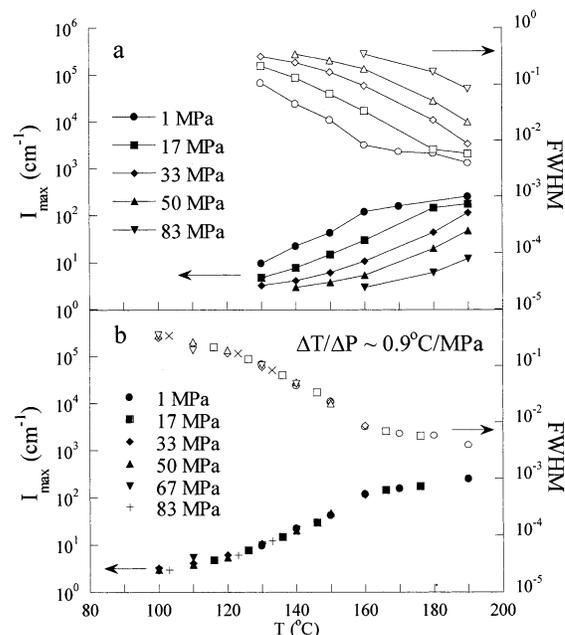


Figure 3. (a) Temperature dependence of I_{max} (filled symbols) and fwhm (open symbols) for 136K PS-*b*-PPMA at indicated pressures and (b) master curves for I_{max} and fwhm generated by pressure–temperature superposition around a reference pressure of 1 MPa using the indicated P – T coefficient. The temperature axes in (a) and (b) are identical. Note that the lack of data points in (a) at 170 °C was due to a temporary malfunction of the pressure cell.

where P_0 is the reference pressure (1 MPa) and the negative sign results from the fact that higher pressure is equivalent to lower temperature for LDOT-exhibiting systems. Pressure–temperature superposition using a constant value for dT/dP of 0.90 °C/MPa results in substantial overlap of the data taken at successive pressures. This yields master curves for I_{max} and fwhm over an extended temperature range which, again, display a distinct change in slope at ~ 155 °C, the LDOT at atmospheric pressure. The coefficient dT/dP used in eq 1 quantifies the equivalence between pressure and temperature for this material, yielding a more accurate estimate of $dT_{\text{LDOT}}/dP = 0.9$ °C/MPa (90 °C/kbar). Analogous results were obtained for 79K PS-*b*-PEMA, yielding a pressure coefficient $dT_{\text{LDOT}}/dP = 1.0$ °C/MPa (100 °C/kbar). Although these values are somewhat lower than the 1.47 °C/MPa (147 °C/kbar) obtained for PS-*b*-PBMA, the effect of pressure on these three LDOT-exhibiting block copolymers is comparable, as would be expected on the basis of the similarity of their phase behavior as a function of temperature.¹⁹

In earlier studies, we showed that thermodynamic compatibility between styrene and *n*-alkyl methacrylates is not restricted to ethyl, butyl, or propyl methacrylate. In fact, any combination of two or more methacrylate monomers copolymerized in such proportions as to match the density of the statistical copolymer to that of polystyrene, i.e., within the bounds of ethyl to butyl methacrylate, displays a similar behavior. In this manner, styrene/methacrylate block copolymers where the methacrylate block consists of a random copolymer of short and long side chain methacrylates, namely MMA and LMA, display an LDOT over a composition range predicted and experimentally verified to span 51–82% mass fraction MMA.^{19,40,41} The effect of pressure on the LDOT of such block copolymers is, as expected, similar to that obtained for PS-*b*-PEMA,

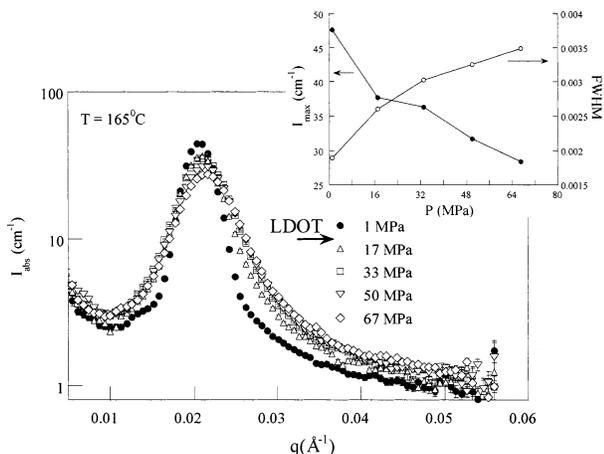


Figure 4. Scattering intensity profile for 80K PS-*b*-P(MMA-*r*-LMA) at 165 °C and indicated pressures.

PS-*b*-PPMA, and PS-*b*-PBMA. Figure 4 shows the SANS profiles obtained as a function of pressure at a temperature of 165 °C for 80K PS-*b*-P(MMA-*r*-LMA) where the methacrylate block contains 53% mass fraction MMA, a composition chosen to match the density of PS. At 165 °C and atmospheric pressure, the system should be weakly microphase separated.¹⁹ The narrow first-order reflection observed at 165 °C and 1 MPa confirms this. However, at this temperature, the application of as little as 17 MPa is sufficient to drive the block copolymer into the segmentally mixed state, as evidenced by the distinct decrease in I_{\max} and increase in fwhm between atmospheric pressure and 17 MPa (see inset of Figure 4). Superposition of the data obtained as a function of pressure at various temperatures yields a strong pressure coefficient of roughly 1.50 °C/MPa (150 °C/kbar) for PS-*b*-P(MMA-*r*-LMA), which coincides precisely with that obtained for PS-*b*-PBMA. This is quite a remarkable result, given that, at 53% mass fraction MMA, the statistical copolymer should have cohesive properties similar to PBMA on the basis of simple group contribution calculations.^{19,42} Thus, by preparing the methacrylate block as a random sequence of short and long alkyl side chain methacrylates, new materials can be designed which exhibit a phase behavior similar to that obtained for block copolymers with intermediate side chain methacrylates, namely, the LDOT and pressure-enhanced miscibility. More importantly, this experiment points to a general molecular design approach by which the pressure properties of a block copolymer could be more precisely optimized by changing the ratio of two or more monomer components in a single block.

The results presented above indicate that hydrostatic pressure is a very effective means of driving LDOT-type styrene/methacrylate block copolymers from the highly viscous ordered state to the fluid disordered state. In terms of rheological properties, this means that pressure applied at a constant temperature can be used to induce the material to flow. The ability to design such “baroplastic” behavior into thermoplastic elastomers (block copolymers with one glassy and one rubbery block component) would be highly advantageous from a processing viewpoint.¹⁶

Figure 5 shows the effect of pressure at a temperature of 140 °C on 34.3K PS-*b*-PHMA. At atmospheric pressure, this block copolymer undergoes a UDOT at 162 °C and is hence fully ordered at 140 °C.¹⁹ However, upon the application of hydrostatic pressure at 140 °C, the

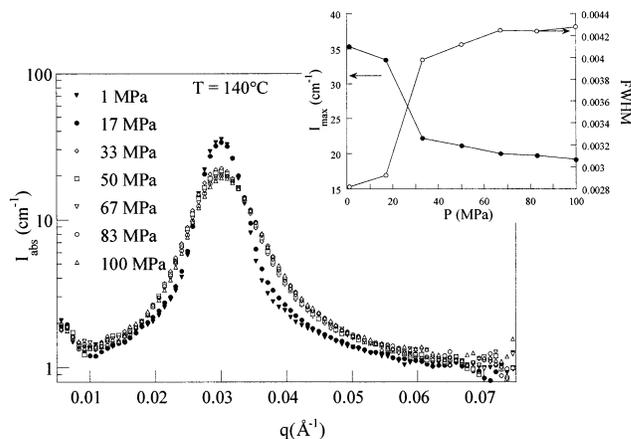


Figure 5. Scattering intensity profile for 34.3K PS-*b*-PHMA at 140 °C and indicated pressures.

material undergoes an order–disorder transition, as evidenced by the strong decrease in peak intensity and increase in peak width between 17 and 33 MPa (see inset of Figure 5). From the data taken at various pressures and temperatures, master curves were constructed for I_{\max} and fwhm, as described above. A constant dT_{UDOT}/dP of -0.60 °C/MPa (-60 °C/kbar) was found to result in substantial overlap of the curves obtained at a series of pressures.¹⁶ Despite its UDOT-type nature, this block copolymer is thus characterized by strong pressure sensitivity, in fact, closer to that of LDOT-exhibiting systems.

The pressure coefficient of the order–disorder transition, dT_{ODT}/dP , is related to the change in volume and the change in enthalpy upon disordering of the copolymer, ΔV_{dis} , and ΔH_{dis} , through the Clausius–Clapeyron equation:

$$\left. \frac{dT_{\text{ODT}}}{dP} \right|_x \cong \Delta V_{\text{dis}} / \Delta S_{\text{dis}} = T_{\text{dis}} \Delta V_{\text{dis}} / \Delta H_{\text{dis}} \quad (2)$$

Since ΔH_{dis} is positive for the enthalpically driven UDOT, the observed pressure-induced miscibility in PS-*b*-PHMA implies a negative change in volume upon disordering (segmental mixing) for this block copolymer ($\Delta V_{\text{dis}} < 0$). Hence, although segmental mixing at atmospheric pressure is enthalpically unfavorable at low temperatures, efficient packing in the segmentally mixed state leads to a strong increase in thermodynamic compatibility upon applying pressure to this material. In PS-*b*-PEMA, PS-*b*-PPMA, and PS-*b*-PBMA, this effect overwhelms the unfavorable enthalpic interactions between the two segment types and therefore governs the phase diagram, yielding LDOT behavior.

On the basis of temperature studies alone, PS-*b*-POMA displays a behavior quite similar to PS-*b*-PHMA, though with less compatibility since the 27K symmetric block copolymer undergoes a UDOT at ~ 135 °C.¹⁹ Yet, the effect of pressure on this UDOT is quite different than the one described above. Starting from the disordered state close to the UDOT, miscibility first increases with the application of small pressures (composition fluctuations in the disordered state are first weakened), again pointing to a $\Delta V_{\text{dis}} < 0$ for this system. The effect is very small, though, since a coefficient of only of -0.05 °C/MPa (-5 °C/kbar) is obtained from P – T superposition of data collected at small pressures. More notably, as pressure further increases, the trend is actually reversed: thermodynamic incompatibility and composi-

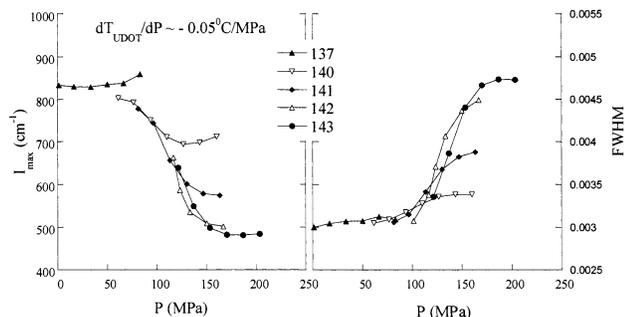


Figure 6. Master curves for I_{\max} and $fwhm$ as a function of pressure at a reference temperature of 137 °C for 27K PS-*b*-POMA.

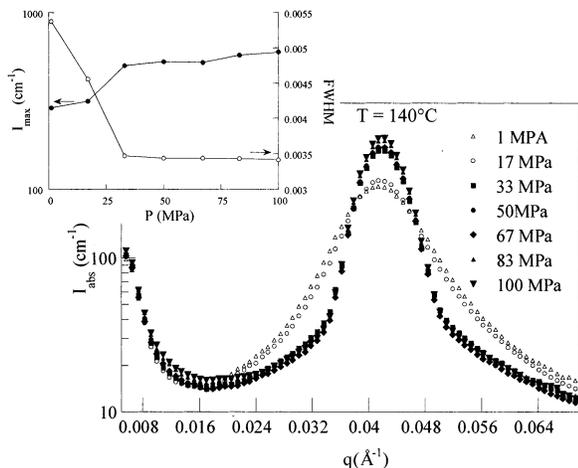


Figure 7. Scattering intensity profile for 19K PS_{d8}-*b*-PLMA at 140 °C and indicated pressures.

tion fluctuations are enhanced by pressure. This is evident from the master curves for I_{\max} and $fwhm$ shown in Figure 6, constructed this time by shifting various isotherms along the pressure axis around a reference temperature of 137 °C. At elevated pressure, the peak intensity is seen to increase. This departure from the low-pressure trend indicates that, at high pressure, the phase behavior is governed by the increase in unfavorable interaction energy that results from the decrease in free volume. Similar behavior has been reported by Schwann and co-workers for block copolymers of PEP and PDMS.²⁰

The decrease in magnitude of dT_{UDOT}/dP upon lengthening the alkyl side chain from 6 to 8 carbon atoms is consistent with a simultaneous increase in the unfavorable enthalpic interactions between the two segment types and decrease in packing efficiency in the segmentally mixed state (ΔV_{dis} negative but smaller in magnitude). On the basis of these observations, it is thus not surprising that, upon further increasing the alkyl side chain length of the methacrylate block to 12 carbon atoms, the pressure coefficient for the UDOT, dT_{UDOT}/dP , actually becomes positive. In contrast to the strong increase in compatibility with pressure observed for ethyl, propyl, butyl, and hexyl methacrylate, pressure drives microphase separation in PS-*b*-PLMA. Figure 7 shows the effect of pressure on 19K PS_{d8}-*b*-PLMA. This material undergoes a UDOT at atmospheric pressure at around 135 °C and is therefore segmentally mixed at 140 °C.¹⁹ However, upon the application of pressure, the system becomes incompatible and undergoes an ordering transition between 17 and 33 MPa at this temperature (see inset of Figure 7). Upon constructing

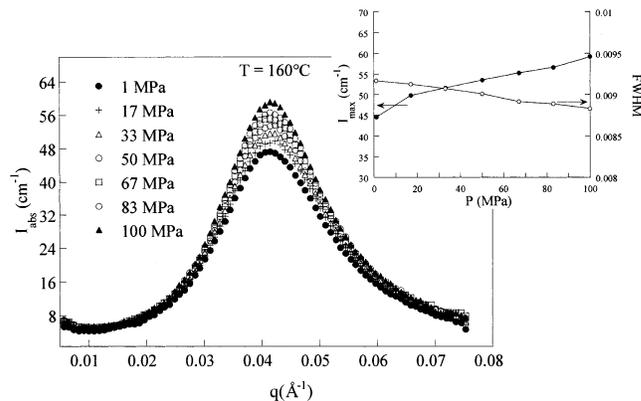


Figure 8. Scattering intensity profile for 27.6K PS_{d8}-*b*-PMMA at 160 °C and indicated pressures.

Table 2. Thermodynamic Characteristics of Diblock Copolymers Investigated

copolymer	type of behavior	sign of ΔV_{mix}	press. coeff dT_{ODT}/dP (°C/MPa)
PS _{d8} - <i>b</i> -PLMA	UDOT	+	0.13
PS- <i>b</i> -POMA	UDOT	-	-0.05
PS- <i>b</i> -PHMA	UDOT	-	-0.6
PS _{d8} - <i>b</i> -PBMA	LDOT	-	1.47
PS- <i>b</i> -PPMA	LDOT	-	0.90
PS- <i>b</i> -PEMA	LDOT	-	1.00
PS _{d8} - <i>b</i> -PMMA	UDOT	+	0.23

the master plots for I_{\max} and $fwhm$, a positive pressure coefficient of $dT_{UDOT}/dP = 1.3$ °C/MPa (13 °C/kbar) is obtained for this material, i.e., similar to polystyrene-*b*-polyisoprene and other strongly incompatible block copolymers.^{22–25} For this highly branched methacrylate, the incompatibility between the two blocks results from increasingly unfavorable enthalpic interactions combined with inefficient packing in the segmentally mixed state ($\Delta V_{dis} > 0$).

Similar results were obtained for PS-*b*-PMMA, the first member of the series of styrene/alkyl methacrylate block copolymers. Figure 8 shows the effect of pressure on 27.6K PS_{d8}-*b*-PMMA at 160 °C. Although this block copolymer is always disordered, the distinct increase in I_{\max} and decrease in $fwhm$ points to a decrease in thermodynamic compatibility (strengthening of composition fluctuations) with increasing pressure for this system. Unfortunately, the ordering transition is not accessible for this material since it lies below the glass transition in the mixed state. However, an estimate of the pressure coefficient in the segmentally mixed state can still be obtained by superimposing the data from various pressures as a function of temperature. In this manner, a rough pressure coefficient of $dT_{UDOT}/dP = 0.23$ °C/MPa (23 °C/kbar) was extracted for PS_{d8}-*b*-PMMA.

Conclusion

The effect of pressure on the phase behavior of the styrene/*n*-alkyl methacrylate block copolymers is summarized in Table 2 where the type of phase behavior, the sign of ΔV_{dis} (change in volume upon segmental mixing or disordering), and the pressure coefficient of the order–disorder transition, dT_{ODT}/dP , are given. It is important to note that, in our experiments, ΔV_{dis} is not a measured quantity; only its sign was deduced from the coefficient dT/dP through the Clausius–Clapeyron equation (eq 2). The results summarized in Table 2 point to a distinct linkage between packing and

energetics, which, for intermediate side chain lengths, is favorable to mixing at low temperatures and leads to the LDOT. For copolymers with longer alkyl side chains, on the other hand, the loss of compatibility at low temperatures can be ascribed to a simultaneous increase in unfavorable enthalpic interaction energy and decrease in packing efficiency in the segmentally mixed state. This premise is further supported by examining the contributions of enthalpy and compressibility to the free energy of mixing for this family of PS/poly(*n*-alkyl methacrylate) mixtures, employing the recently developed compressible regular solution model.^{16,29} The predominantly enthalpic term, always unfavorable to mixing, shows a minimum as a function of methacrylate side chain length for $n = 6$ (PHMA), while the term arising solely from compressibility is minimized for $n = 2$ (PEMA), favoring mixing for small n values but becoming positive for long side chains ($n > 6$). Perhaps the most interesting system in the series remains to be studied for $n = 5$ —recent investigations by Kim and co-workers on PS-*b*-poly(pentyl methacrylate) have demonstrated a unique closed-loop phase diagram for this material,⁴³ which is expected to exhibit substantial pressure dependence.

The experimental results obtained for PS-*b*-PHMA ($dT_{UDOT}/dP = -0.6$ °C/MPa) illustrate that UDOT-exhibiting block copolymers can also be characterized by large pressure coefficients. From an engineering standpoint, such large pressure coefficients could be particularly valuable, providing an effective means to force segmental miscibility and, hence, liquidlike rheological properties.¹⁶ Given the fact that current polymer processing technologies generally involve the application of significant pressures on the polymer melt, the discovery of such pressure and temperature-tunable behavior in toughened thermoplastics or elastomers could have a direct industrial impact.

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- Note that, usually, a discontinuity in I_{max} and fwhm is observed at the order/disorder transition (see for example Figure 5). For PS-*b*-PPMA, however, the continuous and very steep decrease in I_{max} and increase in fwhm even far into the disordered state translates into a change in slope rather than a discontinuity.
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