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Composition Fluctuations and Coil Conformation in a Poly(ethylene−propylene)−Poly(ethylethylene) Diblock Copolymer as a Function of Temperature and Pressure

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ABSTRACT: The disordered and ordered states of a PEP−PEE diblock copolymer have been studied at different temperatures and pressures by small-angle neutron scattering, with the main goal to determine the relation between hydrodynamic pressure and the Flory−Huggins interaction parameter of a diblock copolymer melt. The structure factor has been analyzed in terms of the Fredrickson−Helfand theory, which gives the Flory−Huggins parameter, the spinodal temperature T_S, the order−disorder temperature T_{ODT}, and the order−order temperature T_{OOT}. A decrease of T_{ODT} and T_S with increasing pressure of $\sim 2 \times 10^{-2}$ K/bar is observed experimentally and is related to a decrease of the enthalpic term of the Flory−Huggins interaction parameter. No change of the T_{OOT} temperature with pressure was observed. The coil size as analyzed from the peak position of the structure factor shows stretching at lower temperatures. The compressibility of the coils changes with temperature and shows a maximum at the T_{OOT} temperature. Overall, diblock copolymers and binary homopolymer mixtures show distinct differences with respect to thermodynamic and conformational changes with varying temperature and pressure.

I. Introduction

Diblock copolymers form ordered phases if the two blocks are sufficiently immiscible, i.e., when the Flory−Huggins parameter Γ times the molecular volume V is larger than 10 or so.[1] In the ordered state, the two blocks of the polymers' microphase separate into two phases which form a periodic structure whose characteristic lattice spacing is of the order of the polymer radius of gyration R_g of the polymers. For a review of diblock copolymers see refs 2−4. The driving force for this process is similar to that of phase separation in blends of homopolymers. In the case of a symmetric mixture of homopolymers A and B ($V_A = V_B$) phase separation occurs at $(\Gamma V) \cong 2$. The equivalent microphase separation of symmetric diblock copolymers occurs at $(\Gamma V) \cong 10.5$ (mean field). While both upper critical (UCST) and lower critical solution temperatures (LCST) frequently are observed in binary blends of homopolymers, most block copolymers studied so far have an ordered phase at low temperatures and a disordered phase at high temperatures.[4−12] Only a few systems studied have shown reversed temperature dependence.[13,14]

In this paper we present small-angle neutron scattering (SANS) experiments on a partially deuterated poly(ethylene−propylene)−poly(ethylethylene) (PEP−PEE) diblock copolymer that contains 65% by volume PEP ($f = 0.65$). The total molecular volume is V_n = 83 400 cm^3/mol, corresponding to a degree of polymerization $N = 1100$. We have studied the structure factor $S(Q)$ (Q is a scattering vector) as a function of temperature and pressure in the disordered and ordered states. The same system was previously examined as a function of temperature, as reported in a series of papers by Bates and co-workers.[4−9] In addition to the temperature- and pressure-dependent $S(Q)$ results, we present experimental results for the pressure dependence of the spinodal temperature T_S, of the order−disorder temperature T_{ODT}, of the order−order temperature T_{OOT} between hexagonal and modulated lamella phases, and of the enthalpic (Γ_h) and entropic (Γ_σ) terms of the Flory−Huggins parameter ($\Gamma = \Gamma_h/T - \Gamma_\sigma$). To our knowledge these are the first experimental results on the relation between hydrostatic pressure and thermodynamic parameters such as the Flory−Huggins parameter for diblock copolymers. Furthermore, information about chain compressibility in the disordered and ordered states is obtained from the temperature and pressure dependence of the scattering peak position.

These experiments have to be seen in connection with corresponding pressure/temperature SANS studies on binary blends of homopolymers.[15,16] Generally, binary homopolymer blends are relatively well described by the Flory−Huggins mean-field theory, where the structure factor and the phase diagram can be evaluated in terms of a "segmental" Flory−Huggins parameter Γ. However, as discussed in refs 17 and 18, the effect of composition fluctuations cannot be neglected. The Flory−Huggins parameter, as obtained from the mean-field model, can only be considered as an "effective" quantity useful for the qualitative interpretation of phase diagrams. The study of the mean-field/Ising crossover leads to a better understanding and a more confident evaluation of the Flory−Huggins parameter, which may differ strongly from its value obtained within the mean-field formalism.

In diblock copolymers, the influence of fluctuations has more dramatic effects since it completely changes the mean-field phase diagram as formulated by Leibler.[19] The refined theory of Fredrickson and Helfand[20] goes beyond the mean-field approximation by including fluctuations. The Flory−Huggins parameter as obtained from the structure factor in the framework of this refined theory may lead to a Flory−Huggins parameter Γ which is more consistent with the value obtained for the corresponding binary homopolymer blends, including fluctuations. More recently, it has been shown both

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theoretically[26] and experimentally[4,9] that conformational asymmetry in the molecular characteristics of the two blocks has important implications for more complex phase behavior. We do not, however, have any prior knowledge of a possibly related asymmetry dependence in compressibility and in fluctuations. In the present work, we therefore have to disregard the asymmetry between PEP and PEE.

The discussion of the Flory–Huggins parameter has two aspects: First, the evaluation of Γ from the structure factor must include fluctuations, which seems to be properly described for homopolymer blends[17,18] but which might still be less understood for diblock copolymers.[20] Second, the Gibbs free energy of mixing in the Flory–Huggins model is described by the entropy of mixing in the usual form $\sum(\phi_i/V_i)\ln\phi_i$ where ϕ_i is the volume fraction of component i, and by the Flory–Huggins interaction parameter Γ. The interaction parameter Γ was originally introduced as a segmental enthalpic term.[3,21] Experiments, however, have shown that Γ rather has the meaning of a phenomenological free energy of mixing, additionally influenced by end-group effects, by free volume, and probably by other still unknown properties. These influences might differ for binary homopolymer mixtures and diblock copolymers. Lattice cluster theory (LCT) calculations of diblock copolymers by Freed and Dudowicz[22,23] lead to a Flory–Huggins parameter composed of two contributions: (i) a segmental part (independent of the degree of polymerization), which should agree with Γ for a binary polymer blend, and (ii) a contribution due to the effects of the diblock link. This term disappears when $V \rightarrow \infty$. We will see that the agreement between the LCT calculation and our experimental results for Γ, using the Fredrickson–Helfand theory for the structural data analysis, is qualitatively better than the corresponding Γ form of homopolymer blends.

The use of high pressure has opened the possibility of controling one component of the Flory–Huggins parameter, the entropic part Γ_σ, which according to equation of state (EOS) theories is strongly related to the free volume, which means to compressibility or packing of the polymers.[15] In homopolymers, Γ_σ plays a central role by its influence on the phase diagram[15] and on the strength of composition fluctuations.[18] For instance, phase decomposition at high temperatures is an entropy-driven process because of a negative Γ_σ, which means that the packing of the polymers in the segregated phases is less compact than in the homogeneous phase. Furthermore, the strength of composition fluctuations described by the Ginzburg number, Gi, strongly increases with Γ_σ.[18] The value of Gi estimates the crossover temperature between the validity of the Flory–Huggins theory far from the critical temperature T_C and the critical regime of the 3d-Ising regime near T_C where composition fluctuations have to be included. For homopolymer blends, it has been observed that the influence of Γ_σ causes an increase in Gi by more than 1 order of magnitude.[17] It will be interesting to compare this strong entropic contribution for homopolymer blends with the corresponding effect in diblock copolymers. The comparison should further be made with respect to the pressure dependence of the polymer radius of gyration in the diblock copolymer melt and in the corresponding homopolymer blend. Such comparisons will give a better understanding of phase behavior, and in particular the description of polymer interactions as described by a simple segmental quantity, the Flory–Huggins parameter, and it might provide the basis for a refined theory including fluctuations.

II. Structure Factor for Diblock Copolymers

The structure factor $S(Q)$ for A–B diblock copolymers in the disordered state was first developed by Leibler[19] in the mean-field approximation as

$$S(Q) = V/[F(x,f) - 2(\Gamma V)] \tag{1}$$

where Q is the scattering vector, V the molecular volume, and Γ the effective Flory–Huggins parameter as above. The function $F(x,f)$ is a combination of Debye functions for unperturbed Gaussian coils and depends on the volume fraction f for one of the blocks and on the squared product of Q and the overall radius of gyration R_g: $x = (QR_g)^2$. In the limits $QR_g << 1$ and $QR_g >> 1$ the value of the structure factor $S(Q)$ approaches zero as

$$S(Q) \cong 2Vf^2(1-f)^2(QR_g)^2/3 \tag{2}$$

and

$$S(Q) \cong 2Vf(1-f)/(QR_g)^2 \tag{3}$$

respectively. For $QR_g >> 1$, the structure factors of block copolymers and homopolymers are similar. In diblock copolymers, $S(Q)$ has a maximum at a finite scattering vector Q^* which occurs for $F(x^*,f) = 2(\Gamma_s V)$. Γ_s is the Flory–Huggins parameter at the spinodal temperature. The structure factor $S(Q)$ at $Q = Q^*$ is then given by

$$S(Q^*) = V/2[(\Gamma_S V) - (\Gamma V)] \tag{4}$$

$S(Q^*)$ is a susceptibility which has the same form and meaning as $S(Q=0)$ for binary homopolymer blends. Its temperature dependence is hidden in the product (ΓV) and it becomes infinite at the spinodal. The Flory–Huggins parameter Γ is a free enthalpy of mixing according to $\Gamma = (\Gamma_h/T - \Gamma_\sigma)$, where Γ_h and Γ_σ are the enthalpic and entropic terms, respectively. The Fredrickson–Helfand theory assumes an incompressible medium. The pressure dependence of the system is therefore described by the phenomenological Flory–Huggins parameter. The behavior of $S(Q^*)$ at the spinodal represents a second-order phase transition between the disordered and ordered states. It is experimentally accessible only for $f = 0.5$ e.g., for the blocks with equal molecular weight. For $f \neq 0.5$ the order–disorder phase transition is a weak first order one and the spinodal phase boundary is inaccessible. According to eq 1, the peak position is independent of Γ or temperature and is purely determined by the polymer parameters f and R_g.

Composition fluctuations are neglected in $S(Q)$ of Leibler's theory in eq 1. This approximation is only valid in the limit of very large V, i.e., for a very large degree of polymerization N, as for binary homopolymer blends.[21] Fluctuation effects were included into $S(Q)$ by Fredrickson and Helfand[20] on the basis of the Hartree approximation as employed by Brazovskii.[24] The corresponding structure factor has the form

$$S(Q) = V/[F(x,f) - 2(\Gamma_{ren} V)] \tag{5}$$

which is formally the same as Leibler's mean-field expression in eq 1; however, with a renormalized Flory–Huggins parameter

$$\Gamma_{ren} V = (\Gamma V) - \tilde{c}\sqrt{S(Q^*)/(V\bar{N})} \tag{6}$$

with $\tilde{c} = c^3 d\lambda/2$ and $\bar{N} = (R_0{}^3/V)^2$. Here, R_0 is the end-to-end distance of the overall polymer ($R_0{}^2 = 6R_g{}^2$) and $\tilde{c}$ depends on the molecular parameters given in Table 1 and on relations in ref 20. The parameter $\tilde{c}$ has been

Table 1. System Parameters of the Diblock Copolymer PEP–PEE

	polymer	
	PEP	PEE
chem struct	$C_5H_5D_5$	$C_4H_6D_2$
T_G (°C)	−56	−20
m (g/mol)	75.2	58.1
Ω (cm^3/mol)	81.9	64.8
Σb_i (10^{-12} cm)	4.79	1.75
f	0.65	0.35
N	1100	
M_n	76000	
V_n (cm^3/mol)	83400	
$\Omega \equiv V_n/N$ (cm^3/mol)	75.8	
σ (Å); $T = 120$ °C	8.12	

derived from $F(x,f)$ (eq 2.14 of ref 20), d from R_gQ^* (eq 3.11 of ref 20), and λ from the vertex function γ_4 of an effective Hamiltonian for diblock copolymers (eq 2.2 of ref 20). The parameter $\bar{N}$ corresponds to the Ginzburg parameter as used for homopolymers.[25,5] Here, it is explicitly defined by $P = \bar{N}^{1/2}$ (p 112 of ref 21), which characterizes the average number of chains in the volume R_0^3. It can be shown that the mean-field approximation of binary blends holds in the limit of $\bar{N} >> 1$. The same holds for diblock copolymers. According to eq 6, the mean-field theory becomes valid for $S(Q^*)/V << 1$ and/or $\bar{N} >> 1$, which is fulfilled for temperatures very far from T_S and/or in case of large V. With $S(Q^*) = 1/2[\Gamma_S - \Gamma_{ren}]$ one finally obtains for the product of the Flory–Huggins parameter and the molecular volume

$$\Gamma V = (\Gamma_{ren} V) + \frac{\tilde{c}}{\sqrt{2[(\Gamma_S V) - (\Gamma_{ren} V)]}} \frac{1}{\sqrt{\bar{N}}} \qquad (7)$$

In the following, we analyze the scattering data with eq 5, which yields the renormalized Flory–Huggins parameter. Then, with eq 7 the Flory–Huggins parameter in the framework of the mean-field theory is obtained.

III. Phase Diagrams of Diblock Copolymers

In Figure 1 two phase diagrams of diblock copolymers are shown: (A) evaluated on the basis of Leibler's mean-field theory,[5,19] and (B) with the Fredrickson–Helfand theory including fluctuations.[20] As mentioned above, we have in the present work disregarded the dependence on conformational asymmetry, even though we are aware that this parameter may be important for the modulated lamellar structure of the diblock copolymer being studied. In the mean-field approximation, the product (ΓV) and the volume fraction f are sufficient for a complete evaluation of the phase boundaries. For the Fredrickson–Helfand theory,[25] the parameter $\bar{N}$ is additionally needed. As already discussed, $\bar{N}$ quantifies the deviation from mean-field approximation. In the limit of $\bar{N} \rightarrow \infty$, the phase diagrams A and B become similar. The introduction of fluctuations characteristically changes the theoretical phase diagrams: (i) It stabilizes the disordered regime with a larger ($\Gamma_{ODT}V$). This is a general phenomenon also observed for binary polymer blends. (ii) No *bcc* structure appears for a system with $\bar{N} = 20\,000$. (iii) The disorder–order transition is of first order for all f. (iv) A larger f range for disorder–(lamella)order transitions is obtained. Experimentally, the phase behavior appears more complex with a variety of ordered phases beyond those two in the Fredrickson–Helfand theory, including modulated lamellas and ordered bicontinuous phases.[4]

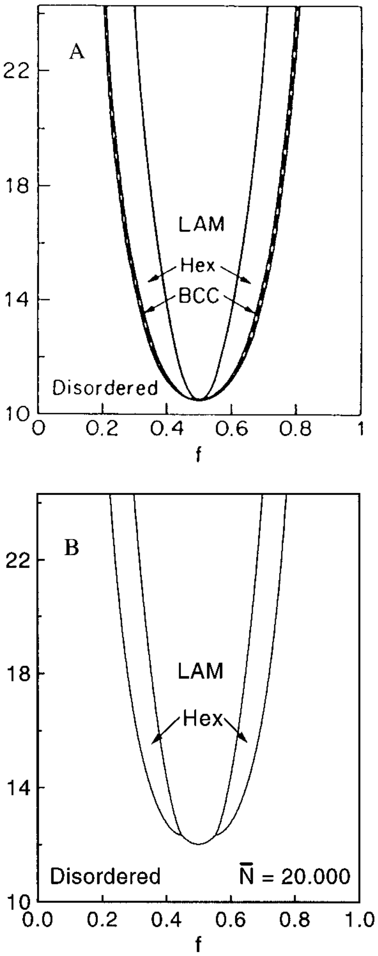

Figure 1. Phase diagram of diblock copolymers according to Leiblers' mean-field approximation (A) and according to the fluctuation theory of Fredrickson–Helfand (B) as taken from ref 4. The parameter $\bar{N}$ corresponds to the Ginzburg parameter. In the limit of $\bar{N} \rightarrow \infty$, the mean-field theory holds and both phase diagrams coincide.

In this paper we present studies of a diblock copolymer with the parameters $f = 0.65$ and $\bar{N} = 2 \times 10^4$. We expect a phase diagram as in Figure 1B. It reveals a transition from the disordered to the hexagonal ordered state at the temperature T_{ODT}, and a transition from the hexagonal ordered to the lamella or modulated lamella ordered state at the order–order temperature T_{OOT}.[4,9] In order to better compare our experimental results with the fluctuation theory of Fredrickson–Helfand, we have evaluated $\Gamma_{ODT}V$ and $\Gamma_{OOT}V$ for the parameters of our sample with the formalism of ref 20. In Figure 2 the correspondingly evaluated thermodynamic potentials Φ (see eq 3.19 in ref 20) of the hexagonal and lamellar phases are plotted versus $\tau = [(\Gamma_S V) - (\Gamma V)]$. The potential is a function of the order parameter and depends on the temperature. At $\tau = 0$ one obtains the spinodal. The order–disorder temperature T_{ODT} or τ_{ODT} appears at $\Phi = 0$. For the hexagonal phase, this yields $\tau_{ODT} = -1.45$. Below $\tau_{ODT} = -5.1$ the lamella phase becomes the stable one because of $\Phi_{LAM} < \Phi_{HEX}$. With $\Gamma_S V = 12.32$ for $f = 0.65$ (see Figure 4 of ref 19) we evaluate $\Gamma_{ODT}V = 13.8$ and $\Gamma_{ODT}V = 17.4$ for the order–disorder and order–order transitions expected for our sample.

IV. Experimental Section

The SANS experiments were performed at the DR3 reactor at the Risø National Laboratory. A steel-bodied pressure cell was used which allows an in situ change of pressure and

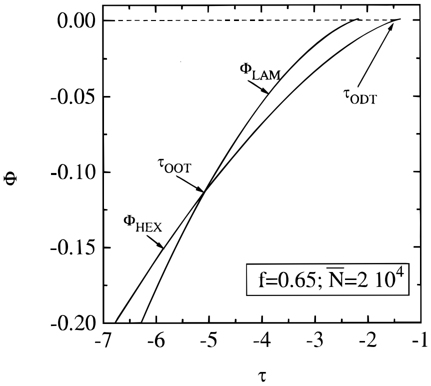

Figure 2. Thermodynamic potential of the lamellar and hexagonal phases of diblock copolymers according to the Fredrickson–Helfands' theory from which the parameter $\tau = [(\Gamma_S V) - (\Gamma V)]$ at the ODT and OOT temperatures is obtained.

temperature in the range of $1 \leq P$ (bar) ≤ 1500 and $-20 \leq T$ (°C) ≤ 200, respectively. This pressure cell is an improved version of the cell described in ref 15 insofar as the new steel body can directly be cooled or heated. In this way, a much better temperature control of ±0.1 K could be achieved. The scattering data were corrected for background and detection probability of the single detector cells and calibrated in absolute units by a Lupolen standard. The resulting absolute macroscopic cross section $d\Sigma/d\Omega$ is related to $S(Q)$ according to $d\Sigma/d\Omega(Q) = S(Q)\Delta\rho^2/N_A$, where $\Delta\rho$ is the difference of the coherent scattering length densities of the components $\sum b_i/\Omega$ (for numerical values of the coherent scattering lengths b_i and monomer volumes Ω, see Table 1). The experiments were performed in the Q range of $0.005 \leq Q$ (1/Å) ≤ 0.05 using the settings of $\lambda = 6.1$ Å as neutron wavelength and a 6 m detector-to-sample distance.

Our sample was a melt of partially deuterated poly(ethylene–propylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer containing a volume fraction PEP of $f = 0.65$ with a total molecular volume of $V_n = 83\,400$ cm^3/mol (degree of polymerization $N = 1100$). The synthesis and characterization of this block copolymer is found in ref 9 and the parameters are given in Table 1. To obtain safely equilibrated conditions in the pressure cell, we waited ~30 min after each temperature setting before a new measurement was started.

V. Experimental Results

Two representative sets of experimental data are plotted in Figures 3 and 4. In Figure 3, the structure factors $S(Q)$ of a sample at two pressures of 1 and 800 bar and at two temperatures of 175 and 95 °C are plotted versus Q in a semilogarithmic scale. This sample was first heated to 175 °C and then cooled stepwise in order to perform the pressure experiments. In Figure 4 the data for two samples are shown. Before being mounted in the pressure cell, the polymer was sheared at room temperature to generate a single-domain sample. The shearing direction was always chosen perpendicularly to the neutron beam axis. The experiments were performed at constant pressure and at various increasing temperatures. The two samples were measured at pressures of 1 and 1000 bar. The data in Figure 4 were integrated over the range of $0.01 \leq Q$ (Å^{-1}) ≤ 0.025. They are plotted versus the azimuthal angle. The structure factor is anisotropic and shows texture due to the shear. The phase transitions lead to strong changes of $S(Q)$, which were observed during heating at 1 bar, but they appear much weaker at 1000 bar.

Figure 3 shows scattering from the disordered state at 175 °C and the hexagonal ordered state at 95 °C. For the analysis these data were fitted with eq 5 of the Fredrickson–Helfand theory from which the renormal-

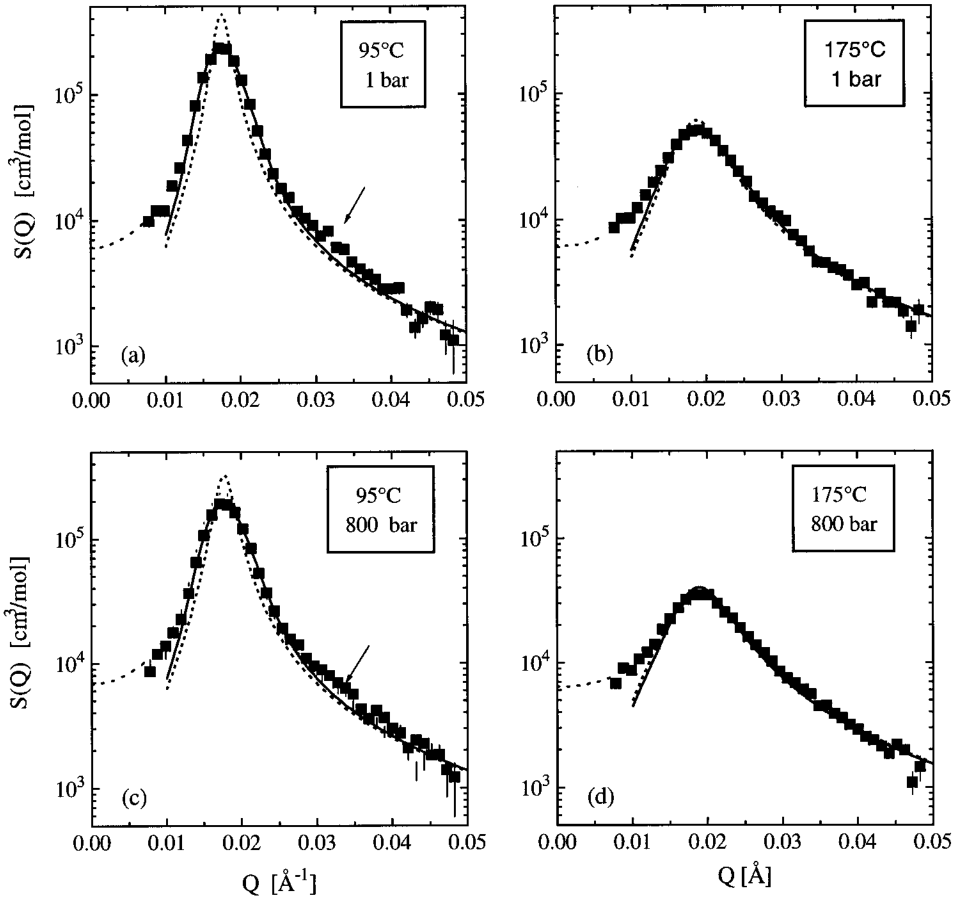

Figure 3. Structure factor at two temperatures and pressures. At 95 °C, a second-order reflection peak caused by ordering is observed (see Figure 5).

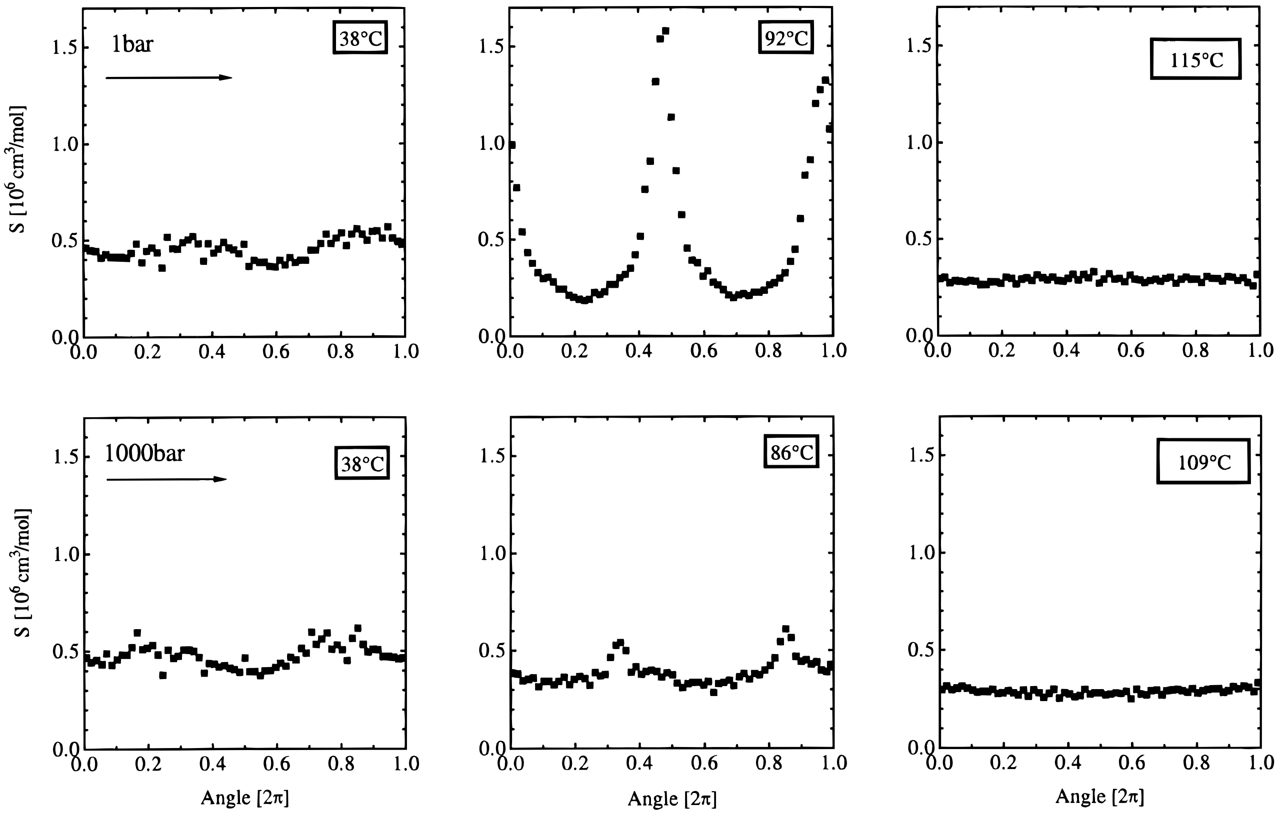

Figure 4. $S(Q)$ of a sheared sample versus the azimuthal angle at fixed Q integrated over the interval from 0.01 to 0.025 Å . $S(Q)$ is shown at three temperatures for 1 and 1000 bar. The strong changes of intensity are caused by the phase transitions.

Table 2. Thermodynamic Parameters of a Diblock Copolymer with $f = 0.65$ and $V = 83\ 400$ cm^3/mol

$x^* \equiv (Q^*R_g)^2$	$\bar{N}$	$\bar{c} = c^3dl/2$	$\Gamma_S V$	$\Gamma_{ODT} V$	$\Gamma_{OOT} V$
3.902	20000	231.2	12.32	13.8	17.4

ized Flory–Huggins parameter Γ_{ren} and, according to the relation $QR_g = 3.902^{1/2}$ (Table 2),[19] the radius of gyration R_g was obtained. The scattering data were corrected for resolution effects. The theoretical function of eq 5 is represented by the dotted curves in Figure 3. They were convoluted with the resolution function of the instrument (solid lines in Figure 3) and fitted to the experimental data shown as solid squares.[27] There are two pronounced deviations from the theoretical data: The structure factor $S(Q)$ should approach zero in the limit of $Q = 0$ (eq 2), in contrast to the experimental data which remain finite and are practically independent of temperature and pressure. Polydispersity of the polymers leads to fluctuation effects on larger scales which, therefore, might be responsible for the observed deviation. The second discrepancy is a second-order peak from the periodic structure observed at 95 °C in the hexagonally ordered regime (see arrows in Figure 3).

VI. Analysis and Discussion of Experimental Results

Two parameters are obtained from $S(Q)$, namely, the susceptibility $S(Q^*)$ and the radius of gyration R_g. Both will be analyzed and discussed in this section.

A. Susceptibility. In Figure 5, the inverse susceptibility at 1 and 1000 bar has been plotted versus $1/T$ in a semilogarithmic scale. The full symbols represent the sample, which was cooled from high temperatures as described in connection with Figure 3, and the open symbols represent the shear aligned samples according to Figure 4. In the disordered phase both samples show the same scattering, while below T_{ODT} within the ordered regime quite strong differences were observed.

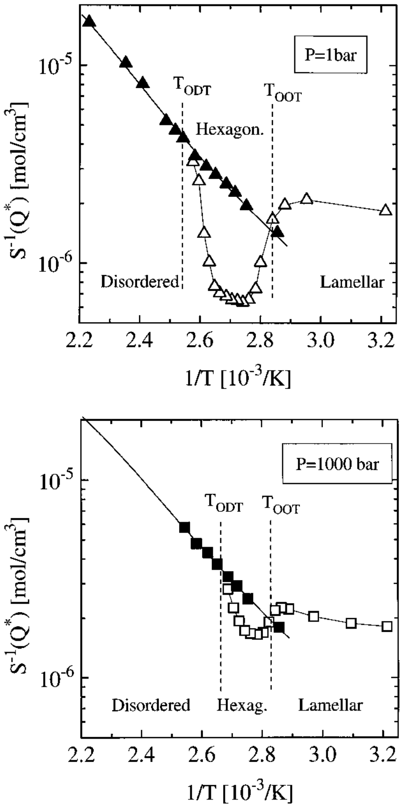

Figure 5. Inverse structure factor (susceptibility) at the peak position for $Q \equiv Q^*$ versus $1/T$ for two pressures. The open symbols represent the sheared samples, the solid symbols the "untreated" sample. Below the temperature T_{ODT}, the untreated sample is undercooled and not in equilibrium. T_{ODT} and T_{OOT} have been determined from this plot.

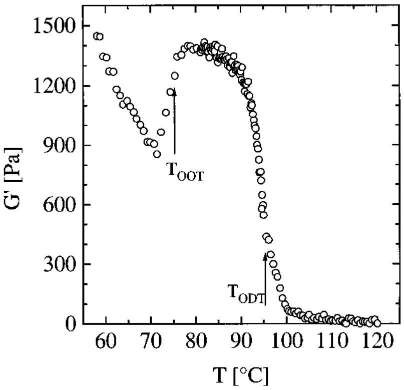

Figure 6. Dynamic elastic modulus G′ of shear-oriented sample. The measurements were performed with increasing temperature. The transition temperatures obtained from the mechanical measurements are $T_{ODT} \cong 95$ °C and $T_{OOT} \cong 75$ °C. With SANS the same T_{OOT}, however, $a \cong 25$ K higher T_{ODT} was found.

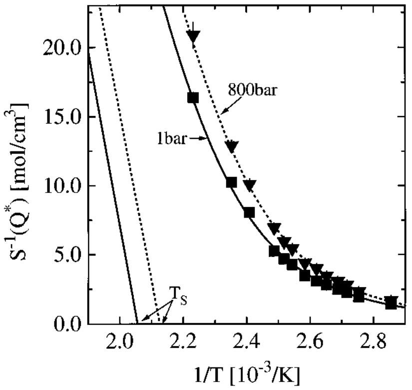

Figure 7. Inverse susceptibility $S^{-1}(Q^*)$ versus $1/T$ for two pressures with the respective fits with the Fredrickson–Helfand theory, plotted as solid and dotted lines. The calculated mean-field susceptibilities for 1 and 800 bar are represented by the straight lines with the respective spinodal temperatures at the intercept $S^{-1}(Q^*) = 0$.

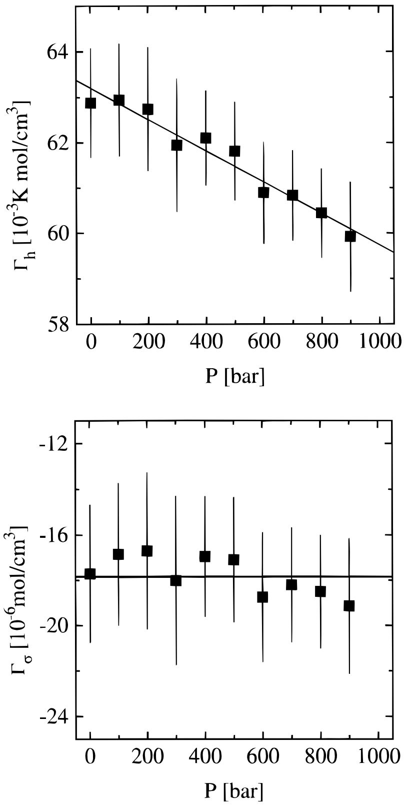

Figure 8. Flory–Huggins parameter for the PEP–PEE copolymer as a function of pressure. The enthalpic part Γ_h (top) decreases with pressure and the entropic part Γ_σ (bottom) is negative and constant. Γ_h is the dominant term in Γ. This behavior differs strongly from the behavior of homopolymers.

They indicate that the continuously cooled sample (full symbols) was possibly not in its equilibrium state. But clearly the sample has crossed the ODT phase boundary, which is evident from the second-order peak (Figure 3).

Two phase boundaries were passed during cooling, namely, order–disorder at T_{ODT} and order–order at T_{OOT}. Both are predicted by the Fredrickson–Helfand theory according to the phase diagram in Figure 1 and to our calculations of the thermodynamic potentials in Figure 2. In analogy with related diblock copolymer melts,[4,9] we ascribe the intermediate phase as hexagonal and the low-temperature phase as modulated lamella, even though we do not have sufficient structural data for unambiguous identification. From the data in Figure 5 we find T_{OOT} between modulated lamellar and hexagonal phases at ≅76 °C independent of pressure and T_{ODT} between the disordered and hexagonal ordered regime at ≅120 °C for 1 bar, and at ≅103 °C for 1000 bar, i.e., a decrease of T_{ODT} with pressure with $\Delta T_{ODT}/\Delta P = -1.7 \times 10^{-2}$ K/bar. Such behavior is unexpected compared with results for binary homopolymer blends with UCST behavior (i.e., decomposition at low temperatures). In this case, $\Delta T/\Delta P$ for binodal and spinodal temperature is always positive due to a positive entropic term of the Flory–Huggins parameter, Γ_σ.[15] The phase transitions as observed in Figure 5 were also measured in a rheological study plotted in Figure 6. These dynamic mechanical experiments were conducted on a Rheometrics RSA II Solids Analyser operated in an oscillatory shear mode using a shear sandwich fixture at a shear rate of $\omega = 0.1$ rad/s. Before experiment the sample was macroscopically aligned at low (ambient) temperature by application of a 100% oscillatory strain at low frequencies. The measurements were performed on increasing temperature as in the SANS experiments. Figure 6 shows the dynamic elastic modulus G′ in the temperature range 55°C to 120°C. The sample shows abrupt changes in the rheological characteristics at two temperatures which can be identified by phase transitions:[6] $T_{OOT} \cong 75$ °C and $T_{ODT} \cong 95$ °C. The measured T_{OOT} is in agreement with the SANS measurements while the T_{ODT} is about 25K lower than the respective SANS value. At the moment we have no explanation for this discrepancy.

Next we discuss the Flory–Huggins parameter and the spinodal temperature as evaluated from the Fredrickson–Helfand theory with eq 7. In Figure 7 the inverse susceptibility has been plotted versus $1/T$ for the 1 bar and the 800 bar measurements of the continuously cooled sample. The solid and dashed lines represent $S(Q)$ according to the Fredrickson–Helfand theory (eq 5). The enthalpic and entropic terms of the Flory–Huggins parameter Γ as obtained from eq 7 are plotted versus pressure in Figure 8. The mean-field susceptibility as calculated from Γ is plotted as straight lines for the pressures at 1 (solid) and 800 bar (dashed). The intercepts at $S^{-1}(Q^*) = 0$ define the spinodal temperatures T_S whose numerical values have been plotted versus pressure in Figure 9. Similar to T_{ODT}, we observe a decrease of T_S with pressure with a slope of $\Delta T_S/\Delta P = -(1.9 \pm 0.04) \times 10^{-2}$ K/bar, in good agreement with $\Delta T_{ODT}/\Delta P$. All the experimental values are summarized in Table 3.

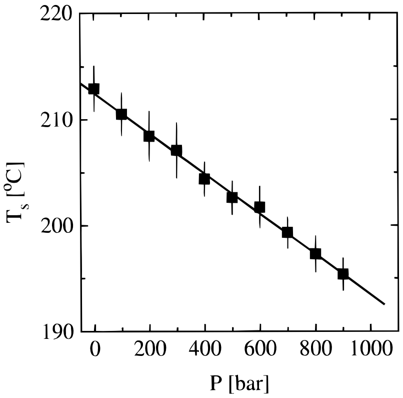

Figure 9. Spinodal temperature as a function of pressure. A linear decrease of T_S with pressure is observed.

Within error bars we find a pressure-independent entropic term Γ_σ and an enthalpic term Γ_h decreasing linearly with pressure. Our 1 bar values for Γ agree with the respectively determined values from Bates et al.[5] These authors have evaluated Γ from a rheological determination of T_{ODT} for three PEP−PEE copolymers with different molecular weights. They found $\Gamma_h = 6.2 \times 10^{-2}$ K·mol/cm^3 and $\Gamma_\sigma = -5.8 \times 10^{-6}$ mol/cm^3. Their Γ_h agrees within error bars with our value whereas their entropic value of $|\Gamma_\sigma|$ is ~3 times smaller than ours. This discrepancy is still in the range of possible systematic errors, considering that the ratio $\Gamma_h/T_{ODT} \cong 1.6 \times 10^{-4}$ mol/cm^3 is 10 times the entropic term.

If we compare the Flory−Huggins parameter of the PEP−PEE block copolymer with the respective ones of binary homopolymer blends we observe three pronounced differences: (i) Γ_h depends on pressure and determines the shift of the transition temperatures with pressure. (ii) Within error bars Γ_σ is constant. Therefore, it does not cause a change of the transition temperature. The opposite holds for binary homopolymer blends investigated so far:[15] The change of the phase boundaries with pressure is mainly caused by Γ_σ. (iii) The value of Γ_σ in Figure 7 is negative. To our knowledge, all homopolymer blends with an UCST investigated so far revealed positive Γ_σ values.

Our results for Γ are qualitatively consistent with lattice cluster theory calculations for diblock copolymers based on the mean-field approximation by Freed and Dudowicz.[22,23] They proposed a Flory−Huggins parameter that combines two contributions: The usual segmental part (index *s*) and a term from the junction connecting the A and B block of the chain (index *j*).

$$\Gamma = (\Gamma_h^s - \Gamma_h^j)/T - (\Gamma_\sigma^s - \Gamma_\sigma^j) \quad (8)$$

The junction obviously reduces the enthalpic and entropic contributions to Γ. This influence is proportional to V^{-1} and disappears for large chains. Obviously, for smaller molecules this term may cause a strong difference with respect to the Flory−Huggins parameter as obtained for the corresponding binary homopolymer. On the basis of experimental data from Bates et al.,[5] Freed and Dudowicz obtain

$$\Gamma = [0.051 - 1322.8/V]/T - [3.84 \times 10^{-5} - 7.04885/V] \quad (9)$$

for the PEP−PEE copolymer (in units of mol/cm^3). In particular for our PEP−PEE system this gives $\Gamma = (3.5 \times 10^{-2}/T + 4.5 \times 10^{-5})$ mol/cm^3.[23] Their enthalpic and entropic terms are smaller and larger by a factor of 2, respectively, but they trend in the same direction. The lattice cluster theory for diblock copolymers also shows a decrease of Γ with increasing pressure[22,23] in agreement with our experimental findings in Figure 8. Remaining discrepancies of Γ between block copolymer and binary blend may contain contributions caused by an insufficient treatment of the fluctuations in the Fredrickson−Helfand theory. Furthermore, there are chain end effects that might also contribute to Γ.

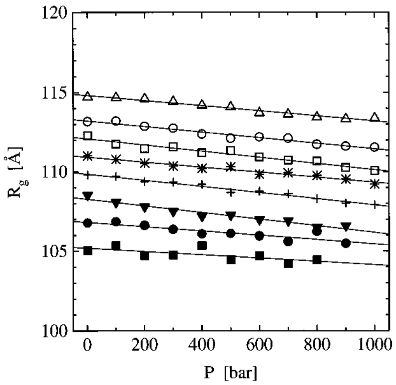

Figure 10. Radius of gyration of the "untreated" sample (Figure 5) as a function of pressure for temperatures at *T* (°C) = (■)175, (●)152, (▽) 129, (+)120, (∗) 108.5, (□) 99, (○) 90, and (△) 77. R_g decreases with increasing temperature and pressure.

Table 3. Thermodynamic Parameters Obtained from SANS and rheology[a]

Γ_h (mol·K/cm^3)	$(6.32 \pm 0.02) \times 10^{-2} - (3.5 \pm 0.3) \times 10^{-6} P$/bar
$\bar{\Gamma}_\sigma$ (mol/cm^3)	$-(1.78 \pm 0.09) \times 10^{-5}$
T_S (°C)	$(212.5 \pm 0.2) - (1.9 \pm 0.04) \times 10^{-2} P$/bar
T_{ODT}(1 bar) (°C)	≅120 (≅95)*
T_{ODT}(1 kbar) (°C)	≅103
$\Delta T_{ODT}/\Delta P$ (*K*/bar)	-1.7×10^{-2}
T_{OOT}(1 bar) (°C)	≅75.7 (≅75)*
T_{OOT}(1 kbar) (°C)	≅75.7
$\Gamma_{ODT}V$(1 bar)	14.9
$\Gamma_{ODT}V$(1 kbar)	14.73
$\Gamma_{OOT}V$(1 bar)	16.6
$\Gamma_{OOT}V$(1 kbar)	15.76

[a] The results from rheology are indicated by an asterisk.

Tables 2 and 3 summarize the theoretical and experimental values of ΓV at the phase boundaries. The spinodal temperatures in Figure 9 were evaluated from the relation $\Gamma_S V = 12.32$ in Table 1. The experimentally determined $\Gamma_{ODT}V$ is ~7% higher whereas $\Gamma_{OOT}V$ is ~7% smaller than the respective theoretical values. Table 3 shows the pressure dependence of the different parameters. With increasing pressure, Γ_{ODT} and the transition temperature T_{ODT} decrease such that $\Gamma_{ODT} = (\Gamma_h/T_{ODT} - \Gamma_\sigma)$ is approximately constant (Γ_σ is nearly pressure independent and small). On the other hand, T_{OOT} is practically pressure independent and Γ_{OOT} decreases with increasing pressure. We emphasize again that the Fredrickson−Helfand theory deals with an incompressible medium and, therefore, cannot describe these effects; e.g., it predicts a constant Γ at the T_{ODT} and T_{OOT} transitions.

B. Conformation. In Figure 10 the radius of gyration R_g is plotted versus pressure for temperatures between 77 and 175 °C. The values for R_g have been evaluated from the peak position at Q^* using the relation $QR_g = 3.902$, as given in Table 2. A decrease of R_g with increasing temperature and pressure was observed. The same trend of the temperature and pressure dependence of R_g was also found in homopolymer binary blends.[16] The observed decrease of R_g with temperature and pressure in diblock copolymers and in

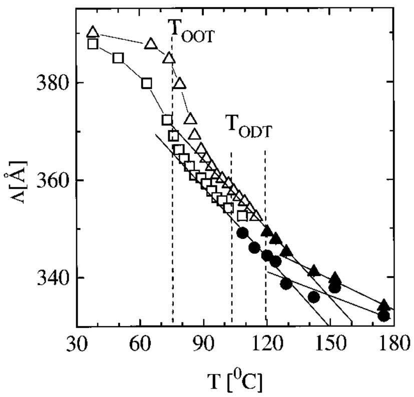

Figure 11. Wavelength of composition fluctuations versus temperature for two pressures of "untreated" and sheared sample: 1 (△), 800 (●), and 1000 bar (□). At T^*, a change of slope is observed which is interpreted as the onset of chain stretching at low temperatures. A further stronger increase of the lamellar period Λ is observed near T_{OOT}.

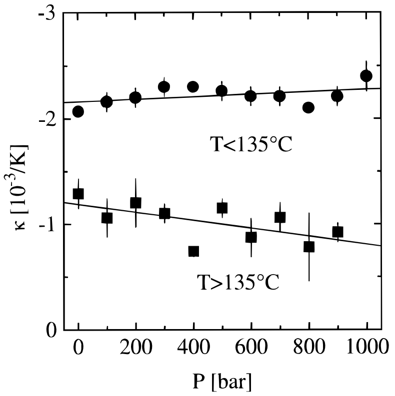

Figure 12. Thermal coil expansion with pressure. Below $T = 135$ °C, the thermal expansion is twice as large as at high temperatures because of the onset of coil stretching. The slope of κ with pressure is different above and below $T = 135$ °C.

binary mixtures of homopolymers contradicts the random phase approximation of Leibler[19] and of de Gennes,[21] where R_g is independent of temperature and pressure. It has been interpreted as a stretching near the order transitions.[28]

In Figure 11, the dominating period of composition fluctuations, $\Lambda = 2\pi/Q^*$, of the shear aligned monodomains (open symbols), and of the polydomain sample (full symbols) is plotted versus temperature for various pressures. The corresponding susceptibilities $S(Q)^*$ are plotted in Figure 5. The characteristic temperatures of the system were investigated, and the following results were obtained.

(i) Below $T^* \cong 135$ °C a stronger increase of R_g with decreasing temperature is observed for all pressures. This is clearly seen in Figure 12, where the thermal expansion coefficient of R_g, namely, $\kappa = \partial \ln R_g^2/\partial T$ has been plotted versus pressure P. Below T^* a value of $|\kappa|$ is found twice as large as above T^*. Furthermore, κ slightly decreases with pressure below T^* whereas it slightly increases above T^*. We interpret the increase of κ below T^* as the onset of coil stretching. The conformation of copolymers has systematically been studied experimentally with SANS by Almdal et al.[28] and numerically with Monte Carlo simulations by Fried and Binder.[29] In both studies, stretching of the coils was observed already in the disordered regime above T_{ODT}. Almdal et al. studied the PEP−PEE copolymer at room temperature for various degrees of polymerization. The authors determined two scaling laws, namely, the $R_g \propto N^{(0.49\pm0.02)}$ and $R_g \propto N^{(0.8\pm0.04)}$ above and below a GST (Gaussian stretched coil transition) temperature, respectively. In our interpretation, the GST coincide with T^*. Therefore, below T^* the conformation of the block copolymers should be non-Gaussian in contradiction to the RPA assumption. On the basis of the numerical calculations Fried and Binder[29] were able to give more detailed information, as the Monte Carlo simulation allows direct determination of Λ and R_g. They found stretching of the coil over a larger temperature interval and interpreted the GST temperature of Almdal et al. as a "smooth crossover from a weak to a strong segregation" regime.

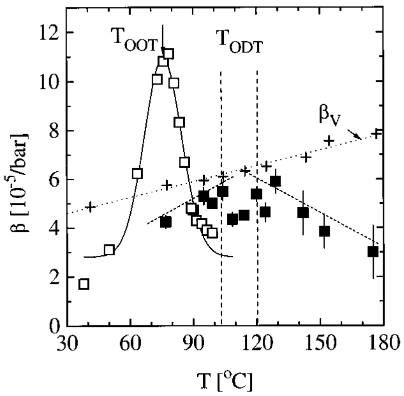

Figure 13. Chain compressibility versus temperature. A rather strong peak at the OOT temperature is observed.

(ii) At T_{ODT}, no change of the thermal expansion coefficient of R_g was observed in agreement with ref 5.

(iii) At low temperatures near the OOT phase transition, a further stronger increase of Λ is observed. At 1 and 1000 bar it mainly appears in the hexagonal and the lamellar phases, respectively. In Figure 13, the compressibility $\beta_\Lambda = -3(\partial \ln \Lambda/\partial P)$ of the fluctuation wavelength evaluated from the data of Figure 11 has been plotted. The open and solid symbols represent the results for the sheared and the "untreated" sample, respectively. For comparison, the volume compressibility $\beta_V = -\partial \ln V/\partial P$ from PVT measurements has been plotted. β_V increases linearly with temperature whereas the chain compressibility β_Λ shows a more complicated behavior. Above $T_{ODT}(1 \text{ bar}) = 120$ °C the β_Λ values are smaller than β_V, and β_Λ values decrease with temperature. Qualitatively, the same behavior was observed for the d-PS/PS homopolymer[16] with a negligible Flory−Huggins parameter, i.e., $\Gamma << \Gamma_S$ (Γ_S, Flory−Huggins parameter at the spinodal). For homopolymer blends with $\Gamma \leq \Gamma_S$, a constant value of β_Λ and larger than β_V was observed.[16] In the ODT transition range for the pressure between 1 and 1000 bar, a slight decrease of β_Λ is observed. This happens because the ODT phase transition occurs in this temperature interval between 1 and 1000 bar and indicates a decrease of Λ during the ODT transition. A change of the radius of gyration of $\Delta R_g \cong 0.44$ Å during the ODT phase transition at 1 bar was estimated from β_Λ measured at $T \cong 110$ °C and extrapolated from higher temperatures . This value is obtained from the difference $(\beta_2 - \beta_1)$ of the relations

$$\beta_1 = 3[R_{g,\mathrm{ord}}(1 \text{ bar}) - R_{g,\mathrm{dis}}(1 \text{ kbar})]/(R_g \times 1 \text{ kbar}) \cong 4.4 \times 10^{-5}/\text{bar}$$

$$\beta_2 = 3[R_{g,\mathrm{dis}}(1 \text{ bar}) - R_{g,\mathrm{dis}}(1 \text{ kbar})]/(R_g \times 1 \text{ kbar}) \cong 5.6 \times 10^{-5}/\text{bar}$$

which yields $[R_{g,\mathrm{ord}}(1 \text{ bar}) - R_{g,\mathrm{dis}}(1 \text{ bar})]/R_g \cong -4 \times$

10^{-3}. A qualitatively similar decrease of R_g due to ordering of the block copolymers at T_{ODT} was reported by Kasten and Stühn.[30] From the change of the sample volume at T_{ODT} they found a value $\Delta V/V = -(3 \pm 1) \times 10^{-3}$.

At T_{ODT}, the compressibility of the sheared sample surprisingly shows a peak whose maximum is roughly 2 times above the value at other temperatures. This means that the coils in their extended direction (or more precisely, the period of composition fluctuations) soften at the order−order phase transition. So far, this peak has no physical interpretation and further studies are needed.

VII. Summary and Conclusions

The structure factor $S(Q)$ of the diblock copolymer PEP−PEE was measured as a function of temperature and pressure in the disordered and in the ordered states.

The structure factor is well described and analyzed in terms of the Fredrickson−Helfand theory[20] even though this theory do not include conformational asymmetry, which may have important implications for formation of a modular layered structure rather than a simple lamellar one in the present diblock copolymer. The Fredrickson−Helfand theory takes concentration fluctuations into account. From the structure factor, the Flory−Huggins parameter Γ was determined as a function of temperature and pressure between 1 and 1000 bar. Γ was separated into a positive enthalpic term Γ_h and a negative entropic term Γ_σ. The enthalpic term is ~90% of Γ at 120 °C. It decreases with pressure whereas the entropic term is practically constant.

These results for $\Gamma(p,T)$ are qualitatively consistent with the lattice cluster theory of Freed and Dudowicz.[22,23] They calculated Γ for diblock copolymers, where an additional nonsegmental term appears; it is caused by the joint of the diblock chains. This term tends to decrease the segmental enthalpy and the entropy of mixing. These results are qualitatively different from the Flory−Huggins parameter Γ obtained for binary homopolymer blends.[15] For example, a negative Γ_σ as in the PEP−PEE copolymer was not observed in UCST blends, and the pressure dependence of the phase diagrams in binary blends is dominated by Γ_σ and not by Γ_h as in the PEP−PEE copolymer. Remaining discrepancies may be due to the deficiencies in the treatment of fluctuations in the Fredrickson−Helfand theory and also due to other effects, e.g., other finite chain contributions.

The spinodal temperature T_S, the order−disorder temperature T_{ODT} and the order−order temperature T_{OOT} were also investigated as a function of pressure. T_{ODT} and T_S decrease with increasing pressure whereas T_{OOT} shows no change with pressure.

The conformation of the coils and the period Λ of the lamella density fluctuations show pronounced changes with pressure and temperature with strong deviations from the Gaussian polymer coils. A stretching of the polymer coils is observed below $T \cong 135$ °C but no change was seen at T_{ODT}. Crossing the T_{OOT}, on the other hand, leads to a strong extension of the coil in the lamellar phase. The compressibility of the fluctuation period (Figure 12) reveals a pronounced maximum at T_{OOT}. The changes of coil conformation in diblock copolymers and in homopolymer blends with pressure and temperature are not yet understood theoretically.

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References and Notes

(1) Γ is defined as $\partial^2[\phi(1-\phi)\chi]/\partial\phi^2$ with the Flory−Huggins parameter χ and is given in units (mol/cm^3) similar to our respective definitions in homopolymer blends.[14] (ΓV) has the same meaning as (χN) usually given in SANS work from other groups.
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