Temperature and Pressure Dependence of the Order Parameter Fluctuations, Conformational Compressibility, and the Phase Diagram of the PEP-PDMS Diblock Copolymer

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The structure factor of a poly(ethylene-propylene)-poly(dimethylsiloxane) diblock copolymer has been measured by small-angle neutron scattering as a function of temperature and pressure. The conformational compressibility exhibits a pronounced maximum at the order-disorder phase transition. The phase boundary shows an unusual shape. With increasing pressure it first decreases and then increases. Its origin is an increase, respectively, of the entropic and of the enthalpic part of the Flory-Huggins interaction parameter. The Ginzburg parameter describing the limit of the mean-field approximation is not influenced by pressure. [S0031-9007(96)01379-8]

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We present small angle neutron scattering (SANS) data of a partially deuteratedpoly(ethylene-propylene)-poly(dimethylsiloxane) (PEP-PDMS) *diblock copolymer.* The structure factor as measured by the scattered neutrons is a measure of the composition fluctuations, and thereby of the fluctuations of the order parameter. The analysis of the structure factor yields the phase transition temperatures, the coil dimension, and the Flory-Huggins interaction parameter. These parameters have been determined as a function of *pressure* and *temperature.* The PEP-PDMS exhibits an unusual phase diagram with respect to the pressure dependence of the order-disorder phase transition temperature T_{ODT}. An interpretation of the phase diagram will be given on the basis of the Flory-Huggins parameter. Furthermore, we show that the conformational compressibility β_{conf} exhibits an anomaly at T_{ODT}. This contradicts the theories which are based on the random phase approximation [1,2]. Finally, no change of the critical range with pressure was observed.

Hydrostatic pressure leads in *binary homopolymer blends* quite generally to a shift of phase boundaries to higher temperatures. This is found for systems with upper as well as with lower critical solution temperature [3–5]. It seems principally to be related to a decrease of the entropic term of the Flory-Huggins parameter with pressure, i.e., $\Delta|\Gamma_\sigma|/\Delta P < 0$ where the Flory-Huggins parameter is written as $\Gamma = \Gamma_h/T - \Gamma_\sigma$; Γ_h and Γ_σ are the respective enthalpic and entropic contributions. This behavior is quite plausible, according to equation of state theories where the entropic term Γ_σ is directly related to the compressibility or the free volume of the sample [6]. The situation is different and more complex in *diblock copolymers.* Most experiments in diblock copolymers show a decrease of the order-disorder temperature T_{ODT} with pressure [7–9], and so far only the polystyrene-polyisoprene (PS-PI) diblock copolymer has been reported to show an increase of the phase boundary with pressure [10]. From theoretical studies based on lattice cluster calculations (LC), Freed and Dudowicz predict that T_{ODT} decreases with increasing pressure as a result of $\Delta|\Gamma_\sigma|/\Delta P$ being negative [11,12]. These calculations assume diblock copolymers which order at low temperatures. Experimental data on a poly(ethylene-propylene)-poly(ethylethylene) (PEP-PEE) diblock copolymer give, however, a negative $\Delta\Gamma_h/\Delta P$ even though $\Delta\Gamma_\sigma/\Delta P \cong 0$ [8]. In order to get a better understanding of the phase behavior in block copolymers, studies of a variety of systems are needed where both the T_{ODT} and the interaction parameters Γ_h and Γ_σ are investigated versus pressure. Such a study will be presented in this Letter for the PEP-PDMS diblock copolymer (see Table I) which shows an even more complex $\Delta T_{\mathrm{ODT}}/\Delta P$ behavior.

Most of the SANS experiments have been performed at the DR3 reactor at the Risø National Laboratory, whereas the 1 bar measurements in the ODT transition range were performed at the SANS diffractometer KWSI at the Jülich FRJ2–research reactor. A steel bodied pressure-temperature cell was used which allows an *in situ* change

TABLE I. System parameters of the diblock copolymer PEP-PDMS. f was determined by ^{13}C and the degree of deuteration by ^{1}H-NMR-spectroscopy. V_n is the number averaged molecular volume.

Polymer	PEP	PDMS
Chem. structure	$C_5H_{5.3}D_{4.7}$	$SiOC_2H_6$
T_G (°C)	−56	−125
m (g/mol)	74.5	74.2
Ω (cm^3/mol)	81.9	75.7
Σb_i (10^{-12} cm)	4.46	0.081
f	0.47	0.53
N	89	
M_n (g/mol)	$6.6 \cdot 10^3$	
V_n (cm^3/mol)	$6.9 \cdot 10^3$	
$\overline{\Omega} \equiv V_n/\mathrm{N}$ (cm^3/mol)	77.8	

of pressure and temperature in the range of 1 bar $\leq P \leq$ 1500 bar and $-20\,^\circ\mathrm{C} \leq T \leq 200\,^\circ\mathrm{C}$, respectively, as described in Refs. [3–5]. The scattering data were corrected for background, detection efficiency 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 the structure factor $S(Q)$ 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 $\Sigma b_i/\Omega$ (for numerical values of the coherent scattering lengths b_i and monomer volumes Ω see Table I). The experiments were performed in the range of 0.01 $\mathrm{Å}^{-1} \leq Q \leq 0.1$ $\mathrm{Å}^{-1}$ (Q scattering vector) using the settings of $\lambda = 7$ Å as neutron wavelength, and a 2 m detector to sample distance. The sample studied is a melt of partially deuterated PEP-PDMS diblock copolymer whose characteristic data are given in Tables I and II. To obtain safely equilibrated conditions in the pressure-temperature cell, we waited about 30 min after each temperature setting before a new measurement was started.

The experimental data, eg., each $S(Q)$, were analyzed using Leibler's formula of A-B diblock copolymers in the disordered regime within the mean-field approximation [1]

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

where V is the molecular volume. The function $F(x,f)$ corresponds to a combination of the Debye function for unperturbed Gaussian coils, depending on the volume fraction f and on $x = (QR_g)^2$, the squared product of Q and the overall radius of gyration R_g. $S(Q)$ shows a maximum at a scattering vector Q^*which occurs for $F(x^*,f) = 2\Gamma_S V$. Γ_S is the Flory-Huggins parameter at the spinodal temperature. It was observed that, with increasing pressure, $S(Q)$ first decreases and then increases, whereas the peak position Q^* continuously shifts to larger values. The structure factor $S(Q)$ at $Q = Q^*$ is a susceptibility whose temperature dependence is determined by the product ΓV. Within mean-field approximation the inverse susceptibility is a linear function of the reciprocal temperature and becomes zero at the spinodal. In Fig. 1 the experimentally determined inverse value of $S(Q^*)$ is plotted versus the inverse temperature for three pressures. The strong deviations from a straight line show that fluctuations of the order parameter are important.

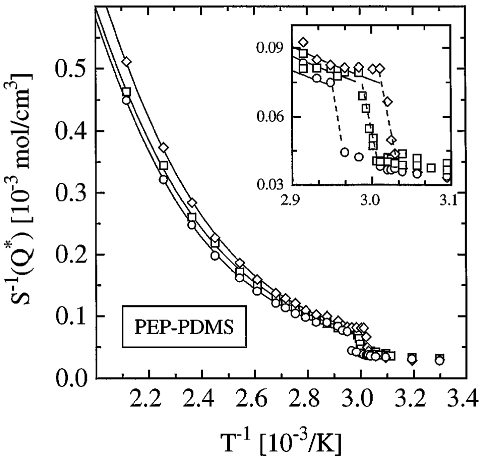

FIG. 1. Inverse peak intensity $S(Q^*)$ versus $1/T$ [1 bar (□), 515 bar (◇), and 1365 bar (○)]. Statistical error bars are within the size of the symbols. $S(Q^*)$ shows a discontinuity at the order-disorder phase transition. The solid lines represent the fit of $S(Q^*)$ with the Fredrickson-Helfand theory.

The effects of fluctuations were included into $S(Q)$ by Fredrickson and Helfand [2] on the basis of the Hartree approximation [13]. The corresponding structure factor has the same form as Leibler's mean-field expression in Eq. (1), but with a renormalized Flory-Huggins parameter instead

$$\Gamma_{\mathrm{ren}} V = \Gamma V - \tilde{c}\sqrt{S(Q^*)/V\overline{N}} \tag{2}$$

with $\tilde{c}$ depending on molecular parameters [2]. The degree of fluctuations is determined by the generalized polymerization parameter defined by $\overline{N} = (R_0^3/V)^2$. The quantity $\overline{N}$ characterizes the average number of chains in a volume R_0^3, where R_0 is the end-to-end distance of the linear polymer ($R_0^2 = 6R_g^2$). The parameter $\overline{N}$ (defined as P^2 on p. 112 of Ref. [14]) can be viewed as the Ginzburg parameter used for homopolymers [15,16]. According to Eq. (2) the mean-field theory is valid for $S(Q)/V \ll 1$ and/or $\overline{N} \gg 1$, which is fulfilled for temperatures very far from T_S and/or in case of large V. With the susceptibility $S(Q^*) = V/2[\Gamma_S V - \Gamma_{\mathrm{ren}} V]$, the product of the Flory-Huggins parameter and the molecular volume can be expressed as

$$\Gamma V = \Gamma_{\mathrm{ren}} V + \frac{\tilde{c}}{\sqrt{\overline{N}}}\bigg/\sqrt{2[\Gamma_S V - \Gamma_{\mathrm{ren}} V]}. \tag{3}$$

In the following, we analyze $S(Q^*)$ of the scattering data by the Fredrickson-Helfand theory which yields the renormalized Flory-Huggins parameter Γ_{ren}. Subsequently, we calculate the Flory-Huggins parameter Γ in the framework of the mean-field theory from Eq. (3).

The order-disorder temperature T_{ODT} in diblock copolymers represents a first order phase transition [1,2]. Experimentally, three parameters are obtained from $S(Q)$, namely the peak intensity $S(Q^*)$, the peak width, and the peak position Q^* which all change discontinuously at T_{ODT}. These parameters are related to the susceptibility, the correlation length, and the dimension of the coil, respectively. For the susceptibility $S(Q^*)$ this is demonstrated in Fig. 1. Figure 2 shows the conformational compressibility β_{conf} evaluated from the peak position Q^* according to $\beta_{\mathrm{conf}} = -3\Delta\ln R_g/\Delta P = 3\Delta\ln Q^*/\Delta P$. The ODT phase transition is accompanied by peaks of β_{conf}; it reflects a discontinuous decrease of the coil dimension at T_{ODT} approaching higher pressures. Such a stepwise change of the conformation at T_{ODT} is not expected from the theories of Leibler [1] and Fredrickson

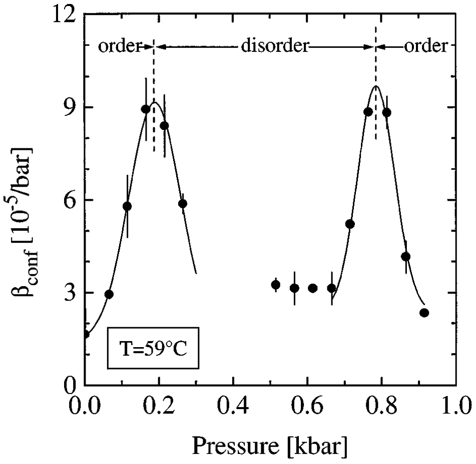

FIG. 2. "Conformational" compressibility β_{conf} at 59 °C in the pressure range between 1 and 1000 bars evaluated from the peak position at Q^*. The two peaks at 189 and 787 bars indicate a order-disorder and a disorder-order phase transition. The origin of the peaks is a discontinuous decrease of the coil dimension at T_{ODT}.

and Helfand [2]. It is, on the other hand, found in computer simulations [17] and predicted in a recent approach for diblock copolymers by Stepanow developed on the basis of a diagram technique avoiding random-phase approximation [18].

The phase diagram of the diblock copolymer PEP-PDMS is depicted in Fig. 3 in a temperature/pressure representation. The T_{ODT} transition line is characterized by different symbols according to the three parameters showing a discontinuity at T_{ODT}. The PEP-PDMS is disordered and ordered at high and low temperature, respectively. The shape of its phase boundary is quite unusual: At low pressure a negative $\Delta T_{\mathrm{ODT}}/\Delta P$ is found as in the majority of the investigated diblock copolymers, while at high pressures (above 500 bars) a quite strong positive $\Delta T_{\mathrm{ODT}}/\Delta P$ is found. No order-order phase transition was observed in PEP-PDMS.

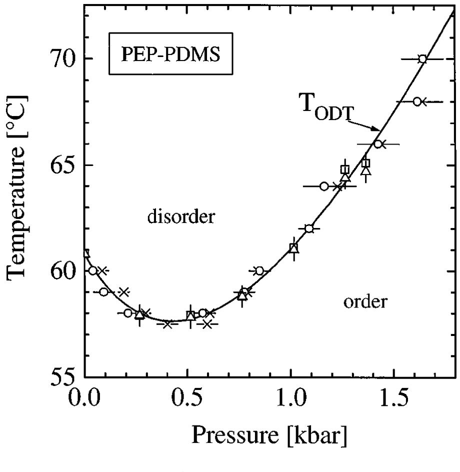

FIG. 3. Phase diagram of the PEP-PDMS diblock copolymer in the temperature-pressure representation. The order-disorder phase transition line has been determined from three parameters of $S(Q)$ which show a discontinuity at T_{ODT}. The behavior of two parameters, namely the susceptibility (isotherm ○ and isobar □) and the conformational compressibility (×), have already been shown in Figs. 1 and 2. The third parameter is the width of $S(Q)$ (isobar △). No order-order phase transition was observed.

The Clausius-Clapeyron equation of classical thermodynamics (p. 349 of Ref. [19]) relates the change of T_{ODT} with pressure to the change of volume and entropy occurring during the phase transition: $\Delta T_{\mathrm{ODT}}/\Delta P = \Delta V/\Delta S$. Since $\Delta V/\Delta P$ must be negative because of stability condition, the experiments give always a gain in entropy ($\Delta S > 0$) when crossing from the ordered to the disordered phase. The sign of $\Delta V/\Delta P$ is the same as the conformational changes with pressure as depicted in Fig. 2. It may seem surprising that the disorder-order phase transition at high pressure leads to a decrease of the coil dimension.

Within the phenomenological thermodynamics, the Flory-Huggins parameter gives an interpretation of the phase diagram shown in Fig. 3. It is determined from the measured $S(Q^*)$ in the disordered phase with Eqs. (2) and (3) as demonstrated by the solid lines in Fig. 1. The enthalpic and entropic terms of the Flory-Huggins parameter have been plotted in Fig. 4 versus pressure. The enthalpic term increases linearly with pressure while the entropic term first increases and then slightly decreases above 800 bar. The increase of Γ_h with P is the origin of an increase of the phase boundary while an increase of Γ_σ with P results in a decrease of the phase boundary. This means that $\Delta T_{\mathrm{ODT}}/\Delta P < 0$ at low pressure has its origin in $\Delta\Gamma_\sigma/\Delta P > 0$ (Fig. 4) while $\Delta T_{\mathrm{ODT}}/\Delta P > 0$ at high pressures has its origin in $\Delta\Gamma_h/\Delta P > 0$ (Fig. 4) and also in $\Delta\Gamma_\sigma/\Delta P < 0$ in the larger pressure regime. It has to be mentioned that the determination of the ODT

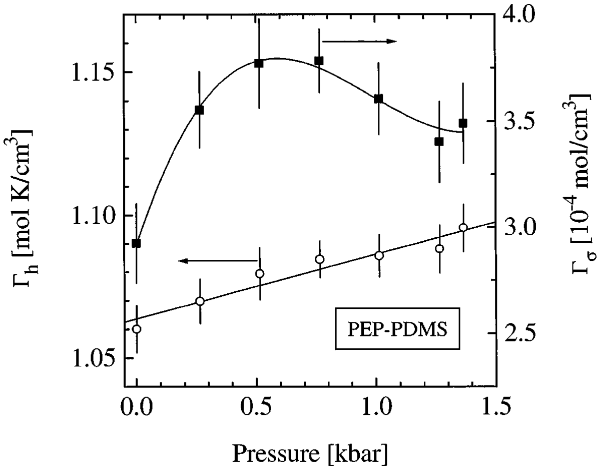

FIG. 4. Enthalpic and entropic terms of the Flory-Huggins parameter. The enthalpic term Γ_h increases linearly with pressure and is the reason for the increase of T_{ODT} with pressure. The observed increase of the entropic term Γ_σ with pressure causes the decrease of T_{ODT}.

temperatures is independent from those of the Flory-Huggins parameter. If one compares these results with former results of the PEP-PEE diblock copolymer, a quite different situation appears but with the same relationship to the Flory-Huggins parameters [8]: In PEP-PEE a $\Delta T_{\mathrm{ODT}}/\Delta P < 0$ was observed which is caused by a $\Delta\Gamma_h/\Delta P < 0$ while $\Delta\Gamma_\sigma/\Delta P \cong 0$. Furthermore, in binary homopolymer blends Γ_σ is related with the volume compressibility and, therefore, a $\Delta|\Gamma_\sigma|/\Delta P < 0$ is expected and observed [5,16]. In PEP-PDMS, however, we observe a $\Delta\Gamma_\sigma/\Delta P > 0$ (Fig. 4) which contradicts a possible relationship with the volume compressibility. These results clearly indicate that in diblock copolymers a microscopic interpretation of the Flory-Huggins parameter, which, for example, would predict a pressure dependence of the phase boundaries, is not yet available.

A further result is related to the pressure dependence of the order parameter fluctuations expressed by $\tilde{c}/\sqrt{\overline{N}}$ in Eq. (3) and which is proportional to the Ginzburg number Gi describing the crossover from mean-field to 3D-Ising behavior in homopolymers [15]. From the fitting routine we obtain a constant value of (5.2 ± 1.1) about 60% larger than the calculated one, indicating that the degree of fluctuations is not influenced by pressure. This finding is in contradiction to similar results of binary homopolymers where a strong decrease of Gi with pressure was observed [5]. Finally, it has to be mentioned that the Flory-Huggins parameter at T_{ODT}, namely $(\Gamma_{\mathrm{ODT}}V) = 18.2$ is independent of pressure and about 60% larger than its theoretical value in Table II.

In summary, the experimentally determined temperature and pressure dependence of the structure factor contributes to four principal different aspects of diblock copolymers: (i) Three parameters can be evaluated from $S(Q)$ which are discontinuous at the order-disorder temperature. This is the peak intensity, the peak width, and the peak position of $S(Q)$. The discontinuous change of the peak position at T_{ODT} leads to a singularity of the conformational compressibility (Fig. 2). (ii) The phase diagram of PEP-PDMS was determined from the three parameters, showing a discontinuity at T_{ODT}, and is plotted in Fig. 3. The phase boundary between disordered and ordered phases has a unique character with re-entrant ordered structure. (iii) The Flory-Huggins parameter of PEP-PDMS is plotted in Fig. 4 versus pressure. The unusual change of T_{ODT} with pressure can be interpreted by the increase of, respectively, the enthalpic and entropic terms. We observed $\Delta\Gamma_\sigma/\Delta P > 0$. This contradicts a simple relationship between Γ_σ and the volume compressibility. (iv) We did not observe any change of the strength of fluctuations with pressure. Therefore, the fluctuations of the order parameter seem much less influenced by the compressibility as compared with binary homopolymer blends [5,16,20].

TABLE II. Thermodynamic parameters of a diblock copolymer with $f = 0.47$ and $V_n = 6300$ cm^3/mol.

$x^* = (Q^* R_g)^2$	$\overline{N}$	$\tilde{c}$	$\Gamma_S V$	$\Gamma_{\mathrm{ODT}} V$
3.79	$1.6 \cdot 10^3$	132.8	10.58	11.41

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