Macromolecules **1995,** *28,* 2555–2560

Coil and Melt Compressibility of Polymer Blends Studied by SANS and *pVT* Experiments

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Received September 9, 1994; Revised Manuscript Received January 9, 1995[⊗]

ABSTRACT: The average radius of gyration R_g for the isotopic blend deuteropolystyrene/polystyrene (d-PS/PS) and for the blends deuteriopolystyrene/poly(vinyl methyl ether) (d-PS/PVME) and deuteropolystyrene/poly(phenylmethylsiloxane) (d-PS/PPMS) has been measured by SANS experiments as a function of temperature (T) and pressure (p) up to 1.2 kbar. Furthermore, the specific volume as a function of p and T has been measured. The resulting compressibilities $\beta_V = -(1/V)(\partial V/\partial p)$ and the compressibility of the radius of gyration, $\beta_{R_g} = -(3/R_g)(\partial R_g/\partial p)$, were compared. For d-PS/PS the following were found: (i) For $T > T_g$ (T_g = glass temperature) R_g changes with pressure less than the macroscopic sample dimensions ($\beta_{R_g} < \beta_V$), whereas β_{R_g} decreases with increasing temperature. (ii) At T_g geometrical affinity is approached ($\beta_{R_g} \approx \beta_V$). (iii) Below T_g there is still an increase of the ratio between β_{R_g} and β_V. This implies that in the glassy regime the polymer chain seems still to be mobile on a "local" scale. Thus, in general, it is concluded that the "matrix effect" in the chain is relatively small both above and below T_g. The value of the temperature coefficient $\kappa = \partial \ln(R_g{}^2)/\partial T < 0$ is consistent with detailed calculations of Yoon et al. For the other blends, where the temperatures are far above T_g, the compressibilities β_V and β_{R_g} differ strongly and the change of their values with temperature is small.

1. Introduction

Flory's argument[1,2] that a polymeric chain in a melt has the same radius of gyration R_g as a random coil in a completely noninteracting environment, i.e., in a Θ-solvent, was experimentally confirmed for the first time by the pioneering SANS studies of Kirste et al.[3] and Cotton et al.[4] Many SANS experiments have been performed so far on polymer solutions and melts under different conditions (see, e.g., ref 5 and references therein).

For an ideal random walk of monomers with a physical length σ one gets

$$R_g{}^2 = \sigma^2 N/6 \qquad (1)$$

where N is the degree of polymerization. Actually, the hindrance potential between monomers in the chain leads to correlations between mutual monomer orientations. This normally tends to an increase of R_g, such that

$$R_g{}^2 = c_N(T,p)\sigma^2 N/6 \qquad (2)$$

where $c_N > 1$ depends on N, temperature T, and density or pressure p. Several temperature-dependent experiments in melts were carried out and $R_g(T)$ or its temperature coefficient

$$\kappa = \partial \ln(R_g{}^2)/\partial T \qquad (3)$$

was measured and compared with the RIS model of Flory which takes the orientational interactions into account.[1] Many SANS and intrinsic viscosity experiments have been carried out on the determination of κ (e.g., refs 6–9). The observed κ values are always negative except for atactic PEE, since typically an increase of temperature favors the population of coiling configurations.

So far, there exist two pressure-dependent SANS studies on polymer blends, namely, our previous[10] and still unpublished work.[11] Both mainly focus on the pressure dependence of the Flory–Huggins interaction parameter χ obtained from the extrapolated scattering intensity for scattering vector $Q \to 0$. In the recent work of Hammouda et al.[11] the authors additionally found a downward trend of the Zimm plot slope ($S^{-1}(Q)$ vs Q^2) (see section 2) with increasing pressure, related to a shrinking of the chain dimensions under pressure.

In connection with our previous measurements[10] we have systematically investigated the pressure dependence of the radius of gyration for pressures up to p = 1.2 kbar by SANS. We have most intensively studied the isotopic blend deuteropolystyrene/polystyrene (d-PS/PS)[12] where the interaction parameter χ is especially small. For this system the pressure dependence of the two isotopic components is supposed to be very similar, which simplifies the interpretation. For the two other blends investigated, namely, deuteropolystyrene/poly(vinyl methyl ether) (d-PS/PVME) and deuteropolystyrene/poly(phenylmethylsiloxane) (d-PS/PPMS), the situation is more involved. Here the measured R_g is an average over the two species, and the Flory–Huggins parameter χ is not negligible. We report these results but even a qualitative interpretation is impossible and detailed computer simulations are needed.

In addition to our SANS measurements of $R_g(p,T)$ we also determined the pressure and temperature-dependent specific volumes, i.e., the *pVT* properties of these blends (for an overview, see refs 13 and 14). The resulting compressibility

$$\beta_V = -\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right) \qquad (4)$$

was then compared with the coil compressibility, which we defined as

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

0024-9297/95/2228-2555$09.00/0

$$\beta_{R_g} = -\frac{3}{R_g}\left(\frac{\partial R_g}{\partial p}\right) \qquad (5)$$

Assuming that the polymeric coil is rigidly embedded in its environment, the deformation of the coil should follow the macroscopic deformation of the sample, like a steel string embedded in a block of rubber; this yields geometrical affinity, which means $\beta_{R_g} = \beta_V$ (strong "matrix packing" effect). In the extreme opposite case, we could assume that a chain keeps its entropy and conformation independently of volume compression. This would lead to $\beta_{R_g} \ll \beta_V$ (R_g is "underaffine").

In section 2 the theoretical concept of the evaluation of the SANS experiments is presented. The SANS and the *pVT* experiments and their results are shown in sections 3 and 4, whereas in section 5 the discussion is presented.

2. Theoretical Concepts

The scattering of a blend is described by the structure factor $S(Q)$ for small-angle neutron scattering (SANS), where Q is the scattering vector or the wave vector of the concentration fluctuations in the blend. $S(Q)$ can be calculated by the random phase approximation (RPA),[15] which is expected to hold sufficiently far from the critical temperature T_c corresponding to R_g values large compared to the correlation length of critical fluctations ξ. By expanding the result of the RPA, we obtain the Zimm approximation for the inverse structure factor

$$S^{-1}(Q) = S^{-1}(0) + AQ^2 \qquad (6)$$

The quantity $S^{-1}(0)$ is related to the Gibbs free energy of mixing ΔG^m by

$$S^{-1}(0) = \frac{\partial^2\left(\frac{\Delta G^m}{RT}\right)}{\partial\Phi^2} \qquad (7)$$

$S(0)$ depends on the Flory–Huggins interaction parameter and the degree of polymerization N. The slope of the Zimm plot A is connected with the geometrical properties of the coil by the equation

$$A = \frac{1}{18}\left(\frac{c_{N1}\sigma_1^{\,2}}{\Phi\Omega_1} + \frac{c_{N2}\sigma_2^{\,2}}{(1-\Phi)\Omega_2}\right) = \frac{1}{3}\left(\frac{R_{g1}^{\,2}}{\Phi V_1} + \frac{R_{g2}^{\,2}}{(1-\Phi)V_2}\right) \qquad (8)$$

where Ω_i is the monomer volume and $V_i = N_i\Omega_i$ is the molecular volume (i = 1 or 2). Φ is the volume fraction of component 1. Thus, from the scattering experiments, genuinely the ratio $c_{Ni}\sigma_i^2/\Omega_i$ is obtained. With the knowledge of the molecular volume $\bar{V}$ from GPC measurements, an effective radius of gyration

$$R_g^{\,2} = 3\Phi(1-\Phi)\bar{V}A \qquad (9)$$

can be calculated with the average molecular volume $\bar{V} = [(1-\Phi)/V_1 + \Phi/V_2]^{-1}$. In our diagrams R_g is presented as obtained from the values of V_i or $\bar{V}$ in Table 1. In the following we maintain the symbol R_g for the average value. Equation 8 is valid for short-range interaction only. If the interation is of longer range (r_0), the Flory–Huggins parameter χ is Q-dependent. This leads to an additional square term $Q^2r_0^{\,2}\chi(T)$ which may cause a T-dependence of the slope A.[16] In all our measurements this effect was not observed and thus neglected.

Table 1. Sample Characteristics

blend	comp 1	comp 2	type	V_1 [cm^3/mol]	u_1	V_2 [cm^3/mol]	u_2	$\Phi_c = \Phi_1$
1	d-PS	PS	UCST	10200	1.05	9050	1.06	0.50
2	d-PS	PPMS	UCST	8800	1.03	2200	1.39	0.31
3	d-PS	PVME	LCST	870000	1.14	63000	1.98	0.13

Obviously, eq 8 shows that there could be a pressure dependence in A, because the densities of the two components of the blend, e.g., Ω, are affected. For the isotopic blend this effect can be corrected, because the deuteration does not significantly influence the compressibility such that the denominators in eq 8 change with pressure in the same proportion. This is not necessarily so for the chemically different components. However, the relative changes of the sample volume with pressure (≈4–6%/kbar) are very similar.[17,18] Therefore, a different compressibility of the components is also negligible in these cases.

A model of the freely jointed chain implies fixed valence angles Φ between subsequent monomer bonds and variable bond rotational angles Θ. For the simplest cases, e.g., for polyethylene, the angular dependence of the conformational energy, i.e., the bond rotation potential $V(\Theta)$, reveals three minima. They correspond to the conformational states trans (lowest energy, Θ = 0°), gauche$^-$ (Θ = −120°), and gauche$^+$ (Θ = +120°). The energy barrier between the trans and gauche states is of the order of kT. Therefore, at room temperature both conformational energy levels are occupied, leading to a flexible Gaussian coil. In the following qualitative interpretation we maintain this trans/gauche model for simplicity, which implies only one activation energy.[23]

3. Experiments

The SANS experiments were performed at the DR3 reactor at the Risø National Laboratory, Denmark. A special steel-bodied pressure cell was constructed, which allows for the in situ change of pressure and temperature in the range 1 bar < p < 1200 bar and 20 °C < T < 200 °C, respectively. The design of the cell has been described elsewhere.[10] The SANS data were corrected for background and calibrated in absolute units by a Lupolen standard. Pressure increases the scattering length density in the sample, with a constant thickness given by the distance of the windows of the pressure cell (niobium or sapphire). For d-PS/PPMS and d-PS/PVME the increase of scattering contrast due to the pressure is canceled within ≈2% by a decrease of sample transmission. Therefore, the product of both which enters the calibration factor is practically constant. The measurements on d-PS/PS were corrected for this effect by normalizing on the scattering signal for $Q \to 0$ neglecting χ.

Consistency was obtained by the fact that the raw data signal for d–PS/PS did not increase more than 2% for pressure changes up to p = 1000 bar. Figure 1 shows typical Zimm plots of our data for different temperatures and pressures.

The *pVT* data were otained from a Gnomix *pVT* apparatus at the Max-Planck-Institut für Polymerforschung, Mainz, FRG. Here, the dilatation and the contraction of a flexible metal bellows serves to measure volume changes of the sample located in a piezometer cell. The experiments covered the same range of p and T as the SANS experiments.

The system d-PS/PPMS was prepared without solvent. Mixing was obtained by mechanical stirring of the two molten components. The two systems d–PS/PS and d-PS/PVME were prepared by solution mixing. Afterwards the solvent was evaporated for several days under an argon atmosphere (d-PS/PVME) or the system was freeze-dried (d-PS/PS). The

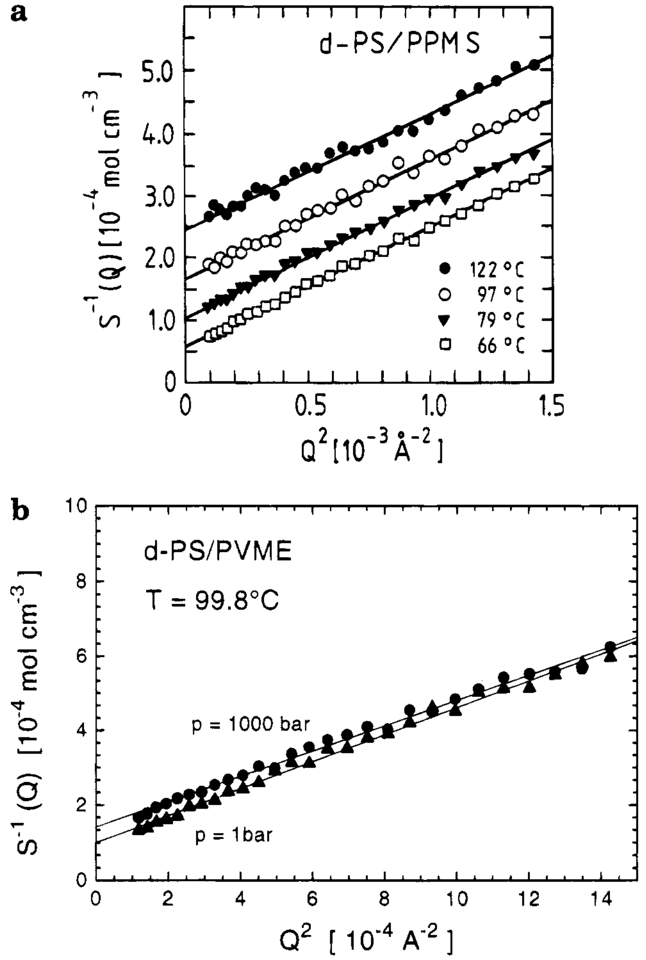

Figure 1. Typical Zimm plots of SANS data for various temperatures and pressures: (a) d-PS/PPMS at four temperatures $T = 122$, 97, 79, and 66 °C and pressure $p = 1$ bar; (b) d-PS/PVME for $p = 1$ bar and $p = 1000$ bar and temperature $T = 99.8$ °C.

characteristic data for three different polymer blends are summarized in Table 1.

4. Experimental Results

We first discuss the pressure dependence of the coil conformation in the isotopic polystyrene blend d-PS/PS. This system exhibits upper critical solution temperature (UCST) behavior[12] with demixing at low temperatures. We have chosen a symmetric system with a molecular volume of $V_w \approx 1 \times 10^4$ cm^3/mol. Due to the relatively short chain length and consequently the large distance to the critical point of demixing, the Flory–Huggins interaction parameter χ reaches values of only ≈1% of the critical value $\chi_c = 2/N \approx 0.02$ in the temperature range of our experiments (80–175 °C). χ was taken from previous SANS experiments[12] on d-PS/PS with a very large V_w of ≈1 × 10^6 cm^3/mol. Therefore the interaction is small and the blend is almost an ideal mixture. From differential scanning calorimetry (DSC) measurements a single glass transition temperature T_g = 86 °C is obtained for the blend at $\Phi = 0.5$.

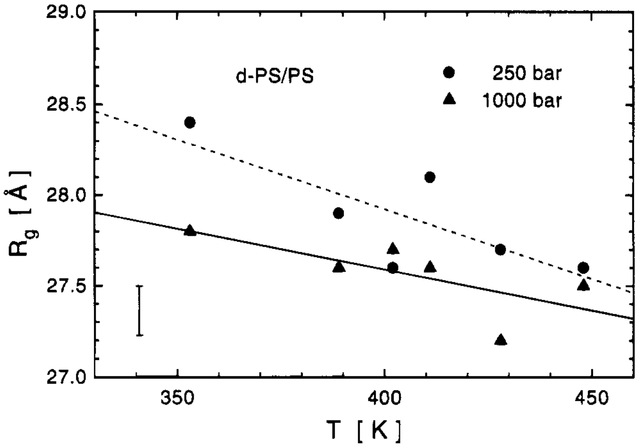

Figure 2. Radius of gyration R_g as a function of temperature T for d-PS/PS from the SANS experiment: circles, 250 bar; triangles, 1000 bar.

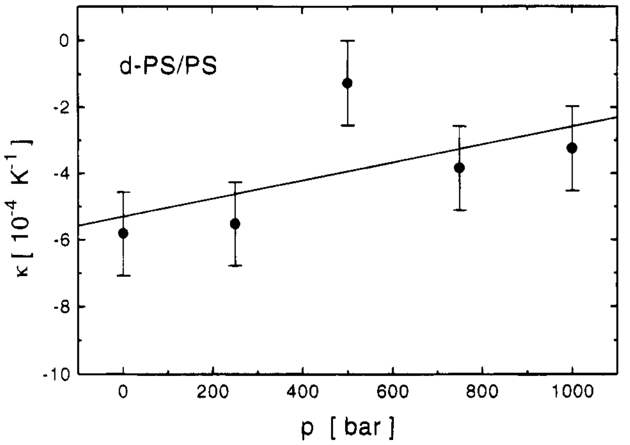

Figure 3. Temperature coefficient κ as a function of pressure p for the isotopic blend. Within the statistical error $|\kappa|$ decreases linearly with p.

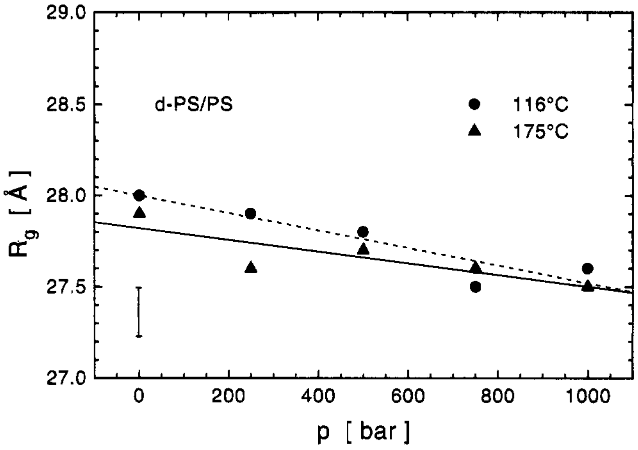

Figure 4. SANS result for R_g vs pressure for d-PS/PS: circles, 116 °C; triangles, 175 °C.

Figure 2 shows the SANS result for the temperature dependence of R_g for two pressures. In total this effect has been studied for the pressures p = 1, 250, ..., 1000 bar. Within experimental error one obtains a linear decrease of R_g with temperature. The statistical error is shown in the figure. By raising the pressure the temperature dependence of R_g gets weaker, which can also be seen from the pressure dependence of κ. This quantity is plotted in Figure 3. For p = 1 bar we obtain $\kappa = (-5.8 \pm 1.3) \times 10^{-4}\ \mathrm{K}^{-1}$. The relatively small error of κ arises from the fact that, for the calculation of κ, six experimental points contribute for each pressure. In Figure 4 our SANS result for the pressure dependence of R_g is presented. Only the data at two temperatures are plotted. As for the temperature dependence (Figure 2), an increase of pressure also leads to a decrease of R_g.

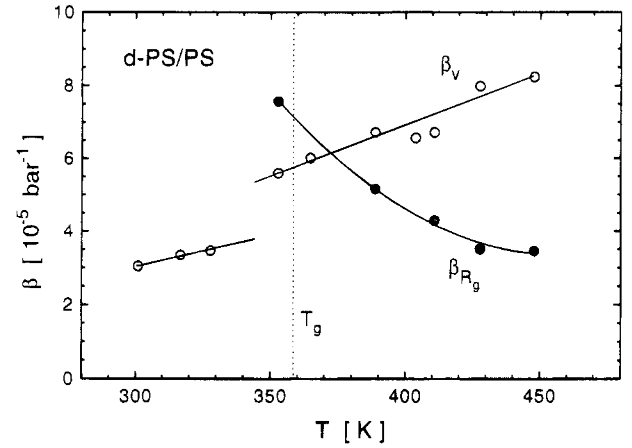

Figure 5. Comparison between the compressibility of the chain β_{R_g} (filled circles) and of the total volume β_V (open circles) as a function of temperature. The glass transition for $p = 1$ bar occurs at ≈359 K.

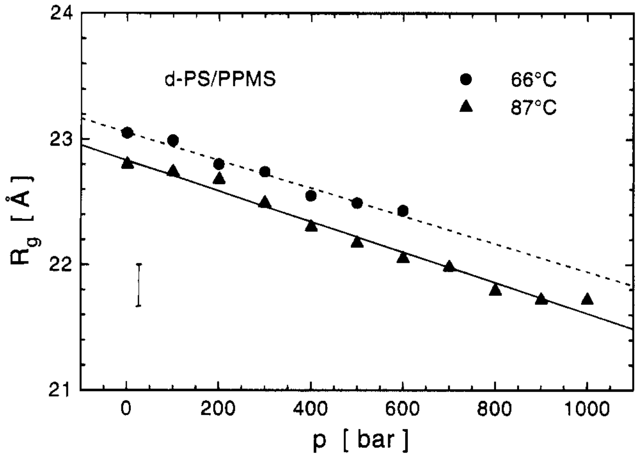

Figure 6. Pressure dependence of R_g at two temperatures for d-PS/PPMS. As for the isotopic blend a linear decrease with pressure is obtained. The bar indicates only statistical error.

In a pVT experiment the specific volume v of the isotopic blend was measured isothermally as a function of pressure up to $p = 1200$ bar. Our measurement of v as a function of p and T is consistent with the detailed measurements of Ougizawa et al.[19] on a pure PS melt. The curves reveal a kink of $v(T)$ around T_g (see Discussion). As in the work of Ougizawa et al., a plateau between $T_g \pm 20$ K for high pressures is observed, which is not yet understood. To our knowledge this effect has not been observed for other blends. From the pVT data the compressibility of the sample volume β_V can be extracted and compared with the compressibility of the chain β_{R_g} as taken from the Zimm plots. Both quantities are plotted in Figure 5. In the whole T-range β_V increases with T. Close to $T_g = 359$ K a step in β_V is observed. The slope $\beta_V(T)$ is larger above than below T_g, consistent with the higher slope of $v(T)$ for $T > T_g$ from the pVT data. On the other hand, the chain compressibility β_{R_g} decreases with rising T. Close to T_g both compressibilities are roughly equal. Above T_g we find $\beta_V > \beta_{R_g}$, whereas below T_g we have one experimental point only which indicates a still higher chain than volume compressibility.

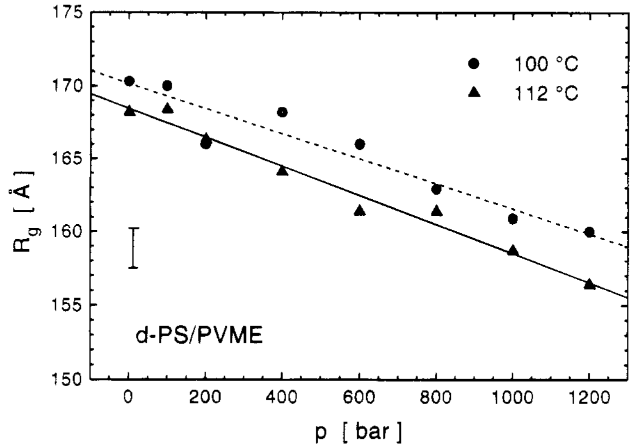

Figure 7. Same as Figure 6 for d-PS/PVME.

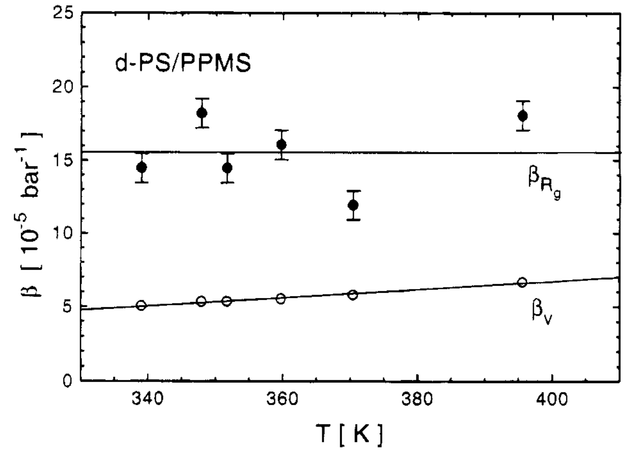

Figure 8. Temperature dependence of compressibilities β_{R_g} and β_V for d-PS/PPMS. β_{R_g} is temperature independent within the experimental error. $\beta_{R_g} > \beta_V$ is obtained for all temperatures.

Figures 6 and 7 show the pressure dependence of R_g for the two polymer blends with chemically different components, namely, d-PS/PPMS and d-PS/PVME, at two temperatures. As for the isotopic blend, the whole studied temperature range was located within the homogeneous one-phase region of the respective phase diagrams. All the temperatures were far above the glass temperature ($T_g \approx 10$ °C for d-PS/PPMS and $T_g \approx -10$ °C for d-PS/PVME). As already observed for the isotopic blend, the pressure-dependent SANS data exhibit a linear decrease of R_g as a function of p. Quantitatively, the pressure dependencies of R_g are stronger by a factor 2–3 compared to the isotopic blend. Therefore, we find larger chain compressibilities β_{R_g} for these two systems. Figures 8 and 9 compare the compressibilities as a function of temperature. In both cases the volume compressibility β_V increases with temperature. The slope $\Delta\beta_V/\Delta T$ is roughly the same as for the isotopic blend. However, no temperature dependence of the chain compressibility is observed in this case. Within the experimental error, β_{R_g} seems to be roughly constant as indicated by solid lines, representing the mean value of the points. Surprisingly, in both cases and for *all* temperatures, $\beta_V < \beta_{R_g}$ is obtained despite the fact that $T > T_g$ in the whole temperature range.

5. Discussion

We first discuss the isotopic blend d-PS/PS. Our pVT results and the detailed studies of Ougizawa et al.[19] show that the slope of the specific volume $v(T)$ vs temperature T markedly increases when the glass temperature $T_g \approx 359$ K is reached. For $T > T_g$ this is supposed to be related to a gradually "using up" of free

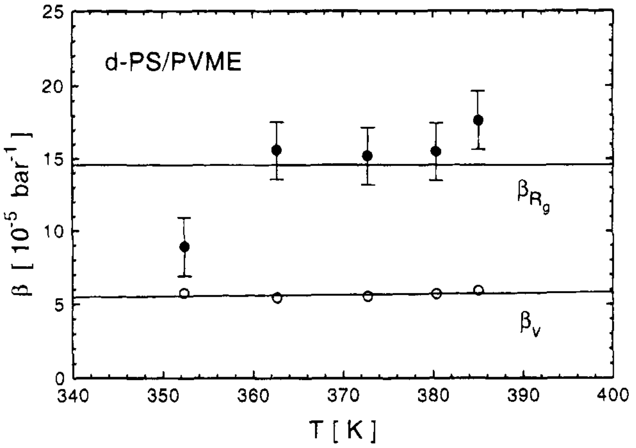

Figure 9. Same as Figure 8 for d-PS/PVME.

or packing volume in the molten state. Below T_g, however, the temperature dependence of the volume is dominated by the heat expansion as for an ordinary solid. Such a behavior was also observed for other polymers.[20-22]

The decrease of the radius of gyration R_g, or of $c_N(T)$ (eq 2) with temperature in Figure 2 can be understood by the existence of different conformational energy minima, which correspond to orientations between monomers which are gauche and trans. Following Yoon et al.,[23] we assume that the gauche conformation corresponds to a higher energy than the trans conformation. In their study based on the first rotational isomeric state (RIS) calculation for the PS chain, the authors calculate the conformational energies of two successive bond conformations. In a simplified RIS model, E_η is the activation energy describing the statistical weight of the trans relative to the gauche state. For different activation energies the values for κ are calculated. Yoon et al. obtained negative temperature coefficients κ between -2.8×10^{-4} and -15.2×10^{-4} K^{-1}. We can compare these theoretical values with our experimental result $\kappa(1\ \text{bar}) = (-5.8 \pm 1.3 \times 10^{-4}\ K^{-1}$; we obtain an activation energy of $E_\eta \approx 0.3$ kcal/mol. From intrinsic viscosity measurements on atactic polystyrene in a Θ-solvent, Kuwahara et al.[24] got $\kappa(1\ \text{bar}) = -1.0 \times 10^{-4}\ K^{-1}$. By SANS on a partly deuterated PS melt Benoit et al.[4,25] also obtained a negative κ. The increase of the population of gauche versus trans conformation leads to stronger coiling and, therefore, to the observed decrease of R_g.

Figure 5 shows that $\beta_V > \beta_{R_g}$ for temperatures above T_g. This means that a pressure increase reduces the sample size more than the coil radius. Near T_g one approximately obtains $\beta_V \approx \beta_{R_g}$, which indicates geometrical affinity for the molecule with respect to the macroscopic sample dimensions. We believe that *above* T_g the applied pressure mainly acts on the free volume.[10] The chain nearly maintains its coil radius (and also its coiling entropy), whereas the free volume (and the corresponding entropy) is diminished by pressure. This means that the coil conformation, i.e., the gauche/trans ratio, is more or less maintained, whereas only packing of the matrix is affected (see Sung et al.[26]). The only experimental point for $T < T_g$ reveals a further reduction of R_g with pressure. From neutron spin–echo measurements[27,28] it is known that near and across T_g the local or short-range motion of the polymer sections persists by the β-process with no change of activation energy, whereas the long-range motion freezes in. This β-process allows the chain to undergo still rearrangements over distances of several segment lengths σ. This could explain the observed reduction of R_g below T_g. On the other hand, this observation somehow contradicts the assumption that free volume freezes in near T_g, which is a short-range or local phenomenon as well. It cannot be excluded that the blend was not fully equilibrated for $T < T_g$ within the time scale of the experiment. However, approaching equilibrium would lead to a smaller R_g and thus an even higher chain compressibility. Unfortunately, we have only one point so far in this region and this needs further investigation. So we conclude that the "matrix effect" on chain conformation is relatively weak for $T > T_g$ and even below T_g.

As can be seen from Figure 4 and 5, R_g decreases with pressure in the whole temperature region. We tentatively assume that the external pressure diminishes the energy difference between gauche and trans, again leading to an increased coiling by the population change of gauche versus trans states. This is consistent with the observed pressure dependence of the temperature coefficient κ. If, at higher pressures, more gauche states are already occupied, the relative increase of gauche population with increasing temperature is diminished. Consequently, the temperature effect of κ should decrease with increasing pressure. So we think that both the dependency of R_g on temperature and on pressure are complementary due to a stronger population of gauche levels in the chain. For the blend d-PS/PS a temperature increase of 100 K corresponds roughly to a pressure increase of about 1 kbar.

For the sake of a theoretical interpretation we assume that there is a trans and a gauche state, where the latter allows coiling. On the basis of a two-state model we assume that the occupancy quotient of both states and therefore $c_N(\phi)$ is only a function of $\phi = E_\eta/kT$, where E_η is the energy difference between both states. The energy E_η depends on the mutual distances r of the interacting atoms in the monomers. During compression r scales as the macroscopic length. Under these assumptions the following relation between the coil and the melt compressibility and the temperature coefficient can be derived:

$$\beta_{R_g} = \frac{1}{2}\frac{\partial \ln E_\eta}{\partial \ln r} T \beta_V \kappa \qquad (10)$$

The quotient $x = \partial \ln E_\eta / \partial \ln r$ yields the power law exponent of the r-dependence of the energy difference E_η. From our experiments we obtain $x \approx -3$ for $T = 450$ K and $x \approx -5$ for $T = 400$ K. Therefore we find a weaker r-dependence of the energy difference at higher temperatures.

In contrast to the results for the isotopic blend d-PS/PS, the results for the blends with chemically different components are not even qualitatively understood. There is a linear decrease of R_g with pressure (Figures 6 and 7) as for the isotopic blend. However, as shown in Figure 8 and 9, β_{R_g} is 3 times larger than β_V, whereas for d-PS/PS the ratio β_{R_g}/β_V ranges from ≈0.4 to ≈1.3. In their recent still unpublished SANS study, Hammouda et al.[11] obtained a decrease of the Zimm plot slope A with increasing pressure for the blend d-PS/PVME. The authors mention that the nonlinear behavior of $A(p)$ is caused by the uncertainties of the extracted slope values. Nevertheless, the data exhibit an obvious tendency of the chain dimensions to shrink with pressure (Figure 6 in ref 11). The authors estimate qualitatively that from their data also $\beta_{R_g} > \beta_V$ is obtained in the complete temperature range as found in our experiments.

It is unlikely that the behavior of β_V and β_{R_g} is related to the change of the mutual interaction. Otherwise we would expect a stronger temperature dependence of β_{R_g}.

If the correlation length reaches the radius of gyration R_g the mean field approximation is no longer valid and a crossover of 3D Ising behavior occurs.[29-31] For d-PS/PS and for d-PS/PVME the measurements were carried out far away from the crossover temperature and we were safely in the mean field region.[12,31] On the other hand, for d-PS/PPMS the experiments were carried out in the Ising and in the transition region, but both d-PS/PPMS and d-PS/PVME show similar behavior of β_{R_g} as a function of T and p. So we can exclude an influence of the non-mean field behavior for d-PS/PPMS.

Acknowledgment. We thank S. Klein from the MPI für Polymerforschung, Mainz, for careful pVT measurements and M. Heiderich from our group for his technical assistance. The neutron scattering experiments were performed at the DR3 reactor at Risø National Laboratory and supported by the commission of the EC through the Large Installation Plan. Finally, we thank Dr. K. Kremer for fruitful discussions and Dr. B. Hammouda for allowing the quotation of their unpublished work.[11]

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MA9450748