Liquid/Gas and Liquid/Liquid Phase Behavior of *n*-Butane/1,4-Polybutadiene versus *n*-Butane/1,2-Polybutadiene

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ABSTRACT: Solutions of 1,4-polybutadiene (1,4-PB, 98% cis) and of 1,2-polybutadiene (1,2-PB) in *n*-butane (*n*-C_4) were studied with respect to their vapor pressure and to their demixing into two liquid phases under isochoric conditions within the temperature range from 25 to 75 °C. 1,2-PB mixes homogeneously with *n*-C_4 at any ratio, in contrast to 1,4-PB, which exhibits a miscibility gap extending from practically pure solvent to approximately 40 wt % polymer. Corresponding to these solubility differences, the vapor pressures for the system *n*-C_4/1,4-PB are considerably higher than for *n*-C_4/1,2-PB at the same concentration and temperature. The experimental results are modeled accurately and consistently by means of a modified Flory−Huggins approach accounting explicitly for chain connectivity and conformational variability of the polymers. The vapor pressures calculated by means of the Sanchez−Lacombe theory agree very well with the experimental data for both systems; this approach fails, however, in the case of the liquid/liquid phase equilibria because it predicts similar miscibility gaps for both polymers. The modified Flory−Huggins approach explains the fundamentally different solubility of 1,2-PB and 1,4-PB in terms of pronounced dissimilarities in their conformational response to dilution, which is in the case of 1,4-PB strongly impeded by the double bonds of the main chain.

1. Introduction

Despite the industrial importance of the different polybutadienes, there is only little known on their thermodynamic behavior in solution apart from an early report on the demixing of solutions of *cis*-1,4-polybutadiene in different alkanes.[1] Both familiar manuals and the web of science yield insufficient data only. It would above all be interesting to obtain information on the differences resulting from the dissimilar structures of 1,4-polybutadiene and 1,2-polybutadiene. For that reason we have studied solutions of these two types of polybutadienes, selecting the chemically very similar *n*-butane as solvent. In particular, we have measured the vapor pressures above solutions of different polymer concentration and studied the phase separation of the liquid mixtures.

The experiments reported here demonstrate fundamental differences in the thermodynamic behavior of the two types of polybutadienes, which are difficult to rationalize on the basis of well-established theories. For that reason we have applied a recently published approach,[2,3] accounting explicitly for chain connectivity and conformational response, to the present problem and propose a plausible explanation of the observations.

2. Theoretical Part

2.1. Molar Volume of Gaseous *n*-Butane. To obtain information on the amount of solvent that is under equilibrium conditions contained in the gas phase, we need to calculate the molar volume $\bar{V}$ of the gaseous *n*-C_4 at the measured pressure p and at the chosen temperature T. For that purpose we have used the cubic equation of Peng and Robinson.[4] This relation reads

$$p = \frac{RT}{\bar{V} - b} - \frac{a\alpha(T)}{\bar{V}(\bar{V} + b) + b(\bar{V} - b)} \tag{1}$$

where

$$\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)](1 - (T/T_{cr})^{0.5})^2 \tag{2}$$

ω is the so-called acentric factor, and T_{cr} represents the critical temperature of the gas. The constants a and b are related to the critical data of the compound by

$$a = 0.45723\frac{(RT_{cr})^2}{p_{cr}} \quad \text{and} \quad b = 0.0778\frac{RT_{cr}}{p_{cr}} \tag{3}$$

2.2. Fugacities of *n*-Butane. Because of the nonideality of *n*-C_4 under the present experimental conditions, we require the fugacity coefficients γ in order to calculate the fugacities f and to get access to the polymer solvent interaction via the equilibrium condition (identical chemical potential of the solvent in the liquid mixture and in the pure gas phase). For that purpose we have again used the relation of Peng and Robinson. The following generally valid expression[4]

$$\ln \gamma = \int_0^p \left(\frac{\bar{V}}{RT} - \frac{1}{p}\right) \mathrm{d}p = \ln \frac{f}{p} \tag{4}$$

becomes

$$\ln \frac{f}{p} = Z - 1 - \ln(Z - B) - \frac{A}{2B\sqrt{2}} \ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{5}$$

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with

$$A = \frac{a\alpha(T)p}{(RT)^2} \quad B = \frac{bp}{RT} \quad Z = \frac{p\bar{V}}{RT} \tag{6}$$

2.3. Phase Equilibria. Modified Flory−Huggins Theory. For most systems it is impossible to model phase equilibria realistically by means of composition-independent Flory−Huggins interaction parameters. To reproduce experimentally determined limits of complete miscibility, one is normally forced to introduce at least two adjustable parameters without clear-cut physical meaning. Furthermore, it is usually impossible to describe liquid/liquid and liquid/gas equilibria with the same set of parameters. The reason for this situation lies in the fact that the original lattice theory does not account for two important features of mixing polymers with low molecular weight solvents, namely the fact that the segments of a given macromolecule cannot be evenly distributed over the entire volume of the system (due to chain connectivity) and the ability of chain molecules to change their conformation in response to changes in their environment (conformational response). These key features have recently been incorporated into the formalism of the normal Flory−Huggins theory.[2,3] Because we are using this new approach to discuss the differences in the liquid/liquid and liquid/gas equilibria for the present systems, the basic relations are briefly recalled.

In terms of the Flory−Huggins theory the segment molar Gibbs energy of mixing, $\Delta\bar{\bar{G}}$, can be written as

$$\frac{\Delta\bar{\bar{G}}}{RT} = (1-\varphi_2)\ln(1-\varphi_2) + \frac{\varphi_2}{N}\ln\varphi_2 + g(1-\varphi_2)\varphi_2 \tag{7}$$

where N is the number of segments of the polymer, calculated from its molar volume dividing it by the molar volume of the solvent, φ_2 stands for the segment fraction of the polymer (in good approximation equal to its volume fraction), and g is the integral Flory−Huggins interaction parameter.

The approach[3] accounting for the two additional features named above yields the following expression for g

$$g = \frac{\alpha}{(1-\nu)(1-\nu\varphi)} - \zeta(1+(1-\lambda)\varphi) \tag{8}$$

The parameter α quantifies the thermodynamic changes resulting from the opening of 1 mol of contacts between polymer segments (by insertion of a solvent molecule) at infinite dilution ($\varphi_2 \to 0$) *without changing the conformation of the polymer chain*. This first step of the mixing process does in the general case not yet describe the total effect. It is only via a *conformational relaxation* of the polymer chain, quantified by the parameter ζ, that equilibria are reached. For normal systems and theta conditions the segments do not rearrange in response to changes in the environment. Under these special circumstances, ζ becomes zero and α assumes the value of 0.5. The parameter ν is required to quantify the changes in g associated with an increase of the polymer concentration beyond the highly dilute state; it accounts primarily for the alterations in the deviation of the entropy of mixing from combinatorial behavior. The parameter λ was introduced to allow for the effects of chain connectivity; it can be calculated from the Kuhn−Mark−Houwink constants K and a (relating the intrinsic viscosity of a given polymer in a certain solvent at specified T and p to its molar mass) according to

$$\lambda = \left(\frac{1}{2} + \kappa N^{-(1-a)}\right) \tag{9}$$

where the factor κ is given by

$$\kappa = K\rho_2\left(\frac{\rho_2}{\rho_1}M_1\right)^a \tag{10}$$

ρ_ι are the densities of the components, and M_1 is the molar mass of the solvent. For sufficiently high molecular weight polymers, λ results so close to 0.5 (the limit for infinite M) that this parameter can in most cases be set equal to 0.5 without noteworthy loss of accuracy.

Sanchez−Lacombe Theory. This approach[5−7] treats the different pure substances as lattice fluids containing vacancies, which account for density changes. The reduced equation of state reads

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{11}$$

Tildes identify reduced quantities, ρ stands for the density, and r stands for the number of mers a molecule consists of.

Each substance is characterized by the three reduction parameters: T^*, p^*, and ρ^* (close-packed mass density). The reduced parameters are given by

$$\tilde{X} = X/X^*; \quad X = p, \nu, T, \rho \tag{12}$$

where ν is the volume one mer occupies under given conditions (T, p = const) and ν^* is the volume of a lattice site. The following relation holds true for r

$$r = \frac{M}{\rho^*\nu^*N_L} \tag{13}$$

where N_L is the Avogadro number. The total interaction energy per mer is given by

$$\epsilon^* = kT^* = p^*\nu^* \tag{14}$$

The characteristic parameters X^* are usually determined by fitting eq 11 to the pVT data measured in the p and T range of interest.

The Gibbs energy of the mixture per mer is according to the Sanchez−Lacombe theory[6,7] given as

$$\left\langle\frac{G}{rN}\right\rangle = \langle\epsilon^*\rangle\left\{-\langle\tilde{\rho}\rangle + \frac{\langle\tilde{p}\rangle}{\langle\tilde{\rho}\rangle} + \langle\tilde{T}\rangle\left[\left(\frac{1}{\langle\tilde{\rho}\rangle}-1\right)\ln(1-\langle\tilde{\rho}\rangle) + \frac{1}{\langle r\rangle}\ln\langle\tilde{\rho}\rangle + \frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2\right]\right\} \tag{15}$$

The parameters inside the angle brackets refer to binary mixtures; in this work they were calculated from the values of the pure components by means of the mixing rules formulated in the literature.[6,7] For the calculation of $\langle\epsilon^*\rangle$ the interaction between the components, ϵ^*_{12}, we have set

$$\epsilon^*_{12} = p^*_{12}v^* = (\varphi_1 p^*_1 + \varphi_2 p^*_2 - \varphi_1\varphi_2\sqrt{p^*_1 p^*_2})v^* \tag{16}$$

The chemical potential μ_1^l of component 1 (presently the solvent) in the liquid mixture reads[7]

$$\mu_1^l = kT\left[\ln \varphi_1 + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + r_1^0\tilde{\rho}X_1\varphi_2^2\right] + r_1^0 kT\left\{-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{p}_1}{\tilde{T}_1\tilde{\rho}} + \frac{1}{\tilde{\rho}}\left[(1-\tilde{\rho})\ln(1-\tilde{\rho}) + \frac{\tilde{\rho}}{r_1^0}\ln\tilde{\rho}\right]\right\} \tag{17}$$

where r_1^0 is the number of the mers calculated according to eq 13 for the pure solvent and X_1 is

$$X_1 = (p_1^* + p_2^* - 2\sqrt{p_1^* p_2^*})\frac{v_1^*}{kT} \tag{18}$$

For prevailing liquid/vapor equilibrium, μ_1^l must be identical with μ_1^{vap}, the chemical potential of the pure solvent in the coexisting gas phase

$$\mu_1^l = \mu_1^{\mathrm{vap}} \tag{19}$$

2.4. Calculation Procedures. In view of the fact that the volume of the system is kept constant throughout the measurements, we have used the Helmholtz energy, A, as the basis for the modeling instead of the usual Gibbs energy. The corresponding interaction parameter χ_A was calculated from the fugacities of n-C$_4$ according to

$$\chi_A = \frac{\ln(f/f_0) - \ln(1-\varphi_2) - (1 - 1/N)}{{\varphi_2}^2} \tag{20}$$

where f_0 is the fugacity of the pure solvent. For the pressure range under investigation, the influences of p on the activity of the solvent remain negligible. Because of the general relation

$$\chi = g - (1-\varphi)\frac{\partial g}{\partial \varphi} \tag{21}$$

the present approach (eq 8) yields the following expression for χ_A

$$\chi_A = \frac{\alpha_A}{(1-\nu_A\varphi_2)^2} - \zeta_A(\lambda_A + 2(1-\lambda_A)\varphi_2) \tag{22}$$

To determine the best representation of the composition dependence of χ_A by eq 22, we have minimized the Helmholtz energy of the entire system as described earlier.[8,9]

The characteristic parameters obtained in this manner from the measured vapor pressures were used to calculate liquid/liquid-phase equilibria by means of the composition dependence of the segment molar Helmholtz energy (expression analogous to eq 7). To this end we have either applied the direct minimization of the Helmholtz energy again or constructed the double tangent to this composition dependence.

3. Experimental Part

3.1. Materials. Both polymer samples were supplied by Bayer AG (Leverkusen, Germany). According to the producer, the weight-average molecular mass of 1,4-polybutadiene (1,4-PB, BUNA CB 22, ca. 98% cis) was 650 kg/mol, and its molecular nonuniformity $U = (M_w/M_n) - 1 = 1.9$; the density of this polymer as a function of temperature is (according to own pycnometric measurements and in agreement with the company's data) given by the expression ρ/kg m^{-3} = 909 − 0.558t/°C. The corresponding data for 1,2-polybutadiene (1,2-PB) read 105 kg/mol, $U = 0.08$, and ρ/kg m^{-3} = 898 − 0.453t/°C.

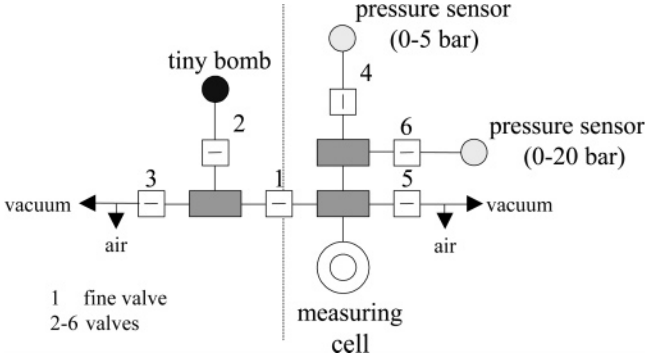

Figure 1. Top view of the apparatus used for vapor pressure measurements.

n-Butane was purchased in purum quality (>99.95%) from Westfalen AG (Münster, Germany). The temperature dependence of its density[10] is ρ/kg m^{-3} = 600.7027 − 1.0042t/°C − 0.0034(t/°C)^2. The solvent THF, used for the preparation of PB films, was supplied by Fluka (Steinheim, Germany) with puriss. p.a. quality. The boiling temperature interval ranged from 66 to 67 °C, and the density at 20 °C was 887 kg/m^3.

3.2. Apparatuses and Procedures. A sketch of the device used for the measurement of vapor pressures is shown in Figure 1. The polymer is deposited inside the cell in form of a thin film deposited on glass beads, and butane is transferred from a tiny gas bomb into the thoroughly evacuated apparatus, determining the amount of added solvent by differential weighing of the bomb. To calculate the composition of the *liquid* mixture from the gross data, it is mandatory to know the exact volumes of the different compartments of the apparatus because of the fact that the solvent is not quantitatively taken up by the polymer, but a nonnegligible part of it will normally be present in the equilibrium vapor phase. With the purpose of determining the different volumes, the different parts of the device (containing the required amount of glass beads, not yet covered with polymer) were filled with argon at 25 °C. From the weight difference of the Ar source (a tiny bomb again) the individual volumes were calculated by means of the ideal gas law. To check the reliability of this procedure, we have also determined the volumes by completely filling the parts with thoroughly degassed water using a calibrated screw press (number of revolutions per unit volume). Both methods (four independent measurements in each case) yielded data which differ only in the third digit after the comma. In a typical experiment the total volumes (right of valve 3, valves 2, 5, and 6 closed) amounted to 26.865 cm^3; shutting valve 4 reduced this volume to 18.125 cm^3. To obtain the volume fraction of the polymer in the liquid mixture, we also require the volume of the polymer films deposited on the glass beads; it was calculated from its known weight and the density of the pure polymer, neglecting possible excess volumes.

The measuring cell consists of a glass tube of 10 cm length with an inner diameter of 1 cm and a wall thickness of 0.5 cm (Schott, Mainz, Germany). The tube is held by metal fittings and sealed by Teflon backings. The glass tubes can withstand pressures up to 10 bar. Valves and connecting metal capillaries were purchased from SITEC (Sieber Engineering AG, Switzerland); the fine valve enables a reproducible adjustment of the opening. The tiny bombs were supplied by B.E.S.T. Ventil + Fitting GmbH (Stuttgart, Germany).

To achieve phase equilibria within reasonable time, we did not fill the bulk polymer into the measuring cell. Instead, we prepared thin films (typically 0.005−0.02 mm thick) on glass beads of 4 mm diameter. To this end the cell was charged with

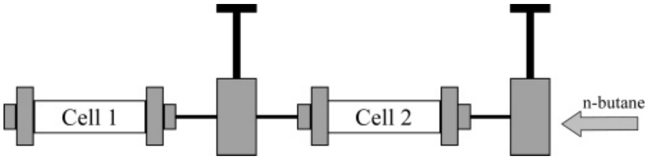

Figure 2. Scheme of the apparatus used for swelling experiments and for the observation of the phase state for the mixtures of PB and n-C$_4$.

the bare beads and sealed on both ends by means of metal grids to keep them in place. Using sufficiently viscous solutions (approximately 10 wt % of the polymer in THF) the voids between the spheres can be filled without seeping. In this manner the solution was evenly distributed to cover all beads, and the cell was loaded with the required amount of polymer. After that the major part of solvent was removed at 40 °C under atmospheric conditions in a drying furnace and the rest by applying vacuum. The amount of deposited polymer (typically some 300 mg) was calculated from the weight gain of the cell.

After assembling the entire measuring device the apparatus was totally immersed in a temperature bath (±1 °C) and thoroughly evacuated. All valves with exception of valves 4 and 6 were closed before the addition of butane, adding the first portion normally at 25 °C by opening valve 2. After closing that valve again fine valve 1 was opened. The attainment of the equilibrium vapor pressures (criterion: constant pressure within the resolution of the pressure sensor) takes typically 15−25 min. In the next step T was raised in the desired increments, and the equilibrium vapor pressures were determined. As soon as the pressure exceeds 5 bar, the sensor of higher sensitivity is uncoupled by closing valve 4. This reduces the total volume of the system by 8.740 cm^3. At the end of each temperature program, the equipment was cooled to 25 °C and the solvent removed quantitatively. This procedure avoids the accumulation of errors because the entire solvent required to realize a certain composition is always added anew. To realize larger volume fractions of solvent, valve 2 was opened at higher temperatures.

A combination of two cells (cf. Figure 2) was used to determine the composition of the coexisting liquid phases for the systems n-butane/PB. Cell 1 was filled with the bulk polymer, and its weight (including the valve, but without cell 2) was determined. After that, the cells were connected again, thoroughly degassed, and filled with n-C$_4$ such that the liquid phase covers the entire polymer. For the attainment of equilibria the systems were typically kept at the desired temperature for 1−2 weeks. To separate the polymer-lean phase from the very viscous polymer-rich phase, it suffices to let the mobile phase flow freely into cell 2. Thereafter, the connecting valve is closed, cell 1 disconnected from cell 2, and weighted again. With the calculation of the composition of the polymer-rich phase we corrected for the gaseous phase of n-C$_4$ in cell 1.

4. Results and Discussion

4.1. Liquid/Vapor Equilibria. Figure 3 and Figure 4 show the vapor pressures measured above the solutions of the two types of polybutadienes for three temperatures; corresponding measurements were also performed at 30, 40, 60, and 70 °C. The amount of solvent contained in the gas phase was taken into account when calculating the weight fraction w_2 of polymer in the mixture. The curves shown in these graphs represent the concentration dependence of the vapor pressure predicted by the Sanchez−Lacombe theory if one uses the reduction parameters collected in Table 1.

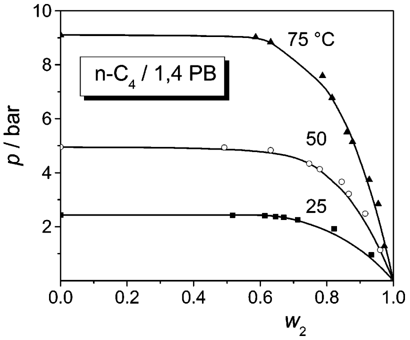

Figure 3. Vapor pressures of n-C$_4$ for solutions of 1,4-PB as a function of the weight fraction w_2 of the polymer at the indicated temperatures. The solid lines are calculated according to the Sanchez−Lacombe theory by means of the parameters collected in Table 1; they are indistinguishable from the fits by means of the modified Flory−Huggins theory (eq 22).

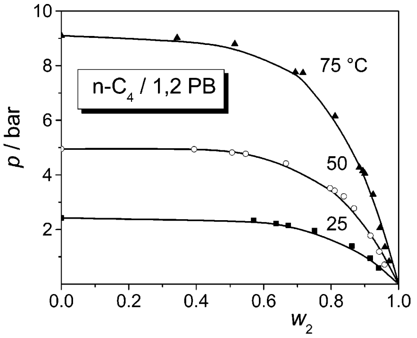

Figure 4. Vapor pressures of n-C$_4$ for solutions of 1,2-PB as a function of the weight fraction w_2 of the polymer at the indicated temperatures. The solid lines are calculated according to the Sanchez−Lacombe theory by means of the parameters collected in Table 1; they are indistinguishable from the fits by means of the modified Flory−Huggins theory (eq 22).

Table 1. Reduction Parameters of the Sanchez−Lacombe Theory (Eq 11)[5,11]

substance	ρ*/g cm^{-3}	p*/MPa	T*/K
n-butane	0.736	322	403
1,2-polybutadiene	0.956	362	615
1,4-polybutadiene	0.960	456	610

The most obvious distinction between the systems n-C$_4$/1,4-PB and n-C$_4$/1,2-PB lies in the fact that the vapor pressure differs from that of the pure solvent down to much lower polymer concentrations in the case of 1,2-PB. These primary data must be corrected because of the nonideality of n-C$_4$ in the gas phase, particularly at the higher pressure and lower temperatures. For the pure solvent the fugacity coefficients γ calculated from eq 5 range from 0.9348 at 25 °C to 0.8415 at 75 °C. Figure 5 and Figure 6 show the results of the vapor pressure measurements in terms of the composition dependence of the reduced fugacities f/f_0, where f_0 is the value for the pure solvent.

To enable a direct comparison of the fugacities of n-C$_4$ in mixtures with the two types of polymers, Figure 7 shows the results for 25 °C in a common graph. From the much lower reduced fugacities for the 1,2-PB it becomes immediately obvious that the interaction with the solvent is for this homologue much better than for 1,4-PB.

On the basis of the equilibrium condition of identical chemical potential of the solvent in the pure gas phase and in the polymer solution, we have calculated the interaction parameter χ_A (differential parameter for the solvent based on the Helmholtz energy instead of the usual Gibbs energy) for all homogeneous solutions for which the fugacities are sufficiently different from that

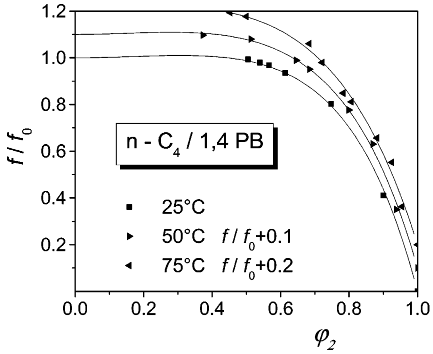

Figure 5. Reduced fugacities of n-butane for the system n-C$_4$/1,4-PB calculated by means of eq 5 from the measured vapor pressures. In view of the modest T dependence, the curves are shifted by the indicated values.

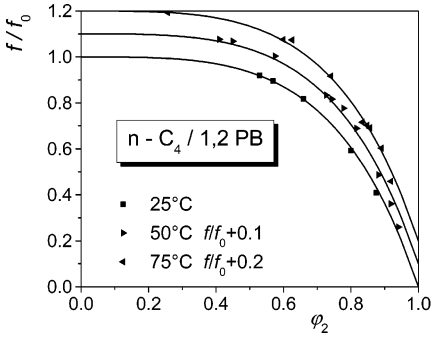

Figure 6. Reduced fugacities of n-butane for the system n-C$_4$/1,2-PB calculated by means of eq 5 from the measured vapor pressures. In view of the modest T dependence, the curves are shifted by the indicated values.

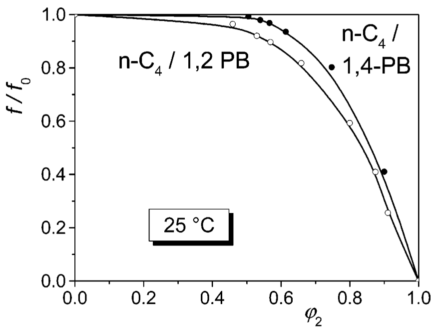

Figure 7. Comparison of the composition dependence of the reduced fugacities of n-C$_4$ for 1,4-PB and 1,2-PB at 25 °C.

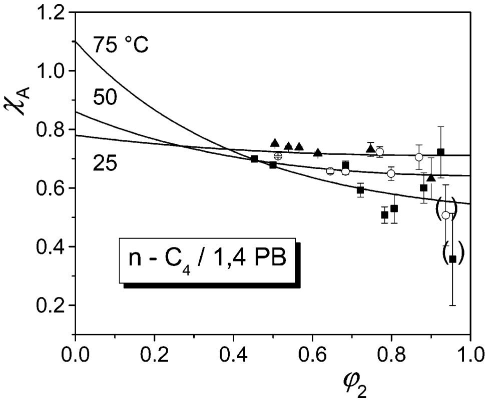

Figure 8. Composition dependence of the differential interaction parameter χ_A of the system n-C$_4$/1,4-PB for the indicated temperatures. The individual points were directly calculated from the measured fugacities by means of eq 20. The lines are best fits to these data by means of eq 22, where λ was set 0.5.

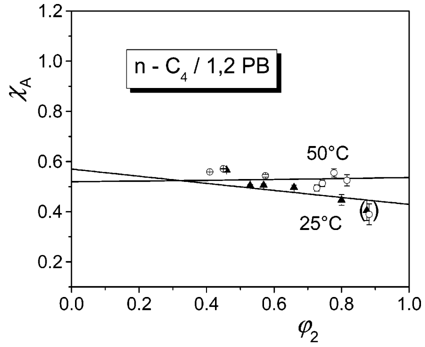

Figure 9. Composition dependence of the differential interaction parameter χ_A of the system n-C$_4$/1,2-PB for the indicated temperatures. The individual points were directly calculated from the measured fugacities by means of eq 20. The lines are best fits to these data by means of eq 22, where λ was set 0.5.

Table 2. Parameters of the Modified Flory–Huggins Relation (Eq 22) Obtained from the Vapor Pressure Measurements

	n-C$_4$/1,4-PB			n-C$_4$/1,2-PB		
T/°C	α_A	ν_A	ζ_A	α_A	ν_A	ζ_A
25	0.651	−0.259	−0.186	0.190	0.035	0.67
50	0.600	−0.520	−0.210	0.049	0.055	0.54
75	0.698	−0.804	−0.155	0.100	0.012	0.53

of the pure solvent. In both cases the lowest polymer concentrations are approximately $\varphi_2 \approx 0.4$, and liquid/liquid phase separation is absent. The results are shown in Figure 8 and Figure 9 for different temperatures using identical scales to ease their comparison. The error bars indicate a marked drop in the accuracy of the data for φ_2 values exceeding 0.9. The reason lies in the increasing difficulties to determine the exact amount of solvent the mixtures contain.

The most prominent difference in the interaction parameters for the two systems lies in the range of their numerical values. For n-C$_4$/1,4-PB they are at all concentrations larger than 0.6, whereas they are smaller than 0.6 for n-C$_4$/1,2-PB. For the former system the heat of mixing is clearly endothermal at high polymer concentrations, and there exist indications that the sign of the heat of mixing changes upon dilution. This behavior is similar to that reported for the system *tert*-butyl acetate/polystyrene.[12] Opposite inversions, i.e., from exothermal at high polymer concentrations to endothermal in the dilute state, have been observed[13] for solutions of PDMS in n-octane. Despite the lack of data at high dilution and despite the significant errors at high polymer concentration, we have fitted the composition dependencies by means of eq 22 because this relation has turned out to be very robust and reliable in the past.[2,3,14,15] To this end we have set $\lambda = 0.5$ (which is a good approximation for reasonably large molar masses) and adjusted the three system specific parameters for each temperature. The corresponding results are collected in Table 2.

The uncertainty of the different parameters describing the composition dependence of χ_A is naturally largest for α because of the lack of experimental data at high dilution. The qualitative differences are, however, beyond doubt. The considerably larger α values for 1,4-PB indicate that the establishment of contacts between the solvent and a polymer segment at fixed conformation is already much less favorable for this polymer than for 1,2-PB. The contributions of the conformational

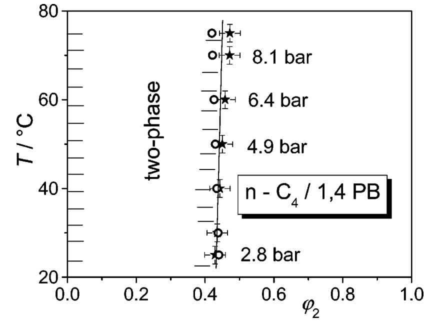

Figure 10. Isochoric phase diagram for the system n-C_4/1,4-PB. The measured data points are drawn as full stars and that calculated by means of the interaction parameters obtained from the vapor pressure measurements as open circles.

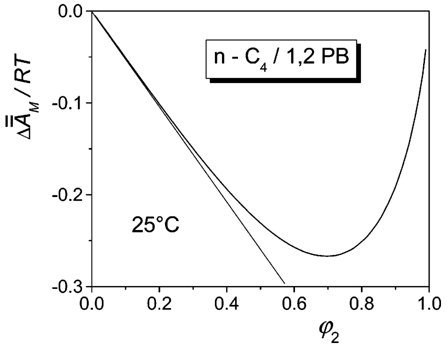

Figure 11. Composition dependence of the segments molar Helmholtz energy of mixing for the system n-C_4/1,2-PB at 25 °C calculated by means of eqs 7 and 8 (replacing the Gibbs energy by the Helmmoltz energy) and using the parameters collected in Table 2. The line is drawn to demonstrate that this curve is always located above its tangent, i.e., that the mixtures do not phase separate.

response amplify these differences. For 1,4-PB the effects of the molecular rearrangement are very adverse, as indicated by the negative sign of ζ, whereas they are very favorable (positive ζ) for 1,2-PB. Similarly to ζ one also observers opposite signs for the parameter ν; a molecular interpretation of this finding is presently still lacking. In any case n-C_4 should be a bad solvent for 1,4-PB but a good solvent for 1,2-PB according to this evaluation of the vapor pressure measurements.

4.2. Liquid/Liquid Equilibria. The composition of the coexisting liquid phases was determined by means of the apparatus shown in Figure 2. Solutions of 1,2-PB in n-C_4 remain homogeneous within the temperature interval from 25 to 75 °C, irrespective of their polymer content. The demixing conditions observed for system n-C_4/1,4-PB and the theoretical prediction of the modified Flory–Huggins theory are shown in Figure 10. In all experiments the liquid phase transferred from cell 1 into cell 2 did not contain measurable amounts of polymer, which means that the highly swollen PB coexists with practically pure n-C_4. The agreement between the experimental findings and the calculations based on the measured vapor pressures appears remarkable.

For n-C_4/1,2-PB the direct minimization of the Helmholtz energy (as calculated by means of the parameters of Table 2) does not result in liquid/liquid demixing. This finding is again in accord with the experimental observations. Plotting the segment molar Helmholtz energy of mixing as a function of composition (Figure 11) makes this situation visible by the fact that the curve is always located above its tangent. The Sanchez–Lacombe theory, on the other hand, does not discriminate between the solubility behavior of the two types of polybutadiene. For n-C_4/1,4-PB the prediction is very accurate, comparable to that of eq 8, but it fails totally for n-C_4/1,2-PB because it yields a miscibility gap, which is in its extension comparable to that for the other isomer.

5. Conclusions

Isochoric demixing experiments and vapor pressure measurements have disclosed fundamental differences in the thermodynamic behavior of 1,4-PB as compared with 1,2-PB. Within the temperature range from 25 to 75 °C the 1,4-isomer exhibits an extended miscibility gap with n-C_4 in contrast to the 1,2-isomer, which is completely miscible with that solvent. This finding is in accord with the considerably higher vapor pressures observed for the solutions of 1,4-PB in relation to that of 1,2-PB at the same temperature and polymer content. The modeling of these results demonstrates that the vapor/liquid equilibria can be described quantitatively by means of established theories, like that of Sanchez and Lacombe. This statement does, however, not hold true for the liquid/liquid equilibria, which are obviously considerably more difficult to describe adequately. It is only by means of a recently established approach, which accounts explicitly for the conformational changes accompanying mixing, that the fundamental differences in the solubility of the two polymers can be modeled. According to that concept the 1,2-isomer interacts favorably with n-C_4 because the flexibility of the polymer backbone (pending double bonds) enables the establishment of suitable contacts to the surrounding solvent molecules. With the 1,4-isomer, on the other hand, such a rearrangement is largely impeded because the double bonds are now located in the main chain and make the conformational response much more difficult.

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