Pressure Dependence of the Flory–Huggins Interaction Parameter in Polymer Blends: A SANS Study and a Comparison to the Flory–Orwoll–Vrij Equation of State

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ABSTRACT: The pressure dependence of the Flory–Huggins interaction parameter of two binary polymer blends was investigated by small-angle scattering of neutrons (SANS). We studied deuteropolystyrene/poly(vinyl methyl ether) (d-PS/PVME) and deuteropolystyrene/poly(phenylmethylsiloxane) (d-PS/PPMS) exhibiting lower and upper critical solution temperatures, respectively. It turned out that in the investigated pressure range between 1 and 1200 bar the enthalpic contribution of the Flory–Huggins parameter is practically independent of pressure. On the other hand, the absolute value of the entropic contribution, which is related to the free volume of the blend, decreases with pressure. Furthermore, *pVT* data of the d-PS/PPMS blend and of its components were measured. From the fits of these data with the Flory–Orwoll–Vrij (FOV) equation of state, the Flory–Huggins parameter was derived and compared with the SANS data. The comparison with the pressure dependence for the entropic contribution is unsatisfactory. The enthalpic contribution is almost pressure independent, as observed in the SANS data.

1. Introduction

Miscible polymers blends exhibit two classes of phase diagrams, namely, decomposition at low temperatures with an upper critical solution temperature (UCST) and decomposition at high temperatures with a lower critical solution temperature (LCST). In recent years the critical concentration fluctuations of different polymer blends in the one-phase region of the phase diagram have been intensively studied by small-angle neutron scattering (SANS) as a function of temperature and the volume fraction of the blend Φ.[1-8] It was found that polymer blends follow the predictions of the mean-field approximation, in particular with a linear dependence of the inverse structure factor $S^{-1}(Q)$ for a scattering vector $Q = 0$ on the reciprocal temperature $1/T$. This holds except in the vicinity of the critical point, where, ruled by the Landau–Ginzburg criterion, a crossover from mean field to 3D Ising behavior occurs.[9,10]

In the mean-field regime the Flory–Huggins model[11] for the calculation of the free enthalpy of mixing $\Delta G_M(\Phi,T)$ has been confirmed. ΔG_M consists of the entropy of mixing ΔS_M, which was calculated in the usual way, and an enthalpic contribution, denoted as the Flory–Huggins interaction parameter. This parameter can be considered as an empirical quantity, which is purely segmental, not depending on the degree of polymerization. The Flory–Huggins interaction parameter was formally divided into two terms, namely, an interaction contribution and an entropic contribution. The latter is a segmental entropy and is supposed to be correlated to the free volume of the blend.

From the literature a great number of theoretical concepts is known as a basis to calculate the partition function for compressible polymer blends.[12-19] From the partition function the Gibbs free energy of mixing ΔG_M and the corresponding equation of state can be derived. Experimental *pVT* data can be fitted with these equations of state and ΔG_M can be evaluated.

Alternatively, SANS has been used in our work to examine the pressure dependence of the Flory–Huggins interaction parameter for an UCST and a LCST polymer blend in the one-phase region of the phase diagram. These two classes of systems were chosen because in an UCST blend the decomposition at low temperatures is essentially induced by the repulsive interaction energy, whereas in the LCST blend the decomposition at high temperatures is related to an increasing entropy connected with an increase of free volume on decomposing. Consequently, for these two classes of systems a characteristically different pressure dependence is expected. The systems investigated were deuteropolystyrene/poly(vinyl methyl ether) (d-PS/PVME) and the blend deuteropolystyrene/poly(phenylmethylsiloxane) (d-PS/PPMS), exhibiting the LCST and UCST behavior, respectively, in a pressure range up to 1.2 kbar.

In addition, we have measured *pVT* data for the d-PS/PPMS blend and for its single components d-PS and PPMS. The results were interpreted with the Flory–Orwoll–Vrij (FOV) model,[12,13] the lattice fluid approach,[14] and the modified cell model (MCM).[19] Although the *pVT* data were fitted best with the MCM theory, we found the best absolute agreement with the SANS results from the FOV model. Thus a comparison of the predictions from this equation of state for the blend d-PS/PPMS with the results for the Flory–Huggins parameter from SANS experiments will be shown. A subject of future work should also be the test of other equation of state theories[15-17] by comparison with our SANS results.

2. Theoretical Concepts

2.1. General Procedures. In a region sufficiently far away from the critical point polymer blends follow the mean-field approximation.[1,2,4,6-9] In this concept the Gibbs free enthalpy of mixing $\Delta G_M = G_{AB} - [\Phi G_A + (1 - \Phi)G_B]$ is given by

$$\frac{\Delta G}{RT} = \frac{\Phi}{V_A} \ln \Phi + \frac{(1 - \Phi)}{V_B} \ln (1 - \Phi) + \Phi(1 - \Phi)\chi \quad (1)$$

Φ is the volume fraction of component A, V_A and V_B are the molecular volumes of polymers A and B, respectively, R is the gas constant, and χ is the Flory–Huggins

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interaction parameter, a segmental quantity not depending on V_A and V_B for sufficiently large molecules.[11]

In the limit where the scattering vector Q is zero, the reciprocal structure factor for scattering on the polymer blend is given by

$$S^{-1}(0) = \frac{\partial^2(\Delta G/RT)}{\partial\Phi^2} \qquad (2)$$

By expanding the results of the random-phase approximation (RPA)[10] for the structure factor of a polymer blend up to the power Q^2, one yields the well-known Ornstein–Zernike form for the structure factor, known as the Zimm approximation in polymer physics, namely

$$S^{-1}(Q) = S^{-1}(0) + AQ^2 \qquad (3)$$

with $A = {}^1/_3(R_{gA}{}^2/\Phi V_A + R_{gB}{}^2/(1-\Phi)V_B)$. In this equation $R_{gA,B}$ are the radii of gyration of the two polymer species. The expansion up to Q^2 holds as long as $QR_g \leq 1$, which is a valid assumption in our experiments. Combining eqs 1 and 2, one obtains

$$S^{-1}(0) = 2(\Gamma_s - \Gamma) \qquad (4)$$

with $\Gamma_s = {}^1/_2(1/\Phi V_A + 1/(1-\Phi)V_B)$. Γ is the generalized Flory–Huggins parameter that is related to χ by

$$\Gamma = -\frac{1}{2}\frac{\partial^2}{\partial\Phi^2}(\Phi(1-\Phi)\chi) \qquad (5)$$

For the case of the original Flory–Huggins theory (where χ should be Φ-independent) one has $\Gamma = \chi$. Thus measuring the reciprocal forward scattering density in a SANS experiment and knowing V_A and V_B, one finds the value of Γ.

In general, Γ depends on T, Φ, and p and can be written as[2,3,6,7]

$$\Gamma(T,\Phi,p) = \frac{\Gamma_h(T,\Phi,p)}{T} - \Gamma_\sigma(T,\Phi,p) \qquad (6)$$

Γ_h is considered as the part of the Flory–Huggins parameter related to the enthalpy of mixing, whereas Γ_σ means the local or segmental entropic contribution. If Γ_σ is correlated to the free volume of the blend, an increase of pressure reduces the free volume and thus leads to a decrease of the absolute value of Γ_σ. By calculations based on equation of state arguments, Patterson and Robard[20] showed that Γ_h is not pressure dependent, whereas $|\Gamma_\sigma|$ is actually a decreasing function of pressure. Recently, for a PS-b-PMMA melt Dudowicz and Freed[21] found a decrease in $|\Gamma_\sigma|$ with an increase of pressure from lattice cluster theory, whereas Γ_h is affected only weakly.

2.2. Equations of State. Many attempts were made to derive the equation of state.[14-19] In polymer physics one of the most widely used equations of state is the Flory–Orwoll–Vrij (FOV)[12,13] equation which reads

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \qquad (7)$$

$\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are reduced quantities. p, v, and T are expressed by these reduced quantities, namely, $\tilde{p} = p/p^*$, $\tilde{v} = v/v^*$, and $T = T/T^*$ with the hard-core or reduction parameters p^*, v^*, and T^*.

By fitting the equation of state to measured pVT data, one obtains p^*, v^*, and T^* as fit parameters. For a given equation of state these parameters are characteristic for a certain blend. The ansatz for the free enthalpy is obtained by the relation $G = -kT \ln Z$ from the knowledge of the corresponding partition function Z. The expression for the free enthalpy of the two compounds A and B is then compared with eq 1. From this expression the Flory–Huggins parameter χ can be extracted and be calculated with the known characteristic parameters p^*, v^*, and T^*. Thus a comparison with the SANS results is possible. In analogy to eq 6 we write χ as

$$\chi = \chi_h/T - \chi_\sigma \qquad (8)$$

with an interaction energy χ_h and a segmental entropy χ_σ, related to the free volume of the blend. Combining eqs 1 and 7, the FOV ansatz for χ_h and χ_σ leads to[22]

$$\chi_h(\Phi,p) = \frac{v^*}{\bar{V}_w R}\left(\frac{X_{12}}{\tilde{v}} + \frac{p_1{}^*}{(1-\Phi)}\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \frac{p_2{}^*}{\Phi}\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right)\right) \qquad (9)$$

$$\chi_\sigma(\Phi,p) = -\frac{v^*}{\bar{V}_w R}\left(\frac{3p_1{}^*}{T_1{}^*(1-\Phi)} \ln\frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{3p_2{}^*}{T_2{}^*\Phi} \ln\frac{\tilde{v}_2{}^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) \qquad (10)$$

$\bar{V}_w = (V_A V_B)^{1/2}$ is the average molecular volume of the blend and X_{12} is an interaction term given by

$$X_{12} = \frac{\Phi p_1{}^* + (1-\Phi)p_2{}^* - p^*}{\Phi(1-\Phi)} \qquad (11)$$

In order to obtain eqs 9 and 10 the enthalpic and the entropic terms, χ_h and χ_σ, were evaluated from χ by the relations $\chi_h = \partial\chi/\partial(1/T)$ and $\chi_\sigma = -\partial(T\chi)/\partial T$.[23] Thus they also contain the implicit temperature dependence of the reduced volumes $\tilde{v}_i$ and $\tilde{v}$. However, from our analysis of the pVT data we found χ to be a linear function of $1/T$. This implies that the implicit temperature dependence of the reduced volumes is so weak that it can be neglected, and χ_h and χ_σ can be treated as temperature independent. After extracting p^*, v^*, and T^* for the individual components and for the blend from the measured pVT data, the equation of state is known for the components and for the blend. In particular, the pVT data yield the reduced volumes $\tilde{v}_A$ and $\tilde{v}_B$ (single components) and $\tilde{v}$ (blend), which are needed to find χ_h and χ_σ.

The pressure dependence of χ_h and of χ_σ is included in the reduced volumes and determined by the equation of state (eq 7). From eq 9 we recognize that the interaction term X_{12} is diminished if $\tilde{v} > 1$, i.e., if the model includes free volume. Physically this results from the fact that the average intermolecular distances increase by the presence of free volume. The other contributions in eq 9, are governed by the difference of the reciprocal reduced volumes of the single components and the blend. The expression for χ_σ (eq 10) is dominated by the logarithm of the ratios $\tilde{v}_i{}^{1/3} - 1$ and $\tilde{v}^{1/3} - 1$. For a LCST blend χ_σ is negative because the sum of both logarithms is positive.

We finally point out that the equation of state formalism yields χ not Γ, as obtained from SANS, i.e., from $S^{-1}(0)$. To evaluate Γ, one had to include the Φ dependence of χ. Consequently, we can only compare Γ from SANS with χ from the FOV equation of state. From our former experiments[2,8] we know that the ratios Γ_h/χ_h and $\Gamma_\sigma/\chi_\sigma$ have values between 0.8 and 1 in a broad concentration range, such that a comparison of Γ and χ is supposed to be a good approximation in a restricted range of Φ.

3. Experimental Section

The neutron scattering experiments have been performed at the small-angle scattering facility at the DR3 reactor at the Risø National Laboratory, Roskilde, Denmark. For these experiments

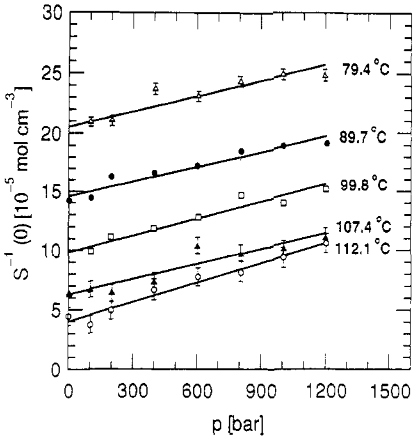

Figure 1. Reciprocal forward scattering $S^{-1}(Q)$ for $Q \rightarrow 0$ vs pressure at different temperatures for the blend d-PS/PVME measured by SANS.

Table I. Sample Characteristics

blend	comp A	comp B	type	V_A (cm^3 mol^{-1})	u_A	V_B (cm^3 mol^{-1})	u_B
1	d-PS	PPMS	UCST	8800	1.03	2200	1.39
2	d-PS	PVME	LCST	870 000	1.14	63 000	1.98

a special steel-bodied pressure cell was constructed.[24] The specimen was fixed within an O-ring between two sapphire or niobium windows depending on the pressure required. A mechanical pressure generator was obtained from NOVA SWISS (Effretikon, Switzerland). The pressure was transmitted via a hydraulic liquid medium onto the sample and was measured with a transducer obtained from BURSTER, Gernsbach, FRG (type 81SG3), which was controlled during the experiments with a calibrated conventional manometer. The scattering data were corrected for background and calibrated in absolute units by a Lupolen standard to obtain $S(Q)$.[8] The pVT measurements were performed with a Gnomix pVT apparatus at the Max-Planck-Institut für Polymerforschung, Mainz, FRG. Changes in the specific volume of 1-g samples were measured for various temperatures isothermally as a function of pressure up to p = 1000 bar.

4. Results and Discussion

4.1. SANS Results. The characteristic data for the two polymer blends used in this work are summarized in Table I. In both cases the experiments have been performed at the critical composition which was $\Phi_{\text{d-PS}} = 0.31$ for d-PS/PPMS[25] and $\Phi_{\text{d-PS}} = 0.13$ for d-PS/PVME.[6] Figure 1 shows the reciprocal forward scattering intensity $S^{-1}(0)$ as a function of pressure for the d-PS/PVME blend. All five temperatures of the measurements are in the one-phase region of the phase diagram. A linear increase with pressure is observed for all temperatures. Within experimental error we obtained the same slope for all temperatures, i.e., $\Delta S^{-1}(0)/\Delta p = (4.72 \pm 0.25) \times 10^{-8}$ mol cm^{-3} bar^{-1}. Table II presents the values for all investigated temperatures.

The slope A of the Zimm plots (eq 3) shows a slight linear decrease with pressure exhibiting a decrease of the radius of gyration R_g, namely, $R_g^2 = {}^1/_6 N_k \sigma_k^2 = {}^1/_6 L \sigma_k$, where σ_k and N_k is the length and the number of the effective segments (Kuhn segments), respectively. L is the contour length of the molecule, which supposedly does not depend on pressure. Affine compression reduces σ_k. This will be the subject of a further investigation.[26]

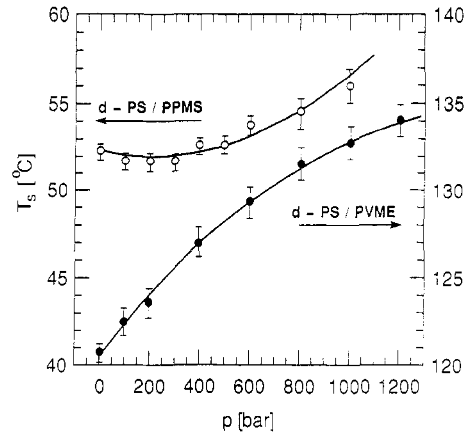

Figure 2. Spinodal temperature as a function of pressure for both investigated polymer blends extrapolated from the SANS data: d-PS/PPMS (left); d-PS/PVME (right).

Figure 2 shows the effect of pressure on the spinodal phase boundary. The spinodal temperature T_S for each pressure was determined by extrapolation of the reciprocal forward scattering as a function of $1/T$ for $S^{-1}(0) \rightarrow 0$. In both cases T_S rises with increasing pressures. For d-PS/PVME T_S increases as $\sim 1.2 \times 10^{-2}$ K bar^{-1}, and for d-PS/PPMS it increases as $\sim 4.3 \times 10^{-3}$ K bar^{-1}. Thus for the UCST blend the range of the two-phase region of the phase diagram increases with pressure, whereas for the LCST blend the one-phase region widens; i.e., the tendency for decomposition gets weaker, because of the respective decrease and increase of the segmental entropy Γ_σ. For d-PS/PVME the spinodal temperature increases over the whole pressure range, with a saturation beginning at ~1000 bar. On the other hand, for d-PS/PPMS T_S first drops slightly to a minimum at ~200 bar before increasing. This behavior was also found by Ougizawa et al.[27] for a PS/PPMA blend from the temperature and pressure dependence of the excess volume of mixing with the use of the FOV equation of state. The solid lines in the diagram are both fits with a second-order polynomial.

The results for the d-PS/PVME system are in good quantitative agreement with could-point measurements of Hiramatsu et al.,[28] who found a linear increase of T_S of $\sim(1-3) \times 10^{-2}$ K bar^{-1} depending on the volume fraction. In contrast to these experimental results Patterson et al.[20] theoretically predicted a value of $\sim 1.3 \times 10^{-1}$ K bar^{-1} which is an order of magnitude too large. They used equation of state parameters from McMaster.[29]

Figures 3 and 4 show separately the enthalpic and the entropic contributions of the generalized Flory–Huggins parameter Γ as a function of p. Obviously, the enthalpic interaction term Γ_h is not influenced by the pressure within the experimental error of ~3% and remains constant at least for pressures up to 600 bar for d-PS/PPMS and 1200 bar for d-PS/PVME. This agrees with the result of Patterson's calculation.[20] Consequently, changes in the Flory–Huggins parameter could only follow from changes in the entropic contribution that we have related to the free volume of the blend. Figure 4 shows that the absolute value of Γ_σ generally decreases with p for both blends, which is consistent with the assumption of a diminishing free volume for increasing pressure. Nevertheless, there are differences in the pressure dependence of Γ_σ for the two blends. For d-PS/PVME the absolute value of Γ_σ

Table II. Slope of $S^{-1}(Q)$, $Q \rightarrow 0$

	T = 79.4 °C	T = 89.7 °C	T = 99.8 °C	T = 107.4 °C	T = 112.1 °C
$\Delta S^{-1}(0)/\Delta p$ (10^{-8} mol/cm^3 bar)	4.36 ± 0.40	4.41 ± 0.31	4.88 ± 0.24	4.38 ± 0.44	5.55 ± 0.73

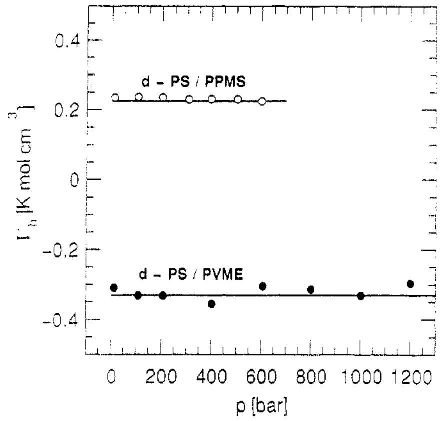

Figure 3. Enthalpic contributions Γ_h to the Flory–Huggins parameter as obtained from SANS. Within statistical error it exhibits no pressure dependence.

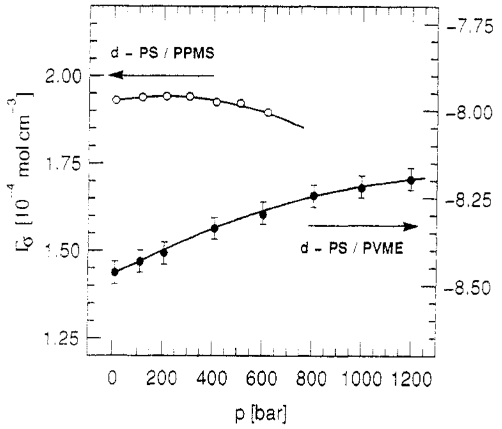

Figure 4. Same as Figure 3 for the entropic contributions Γ_σ. For d-PS/PVME this quantity decreases over the whole pressure range, while it passes a maximum at 200 bar for d-PS/PPMS.

decreases in the whole pressure range and shows saturation at higher pressure, as was also found for the spinodal temperature. For d-PS/PPMS $|\Gamma_\sigma|$ passes a shallow maximum at 200 bar and then decreases continuously. Again the solid lines represent parabolic fits to the experimental data. The change of $|\Gamma_\sigma|$ is as high as $\sim 1 \times 10^{-4}$ bar^{-1} for d-PS/PPMS and $\sim 5 \times 10^{-4}$ bar^{-1} for d-PS/PVME.

To summarize, the value of Γ *decreases* for the LCST blend ($\Gamma_h > 0$, $\Gamma_\sigma > 0$), whereas for the UCST blend ($\Gamma_h < 0$, $\Gamma_\sigma < 0$) Γ increases with rising pressures. In the following paragraph we compare these SANS data for the d-PS/PPMS blend and the predictions of the FOV equation of state theory.

4.2. *pVT* Data. *pVT* data for the d-PS/PPMS blend and for its components have been measured in the pressure range 1–1000 bar isothermally for various temperatures. Figure 5 shows typical results for the pure PPMS component, together with the simultaneous fit of the data sets for five different temperatures (solid curves) by the FOV equation of state (eq 7). From the fitting procedure the reduced parameters p^*, v^*, T^* of the FOV model were obtained. They are shown in Table III. By applying the method described in Chapter 2, these evaluated parameters were used to calculate the expression for χ_h (eq 9) and χ_σ (eq 10) at various temperatures and pressures.

In Figures 6 and 7 the results are compared with the SANS measurements presented in absolute units. One should be aware that the SANS experiments yield Γ_h and Γ_σ, whereas the equation of state yields χ_h and χ_σ (see Chapter 2). Looking at the enthalpic contribution, one finds a discrepancy of a factor 1.7 for the absolute value.

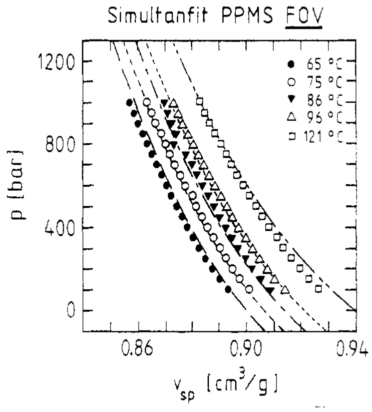

Figure 5. Pressure as a function of the specific volume for five temperatures for the single PPMS component (*pVT* data). The dashed lines represent the simultaneous fit of the data with the FOV equation of state. The estimated reduction parameters are summarized in Table III.

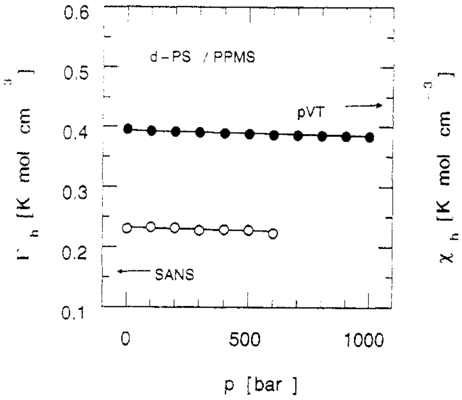

Figure 6. Interaction terms Γ_h from SANS and χ_h from the equation of state versus pressure.

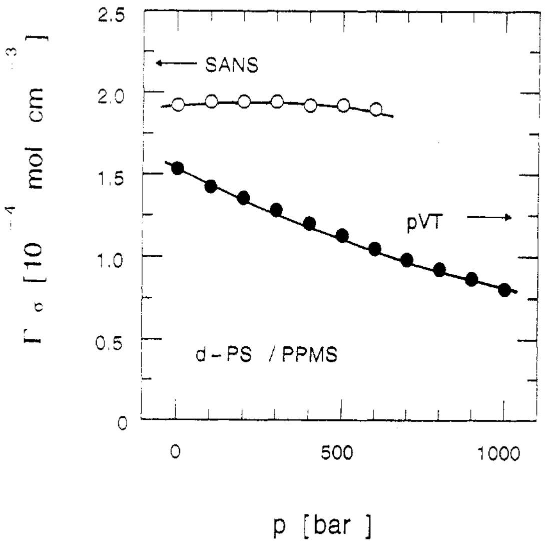

Figure 7. Same as Figure 6 for the entropic contributions Γ_σ and χ_σ, respectively.

Table III. Characteristic Parameters of the Equation of State

	p^* (bar)	T^* (K)	v^* (cm^3 g^{-1})
d-PS	4257	10235	0.7999
PPMS	5391	6609	0.7426
d-PS/PPMS	4540	7055	0.7561

The very small linear pressure dependence of the equation of state result is obtained for Γ_h and χ_h as well. Nevertheless, the slope zero is within the experimental errors of Γ_h.

Comparing the entropic parts Γ_σ and χ_σ (Figure 7), one also obtains a discrepancy of a factor 2 in the absolute values, but in contrast to the enthalpic contribution, here the general trends in the pressure dependence are different. The maximum visible in Γ_σ does not appear in χ_σ, which shows an almost linear decrease. In addition the decrease with pressure of χ_σ is a factor 5 stronger than Γ_σ.

As already mentioned at the end of Chapter 2 the direct measurement of Γ by SANS is the more reliable one, as compared to the more indirect measurement via the *pVT* data and the equation of state formalism. We believe that the discrepancies between $\Gamma(p)$ and $\chi(p)$ (as concerns the absolute values) and trends in the case of the entropic parts are not predominantly caused by inconsistencies in Γ but more by effects not considered in the FOV equation of state. The values of Γ are reliable insofar as the separation of ΔG into a segmental and an entropic contribution (as in eq 1) is well established. This can be seen from experiments by Schwahn et al.[2] where, for instance, the spinodals for the same polymer blend with a different degree of polymerization can be described with the same Flory–Huggins interaction parameter.

5. Conclusions

The generalized Flory–Huggins interaction parameter Γ was measured as a function of pressure and temperature by SANS for the two polymer blends d-PS/PPMS (UCST) and d-PS/PVME (LCST). *pVT* data of d-PS/PPMS were used to evaluate the prediction of the well-known FOV equation of state with respect to the Flory–Huggins parameter χ.

By small-angle neutron scattering it could be shown that for pressures up to 1200 bar the enthalpic contribution Γ_h is not affected by p, as predicted by Patterson et al.[20] The absolute value of Γ_σ is a decreasing function of pressure. Expectedly, this decrease results from its relation to the free volume of the blend, which decreases at rising pressure.

On the other hand, the tentative comparison with predictions of the FOV equation of state evaluated from *pVT* data shows a discrepancy by a factor of 1.7, but it agrees insofar that there is no pressure dependence of the enthalpic contribution. However, the entropic contributions show a qualitatively different behavior, which is not yet understood.

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