Pressure Dependence of the Order-to-Disorder Transition in Polystyrene/Polyisoprene and Polystyrene/Poly(methylphenylsiloxane) Diblock Copolymers

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ABSTRACT: The pressure dependence of the order-to-disorder transition in a polystyrene/polyisoprene (PS/PI) ($M = 17\,000$) and a polystyrene/poly(methylphenylsiloxane) (PS/PMPS) ($M = 29\,600$) diblock copolymer of symmetric composition has been studied using small-angle X-ray scattering. The order−disorder transition is investigated with a temperature resolution of 0.1 K. The transition can be resolved in a two-step process with a roughening of the interface preceding the breakdown of the lamellar order. For both systems a pressure-induced ordering transition is observed at constant temperature. The application of small pressures leads to a decrease of the transition temperature for both systems. High pressure shows the opposite effect. The minimum transition temperature for the PS/PI is located around $p = 8$ bar.

Introduction

The ordering transition in block copolymers has been investigated in great detail in recent years.[1,2] Much attention has been paid to the properties of symmetric diblock copolymers. The basic principles of their transition between the disordered and the ordered state are well understood in the framework of a mean field theory.[3] More elaborate theory is able to take into account the effect of fluctuations.[4] It then describes the ordering phenomenon as a fluctuation-induced first-order phase transition. This picture has been confirmed in particular by scattering experiments.[5,6] So far the influence of pressure on the phase state of a block copolymer was mostly ignored. Recent work, however, has shown that the thermotropic ordering transition of a polystyrene/polyisoprene diblock copolymer leads to an increase of the relative volume by 0.03%.[7] These experiments were performed at atmospheric pressure. On the basis of the Clausius−Clapeyron equation it was concluded that the transition temperature T_{ODT} should decrease with the application of pressure. Subsequent experiments have found both a decrease[8,9] and an increase of T_{ODT} with pressure. In particular for the PI/PS system in a pressure-dependent measurement, a volume change of similar magnitude but of opposite sign was observed.[10]

In this paper we present results which resolve this seeming contradiction. We have investigated the pressure dependence of the ordering transition of a polystyrene/polyisoprene (PS/PI) and a polystyrene/poly(methylphenylsiloxane) (PS/PMPS) diblock copolymer using small-angle X-ray scattering (SAXS) experiments. For both systems we find a pressure-induced transition from the ordered to the disordered state. We also determine the transition temperature of the PS/PI block copolymer in a wide regime of pressures, putting special emphasis on small pressures. As a result we find a decrease of T_{ODT} at small pressures. This trend is reversed in the high pressure regime $p \geq 25$ bar which was studied in ref 10. As it turns out it is not correct to extrapolate the results obtained at high pressures to the low-pressure regime.

I. Experimental Method

The PS/PI diblock copolymer was synthesized anionically using standard high vacuum procedures. The molecular weight of the polymer was $M = 17\,000$ g/mol; its volume fraction of polystyrene was $f = 0.49$. The polydispersity M_w/M_n was determined with gel permeation chromatography to be smaller than 1.04. The PS/PMPS diblock copolymer was similar as the one described in ref 11. Its molecular weight was $M = 29\,600$ g/mol, and the polystyrene volume fraction was $f = 0.56$.

Some of the SAXS experiments were carried out in a Kratky compact camera using slit collimation for pressures of 0 and 1 bar. The high-pressure measurements (1 bar → 500 bar) were performed using the beamline ID2 of the ESRF (Grenoble, France). The scattered intensity was measured with a two-dimensional detector and averaged circularly. The sample is contained in a cylindrical volume with diamond windows. The sample thickness is 3 mm. Pressure is applied via an oil-filled presure line. The oil is strictly separated from the sample by a membrane (Kalrez, Dupont) which is installed in

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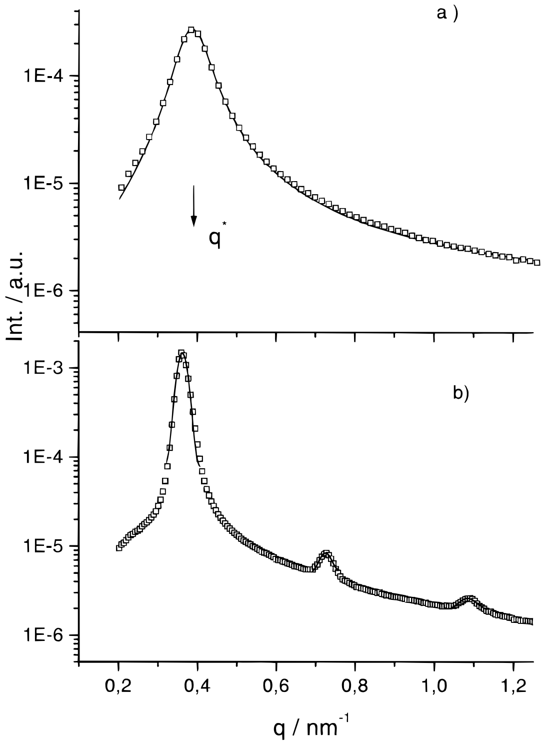

Figure 1. SAXS profiles obtained in pinhole geometry for the disordered (a) and the ordered (b) states of the PS/PI diblock copolymer. (a) $T = 403$ K. For the sake of clarity not all measured points are shown. The full line is a fit of mean field theory. Systematic deviations are observed at large q. (b) $T = 358$ K. The scattering profile in the ordered state exhibits three equally spaced maxima. The full lines are fits with a Gaussian.

the media separator below the cell. The application of pressure is achieved by manual pumping. Fast pressure release is made possible by opening of an automatic valve. The typical time for the release of pressure is less than 0.1 s. Further details of the design of the pressure cell may be found elsewhere.[12] The wavelengths used were $\lambda = 0.1542$ nm (Kratky system) and $\lambda = 0.0989$ nm (ESRF), respectively. The data were corrected for background scattering by subtracting the intensity of an empty container measurement. The Kratky data were desmeared using standard procedures[13] to obtain the scattering cross section whereas the ESRF data were directly obtained in point collimation. Temperature was measured with a platinum resistor and controlled with a computer. The resulting fluctuations of T were smaller than ±10 mK.

II. Results and Discussion

Scattering experiments with X-rays provide a direct measure of the strength of concentration fluctuations at a wave vector q which is experimentally defined by the wavelength of the radiation and the scattering angle θ, $q = (4\pi/\lambda)\sin\theta$. Figure 1 displays the SAXS profile (ESRF) of the diblock copolymer at $p = 1$ bar and $T = 403$ K (a) and $T = 358$ K (b). At the lower temperature one observes a sharp peak at 0.362 nm^{-1}. Two higher orders are clearly observed indicating a lamellar order with a period of 17.36 nm. The nonzero intensity of the second-order peak is a result of the slight asymmetry in the layer thickness of both components.

The high-temperature profile shows only one broad peak with a significantly smaller intensity in its maximum which is characteristic of the disordered state. The full line in Figure 1a is a fit of the structure factor obtained in mean field theory[3] modified to take the polydispersity of the sample into account.[14] The resolution of the camera is convoluted with the theoretical scattering curve. The parameters obtained from this fit are the radius of gyration of the block copolymer $R_g = 4.75$ nm and the product of the Flory–Huggins parameter and the number of segments $\chi N = 9.8$. The result provides a very good description of the experimental data although the temperature is only 0.8 K above the transition. The presence of concentration fluctuations in the sample does not significantly alter the shape of the scattering curve. Systematic deviations between the measured data and the theoretical curve appear at large q where the scattering data are sensitive to short scale variations of concentration.

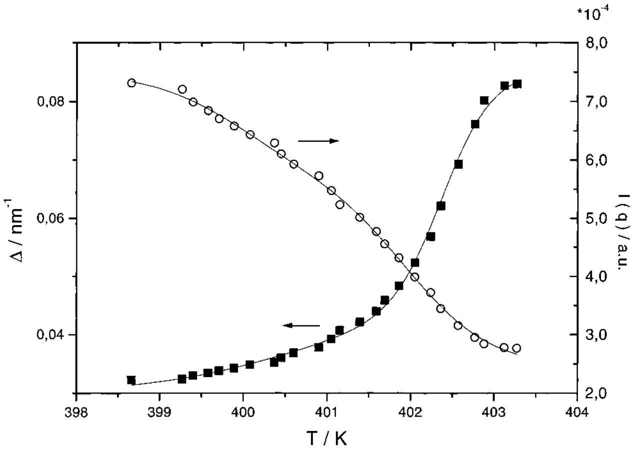

Figure 2. Details of the peak shape variation with temperature for the PS/PI diblock copolymer at 1 bar. Open symbols are the intensity at the maximum $I(q^*)$; filled symbols are the peak width Δ as obtained from a fit of the individual scattering profiles. The errors for both quantities are smaller than the size of the symbol. The full lines show the two-step variation of both quantities (see text).

It has been shown previously[6] that the change in the intensity $I(q^*)$ as well as in the full width at half-maximum (Δ) of the first maximum may be used to determine the transition temperature T_{ODT}. The latter is particularly sensitive to the breakdown of the lamellar structure. The disappearance of the higher order maxima may be taken as an additional indication for the transition from the ordered to the disordered state. It is, however, more difficult to detect experimentally.

A. Thermotropic Transition at $p = 1$ bar. The order-to-disorder transition shows up as a discontinuous decrease in the scattered intensity at a wave vector value q^* which is directly related to the radius of gyration of the block copolymer $q^*=1.946/R_g$.[15] Experimentally q^* is the wave vector of maximum intensity (see Figure 1). As an example for the determination of the transition temperature T_{ODT} we show in Figure 2 the change of $I(q^*)$ and Δ with T. The pressure for this measurement is $p = 1$ bar. The sample is heated at an effective rate of 0.08–0.1 K/min. This slow variation of T is necessary for the sample to equilibrate. It is known, that the glass transition temperature is raised under pressure. For PS this increase is $dT_g/dp = 0.032$ K/bar.[16] Within the range of our experiment this will account for less than 16 K, and T_g is therefore well below T_{ODT} for all pressures.

The registration of a scattering profile takes 30 s. We are therefore able to determine the variation of the scattering profile with extremely high temperature resolution. In between the measurements the X-ray beam is shut off in order to avoid degradation of the sample. Figure 2 shows that the sharp transition in the intensity $I(q^*)$ and the full width at half-maximum Δ that is usually observed in experiments with lower temperature resolution, does indeed consist of a two step process. During heating one finds a first drop of $I(q^*)$ which is accompanied by only a small increase in Δ. Both findings are in accordance with the assumption of a roughening of the interphase between PS and PI. A second step then finally leads to the disordered state as indicated by the strong increase in Δ and a further loss of intensity. The temperature dependence of both properties of the peak is empirically well described by the sum of two subsequent tanh profiles:

$$\Delta(T) = D_0 + \frac{D_1}{2}\left(1 + \tanh\frac{T - T_1}{w_1}\right) + \frac{D_2}{2}\left(1 + \tanh\frac{T - T_2}{w_2}\right)$$

D_0 is the initial value of Δ at low T, and D_1 and D_2 denote the steps of increase at the temperatures T_1 and T_2. The width of the transition is described by w_1 and w_2. An analogous form describes the temperature dependence of $I(q^*)$. Quite similar results for T_1 and T_2 are obtained by a numerical differentiation of the measured $\Delta(T)$ and $I(q^*,T)$.

Repeated measurements with fresh samples were used to assure the reproducibility of this method. Not shown in the figure is the variation of q^* with T. It is seen in Figure 1 that q^* in the ordered state is smaller than that in the disordered state which is taken as an indication for chain stretching in the ordering process. The variation, however, is small (<1%), and we do not use it for the determination of T_{ODT}.

The temperatures T_1 and T_2 are consistently obtained from a fit of Δ and of $I(q^*)$. In the following we use T_2 as the transition temperature T_{ODT}. At 1 bar we determine $T_{\mathrm{ODT}} = 402.5$ K. The roughening of the interphase gives rise to a reduction of the intensity at q^* by about 30%. If we neglect the slight increase in the peak width and assume a Gaussian form of the interface profile, then $I(q^*) \propto \exp(-q^{*2}\sigma^2)$. The interface thickness σ that is acquired at T_1 is then found to be 1.6 nm. It therefore amounts to only 10% of the lamellar period.

B. Pressure-Induced Transition. In order to study the influence of pressure on the phase state of the diblock copolymer we have varied p at constant temperature. The results of a second set of measurements refers to the detection of the thermotropic transition at various pressures. They are reported in the subsequent section.

In Figure 3 we present the results of a series of measurements at T= 401.6 K using the PS/PI diblock copolymer. This temperature is just below the transition temperature that was determined at $p = 1$ bar in the previous section. At 1 bar the scattering profile exhibits a narrow peak which is characteristic of the ordered state. Increasing pressure leads to a broadening of the peak and a loss of intensity at q^*. Further increase of pressure however reverses this trend, and at high pressure the scattering profile is again that of the ordered state. The surprising result is the existence of a disordered regime in between the ordered states at low and high pressure. The detailed analysis of the scattering curves in terms of the peak intensity $I(q^*)$ and the full width at half-maximum Δ is depicted in Figure 4. Both parameters consistently display the sequence order → disorder → order. The shape of the curves in Figure 4 is strongly asymmetric. The pressure induced transition from order to disorder occures within less than 10 bar pressure increase whereas the reverse transition extends up to 250 bar.

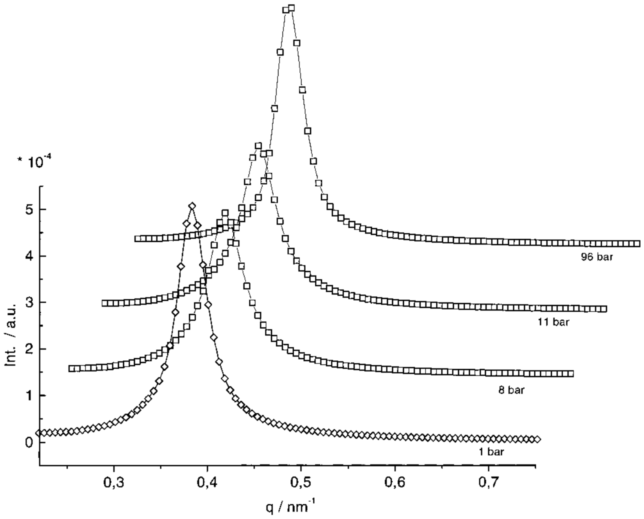

Figure 3. Variation of the scattering profile with pressure at constant temperature T = 401.6 K for the PS/PI diblock copolymer. The transition order → disorder → order is clearly seen in the peak shape.

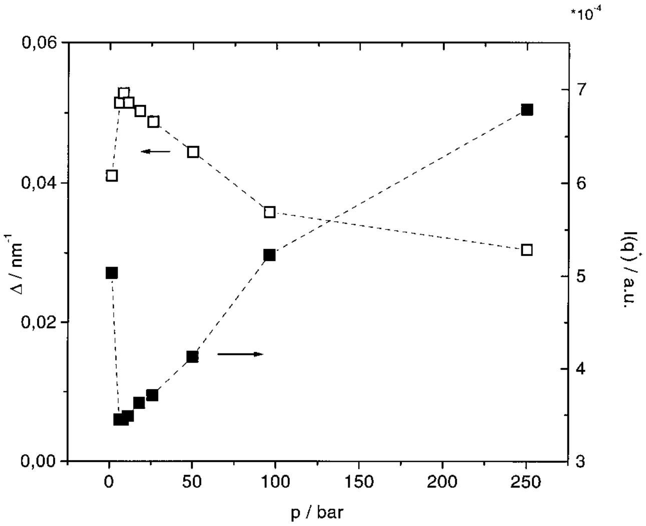

Figure 4. The peak width Δ (open symbols) and the intensity $I(q^*)$ (filled symbol) at T = 401.6 K in dependence on pressure. Both parameters display the transition from disorder to order at low pressure. Further increase of p then leads to the inverse transition.

As a second example for the pressure induced transition between order and disorder we present the result for the PS/PMPS system. The transition temperature for this block copolymer at p = 250 bar is determined as T_{ODT} = 424 K. The measurements are performed at a constant temperature T = 437.7 K, i.e., well above the T_{ODT}. After a sudden release of pressure to p = 1 bar we follow the evolution of structure in a time resolved experiment. The result of this experiment is shown in Figure 5. The scattering contrast of the PS/PMPS system is smaller than in the PS/PI case. In order to emphasize the change of the scattering profile with time, we subtract from each data set the scattering profile obtained at the starting pressure. Consequently the data in Figure 5 show more scatter. The obvious observation, however, is the development of a shoulder

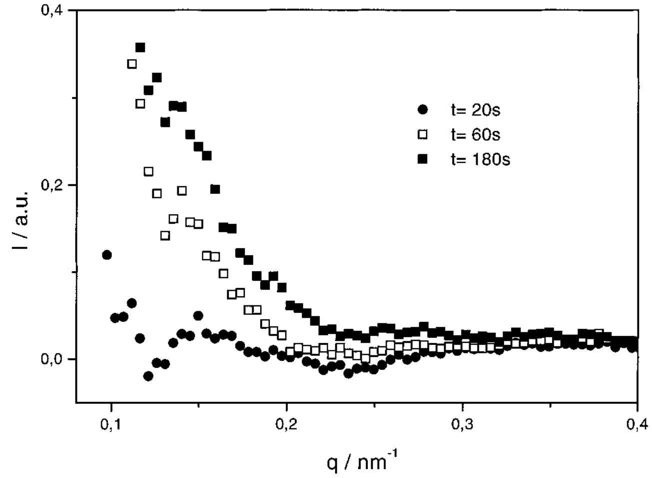

Figure 5. Variation of the scattering profile with time from the PS/PMPS diblock copolymer after a sudden release of pressure from 250 to 1 bar at $T = 437.7$ K. The scattering profile of the initial state is subtracted. The evolution of a peak at $q^* = 0.14$ nm^{-1} is a clear indiation for the transition from disorder to order.

at q^*=0.14 nm^{-1} with time. This is a further indication for the system to pass through its transition from disorder to order. Consequently the transition temperature at 1 bar must be higher than that at 250 bar. We find $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p \approx -0.07$ K/ bar in this pressure regime. Up to 500 bar there is no indication for a change of sign in $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p$.

For both systems studied at constant temperature the application of pressure results in a decrease of the transition temperature. A similar result has been reported for a polystyrene/poly(*p*-methylstyrene) block copolymer.[9]

Our result is seemingly in contradiction to previously reported results for PS/PI.[10] We point out, however, that these measurements were performed in the pressure regime of $25 < p$/bar < 700 and therefore missed the regime that is of interest here.

C. Determination of the Phase Diagram. We now turn to a discussion of a second set of measurements on the PS/PI diblock copolymer which determines the transition temperature at constant pressure from a series of scattering profiles taken at increasing temperature. The experimental procedure at each pressure therfore is the same as described above. In Figure 6 we display the result for the temperature dependence of the full width at half-maximum (FWHM) of the main peak for three values of the pressure p. The figure clearly shows that T_{ODT} does not depend monotonically on pressure. Increasing pressure from 1 (circles) to 5 bar (triangles) leads to a drop of T_{ODT}. Further increase of pressure to 11 bar (squares) reverses this variation. The shift in T_1 and T_2 is the same within error.

In order to extend the range of accessible pressure to 0 bar we have determined the transition temperature in the same way as described above using a Kratky compact camera. The data reported in the literature normally refer to a measurement in an evacuated camera. In our system this correponds to a pressure of 30 mbar. The experiment at 1 bar is possible in a nitrogen atmosphere. Repeated measurements at both pressures were used to ensure stability of the sample. The reversibility of the shift in T_{DOT} was shown by measurements with increasing and decreasing pressure. The unavoidable calibration difference in the temperature measurement of both scattering set-ups was removed by shifting the temperature scale of the Kratky camera such that both data sets agree at 1 bar.

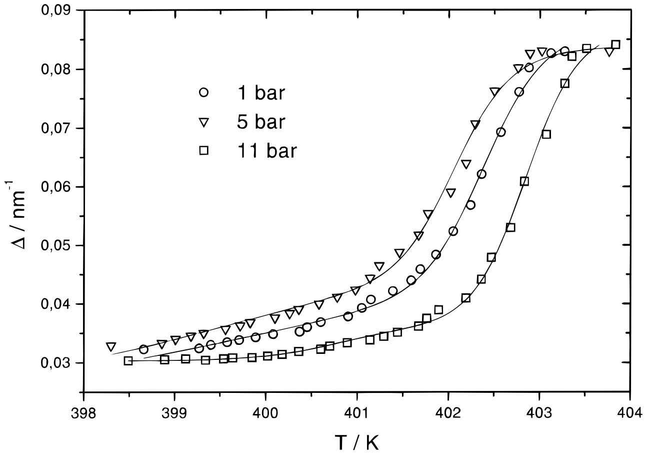

Figure 6. Peak width Δ for the PS/PI diblock copolymer for three pressures. The transition at 5 bar is shifted to smaller T with respect to the 1 bar measurement. At 11 bar an inverse shift is observed.

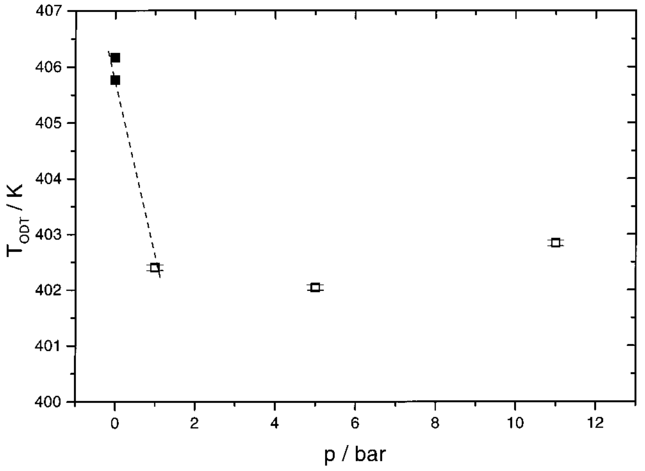

Figure 7. Variation of T_{ODT} with pressure in the regime of small pressures. Filled symbols refer to measurements with the Kratky camera, open symbols are obtained from the ESRF data.

In Figure 7 we present the result for the variation of T_{ODT} with pressure for the PS/PI diblock copolymer. As was already concluded above from the pressure dependence of the structure factor one observes a marked minimum around $p_{\mathrm{min}} = 8$ bar. The variation of T_{ODT} is $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p = -3.6$ K/ bar at 0 bar and changes to $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p = -0.09$ K/bar at 1 bar. The high pressure value agrees well with the result of reference,[10] $\mathrm{d}T_{\mathrm{ODT}}/\mathrm{d}p = +0.019$ K/bar. As was pointed out earlier[7] this slope is related to the latent heat and the volume change of the transition through the Clausius–Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T_{\mathrm{ODT}}\dfrac{\Delta V}{V\rho}} \qquad (1)$$

ρ is the density of the sample. The relative volume change as determined in a capillary densitometer at normal pressure was $\Delta V/V = -3(\pm 0.4) \times 10^{-3}$. The latent heat ΔH as determined from DSC measurements carries a large error. The estimate of reference[7] was

$dT_{ODT}/dp = -0.3$ K/bar. In particular the predicted decrease of T_{ODT} is confirmed by our data in the low-pressure regime.

The change of slope in the coexistence curve implies a change in the sign of the volume change $\Delta V/V$ when going to higher pressure. This is indeed confirmed by the results of reference.[10] With increasing pressure they cross the coexistence curve from the disordered to the ordered state and find a decrease in the specific volume. Their relative volume change is $\Delta V/V = 0.45(\pm 0.15) \times 10^{-3}$.

A minimum in the dependence of T_{ODT} on pressure has previously been found for a PEP/PDMS diblock copolymer.[8] The minimum T_{ODT} in that case was found around 400 bar.

III. Conclusions

The ordering transition in diblock copolymers is in many respects correctly described as a first-order phase transition. Using scattering experiments the transition temperature may be determined with high accuracy if the slow relaxation times of the system are taken into account in the experiment. The transition from the ordered lamellar state to the disordered state is preceded by a roughening of the interphase between both components. The final transition to the disordered state shows up in the scattering profile as a marked increase in the width of the main peak as a result of the loss of long-range order. The transition temperature may thus be determined with a resolution better than 0.1 K.

The application of hydrostatic pressure has very different effect at low and at high pressure. The minimum in dT_{ODT}/dp may be located at very different pressure depending on the block copolymer under study. It may be taken as an indication for the existence of two opposing effects of pressure on the miscibility of the blocks in the diblock copolymer. The essential difference between the ordered and the disordered state is the amount of mixing between the two chemically different blocks. It must be noted, however, that mixing and demixing are both not complete. The disordered state shows composition fluctuations which help to avoid contact between the different monomer species. In the ordered state, on the other hand, one has an interface between the lamellae in which both blocks interpenetrate. This interface is known to amount to a significant volume fraction. As a result the free energy of mixing is reduced.

The initially negative slope of the coexistence curve is therefore considered as a result of an entropic contribution to the free energy of mixing which favors the mixed state. It may be envisaged as a creation of free volume in the mixing process. The observed value of the volume change $\Delta V/V = -3(\pm 0.4) \times 10^{-3}$ is attributed to this effect.

The application of pressure reduces the effect of this mechanism until it is balanced by the opposite volume change caused by the packing density. The latter is responsible for the normally observed reduction of the mixing tendency under the application of pressure. Such behavior was so far found for polymer blends[17] and appears to be a rule for the high pressure behavior of several diblock copolymers.

The question remains open if the observed decrease of T_{ODT} with pressure is a specific phenomenon for a class of block copolymers or a general feature of the ordering transition in block copolymers.

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