Macromolecules **1995**, *28*, 4975−4980

Hitherto Ignored Effects of Chain Length on the Flory−Huggins Interaction Parameters in Concentrated Polymer Solutions

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Received January 6, 1995; Revised Manuscript Received April 21, 1995[⊗]

ABSTRACT: Equilibrium vapor pressures were measured for the systems toluene/poly(dimethylsiloxane) [two different polymers, 35−55 °C] and cyclohexane/poly(vinyl methyl ether) [three polymers, 35−65 °C] by combining a head-space sampler with a gas chromatograph. The Flory−Huggins interaction parameters χ calculated therefrom as a function of the volume fraction φ_2 of polymer were complemented by literature data on inverse gas chromatography and by χ values at high dilution from osmometry in the former case and from light-scattering measurements in the latter. These results demonstrate that the effects of differing chain lengths can still be felt at $\varphi_2 > 0.5$, in contrast to the general perception. This observation is tentatively explained in terms of changes in coil dimension taking place in the region of high polymer concentrations. Furthermore, $\chi(\varphi_2)$ may exhibit a minimum even with the common polymers of present interest. In all cases the concentration dependence of χ is described well by a series expansion of χ with respect to φ_2 up to the fourth term, if two parameters are adjusted. The temperature dependence of χ at different concentrations demonstrates that the heats of dilution generally increase with increasing φ_2, whereas the noncombinatorial entropy of dilution decreases. This situation leads to a linear interdependence of the enthalpy and entropy part of χ. With the system toluene/poly(dimethylsiloxane) one observes an inversion of the heat effects upon an increase of φ_2 from exothermal to endothermal at ca. 13 vol %.

Introduction

The understanding of the concentration dependence of the Flory−Huggins interaction parameter χ for solvents of different thermodynamic qualities and of the role the molecular weight of the polymer plays in this context has in the past been greatly hindered by experimental difficulties. Very laborious and time-consuming vapor pressure measurements were required. To improve this situation, a new method[1] consisting of the combination of a head-space sampler with a normal gas chromatograph was recently developed and applied[2] to a number of systems not previously studied. These new results have demonstrated that—at least with the system cyclohexanone/poly(*n*-butyl methacrylate)—there exist remarkably large and theoretically unexpected influences of chain length on χ at high polymer concentrations. The present study was undertaken to test, by means of the new procedure in combination with osmotic and light-scattering measurements, whether this finding is specific to poly(*n*-butyl methacrylate)—which exhibits some peculiarities since the side groups of its monomeric units are able to intercalate[3]—or whether the features observed with this polymer are general and have merely been overlooked.

Experimental Section

Materials. Toluene (TL) and cyclohexane (CH) were p.a. grade and were dried over 3 Å molecular sieves. The molecular weights of the different polymer samples, their molecular nonuniformities $U = (M_w/M_n) - 1$ (as checked by GPC), and their provenance are collected in Table 1. Poly(dimethylsiloxane) [PDMS] was used as obtained from the producer, whereas the poly(vinyl methyl ether) [PVME] samples were from a fractionation[4] by means of the CPF (continuous polymer fractionation). For the calculation of volume fractions the following expressions describing the temperature dependence of the densities ϱ (g/cm^3) of the components were used.

Table 1. Provenance and Characterization of the Polymer Fractions

polymer	supplier	$10^{-3}\,M_w$	U
PDMS 170	Wacker GmbH, München	170	0.70
PDMS 70		72	0.38
PVME 81[a]	BASF AG, Ludwigshafen	81	0.38
PVME 51[a]		51	0.30
PVME 28[a]		28	0.27

[a] Samples fractionated from Lutonal M40 by means of continuous polymer fractionation.

TL:[5] $$0.8854 - 9.3 \times 10^{-4}\,t/°\mathrm{C}$$

CH:[6] $$0.79774 - 9.528 \times 10^{-4}\,t/°\mathrm{C}$$

PDMS:[7] $$0.97/[1 + 9.2 \times 10^{-4}(t/°\mathrm{C} - 25) + 4.5 \times 10^{-7}(t/°\mathrm{C} - 25)^2]$$

PVME:[8] $$1.0725 - 7.259 \times 10^{-4}\,t/°\mathrm{C} + 4.5 \times 10^{-7}(t/°\mathrm{C})^2$$

For PDMS it is known[7] that the densities are independent of molecular weight for $M > 15 \times 10^3$; similar considerations should hold true for PVME.

Apparatus and Procedures. *Vapor pressures* were measured using a pneumatically driven thermostated head-space sampler (Dani HSS 3950, Milano, Italy) which takes 50 μL of the gas phase (in equilibrium with the polymer solution) and injects this mixture of solvent and air into a gas chromatograph (Shimadzu GC 14A, Kyoto, Japan). The amount of solvent contained in the sample volume—being proportional to the vapor pressure—is detected by a flame ionization detector and recorded by means of an integrator (Shimadzu, Chromatopac C-R6A). The setup of the apparatus, the working conditions, and the procedures were the same as in ref 1 for the system CH/PVME; for TL/PDMS the temperatures of the column (150 °C) and of injector plus detector (170 °C) had to be increased as a result of the higher boiling temperature of the solvent.

Osmotic pressures were determined by means of the Osmomat 090 apparatus (Gonotec, Berlin, Germany) in combination with the control unit 070/090 supplied by the same company and a data recorder (Linseis, Selb, Germany). A two-layer membrane consisting of cellulose acetate (Gonotec, Berlin,

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

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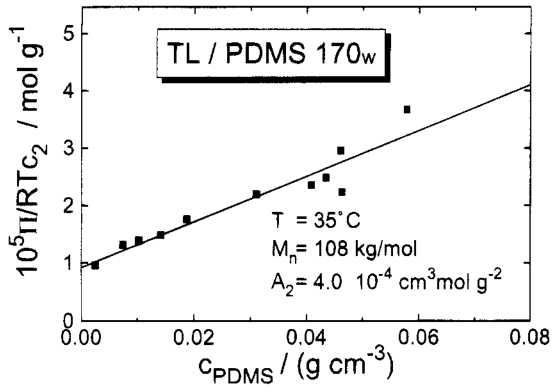

Figure 1. Evaluation of the concentration dependence of the osmotic pressure Π, measured for the system toluene/poly(dimethylsiloxane) 170w at 35 °C.

Germany) with a cutoff at ca. 5000 Dalton was used. The solutions were prepared using dust-free degassed solvents and filtered through a 0.45 μm membrane filter (Millipore Corp., Bedford, MA) directly into the osmometer cell.

Light-scattering measurements were performed on a modified (SLS, G. Baur, Freiburg, Germany) static-light-scattering apparatus Fica 50 (Sofica, Paris) using a laser light source (633 nm) at angles from 20° to 145°. The solutions were prepared 2 days in advance and stirred at ca. 50 °C in an oven. Prior to the measurements, they were filtered through a 0.45 μm membrane filter (Millipore) directly into the thoroughly cleaned optical cells (Hellma, Müllheim, Germany) and thermostated in the light-scattering apparatus for 15 min. The refractive index increment (measured with an apparatus described in the literature[9]) of the system CH/PVME 81 is 0.054 cm^3/g at 35.5 °C and 0.057 cm^3/g at 45 °C.

Results

All experimental data were evaluated according to the Flory–Huggins relation

$$\frac{\Delta\overline{G_1}}{RT} = \ln \varphi_1 + \left(1 - \frac{1}{N_2}\right)\varphi_2 + \chi\varphi_2^{\,2} \tag{1}$$

in which φ_1 represents the volume fraction of the solvent and φ_2 that of the polymer and N_2, the ratio of the molar volumes of solute and solvent, is proportional to the degree of polymerization. The parameter χ (the differential interaction parameter for the solvent) is defined in terms of the partial molar residual Gibbs energy of mixing of this component and is related to the integral interaction parameter g according to

$$\chi = \frac{\Delta\overline{G_1}^R}{\varphi_2^{\,2}RT} = g - (1 - \varphi_2)\frac{\partial g}{\partial\varphi_2} \tag{2}$$

Neglecting small corrections for the nonideality of the vapor, the Flory–Huggins interaction parameter can be calculated from the ratio of p_1 and p_1^0, the vapor pressures of the solution and of the pure solvent, respectively, as

$$\chi = \frac{\ln\left(\frac{p_1}{p_1^0}\right) - \ln \varphi_1 - \left(1 - \frac{1}{N_2}\right)\varphi_2}{\varphi_2^{\,2}} \tag{3}$$

The measured osmotic pressures Π were used to evaluate the analogous expression

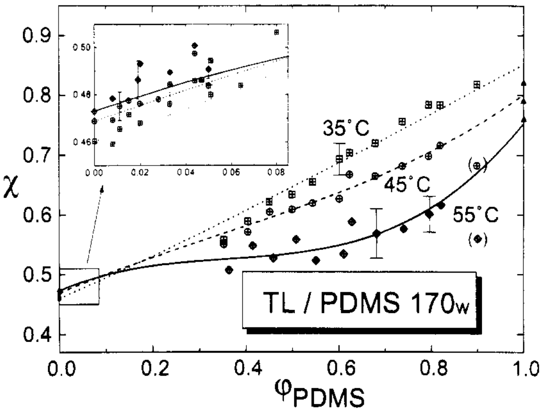

Figure 2. Concentration dependence of the Flory–Huggins interaction parameter χ for the system toluene/poly(dimethylsiloxane) 170w at the indicated temperatures. The insert gives the data resulting from osmometry, the limiting value for the vanishing solvent content is taken from the literature,[11] and all other information stems from vapor pressures. The curves are best fits to eq 5, fixing χ_0 plus χ_1 and adjusting χ_2 plus χ_3.

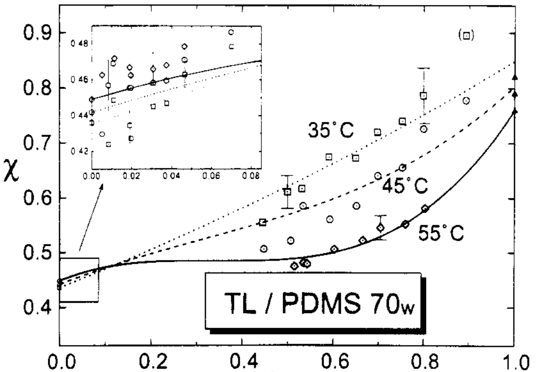

Figure 3. As Figure 2 but for poly(dimethylsiloxane) 70w instead of PDMS 170w.

$$\chi = \frac{\ln\left(\frac{\Pi\overline{V}_1}{RT}\right) - \ln \varphi_1 - \left(1 - \frac{1}{N_2}\right)\varphi_2}{\varphi_2^{\,2}} \tag{4}$$

in which $\overline{V}_1$ is the molar volume of the solvent. For sufficiently small concentrations, $\chi(\varphi_2)$ can be represented by the series expansion

$$\chi = \chi_0 + \chi_1\varphi_2 + \chi_2\varphi_2^{\,2} + \chi_3\varphi_2^{\,3} \ldots \tag{5}$$

where χ_0 is related to the second osmotic virial coefficient A_2 (obtained from osmotic or light-scattering measurements) by

$$\chi_0 = 0.5 - A_2\overline{V}_1\varrho_2^{\,2} \tag{6}$$

(ϱ_2 being the density of the polymer). The corresponding relation for the next term reads $\chi_1 = {}^1/_3 - A_3\overline{V}_1\varrho_2^{\,3}$ which means that χ_1 can be approximated by $^1/_3$, as long as A_3 remains small enough.[10]

Toluene/Poly(dimethylsiloxane). With the system TL/PDMS, vapor pressures and osmotic pressures were measured for two polymer samples in the temperature range from 35 to 55 °C. Figure 1 gives an example of determination of A_2.

Table 2. Parameters of Equation 5 for the Analytical Description of $\chi(\varphi)$

10^3M_w	T (°C)	fits according to eq 5 ($\chi_1 = {}^1/_3$) χ_0[a]	χ_2	χ_3	interpolated χ_∞[b]
		PDMS			
170	35	0.460	0.10	−0.04	0.82
	45	0.468	−0.22	0.22	0.79
	55	0.473	−0.79	0.74	0.76
70	35	0.436	0.07	0.01	0.82
	45	0.442	−0.35	0.38	0.79
	55	0.449	−1.00	0.98	0.76
		PVME			
81	35	0.524	−2.29	2.60	1.20
	45	0.519	−2.58	2.81	1.12
	55	0.482	−3.17	3.34	1.04
	65	0.446	−3.50	3.61	0.96
51	35	0.525	−2.55	2.91	1.20
	45	0.52	−3.02	3.22	1.12
	55	0.48	−3.22	3.40	1.04
	65	0.44	−4.07	4.12	0.96
28	35	0.525	−2.82	3.20	1.20
	45	0.51	−3.21	3.40	1.12
	55	0.47	−3.39	3.54	1.04
	65	0.43	−4.39	4.49	0.96

[a] Fixed at the value determined by osmosis or light scattering. [b] Interpolated from literature data.

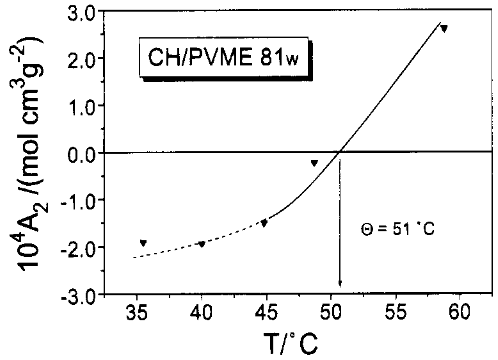

Figure 4. Temperature dependence of the osmotic virial coefficient A_2 as obtained from light-scattering measurements for the system cyclohexane/poly(vinyl methyl ether) 81w. The Θ-temperature resulting from this graph is indicated.

The concentration dependence of χ—calculated from the primary vapor pressure data according to equations presented in the previous section—is depicted in Figure 2 for the higher molecular weight sample of PDMS and in Figure 3 for the lower molecular weight sample; the inserts give the information stemming from osmometry. The curves connecting the data points for the different temperatures are calculated by adjusting the parameters χ_2 and χ_3 of eq 5, fixing χ_0 (given by A_2) and χ_1 (set $^1/_3$) to the present experimental information plus χ_∞ data; the latter information, referring to the limit of $\varphi_2 \to 1$, was obtained from inverse gas chromatography[11] and interpolated as required. The different χ_i values are collected in Table 2.

Cyclohexane/Poly(vinyl methyl ether). With the system CH/PVME vapor pressures were measured for three polymer samples in the temperature range from 35 to 65 °C; light-scattering experiments performed with sample PVME 81w as a function of T (cf. Figure 4) yield a (endothermal, UCST type) Θ temperature of 51 °C.

The concentration dependence of χ for polymers of different chain lengths is depicted in Figures 5–7; the curves are calculated in the same manner as described for PDMS, again including information[12,13] concerning χ_∞. The different χ_i values are again collected in Table 2.

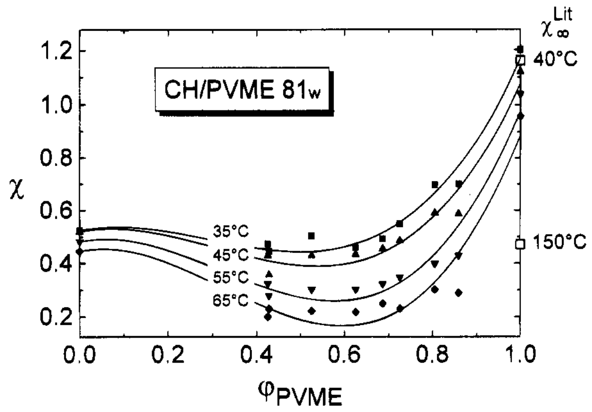

Figure 5. Concentration dependence of the Flory–Huggins interaction parameter χ for the system cyclohexane/poly(vinyl methyl ether) 81w at the indicated temperatures. The limiting values of χ for the vanishing polymer concentration stem from light-scattering measurements, and those for the vanishing solvent content were interpolated from information given in the literature;[12,13] all other data are based on vapor pressures.

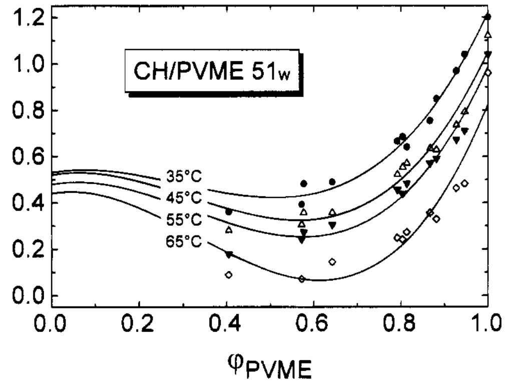

Figure 6. As Figure 5 but for PVME 51w instead of PVME 81w.

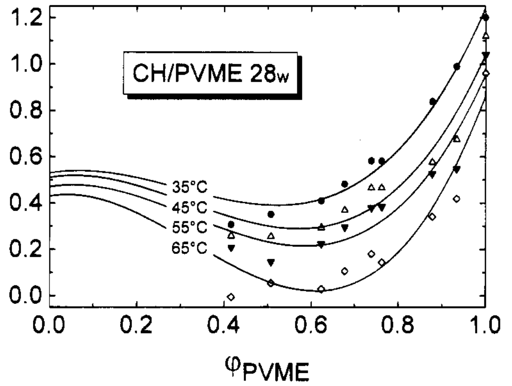

Figure 7. As Figure 5 but for PVME 28w instead of PVME 81w.

Discussion

Before evaluating the influence of chain length on the Flory–Huggins parameter at high polymer concentrations, we compare the present experimental results—as far as possible—with existing data. In addition, the information concerning the Gibbs energy of dilution, contained in the χ values, is split into its enthalpy and entropy part to facilitate the discussion.

The system TL/PDMS is the only one of the two under investigation for which experimental data on $\chi(\varphi_2)$ could be found in the literature;[14–16] Figure 8 collects all facts. Although the data scatter considerably, especially at high polymer content, the agreement is reasonable if

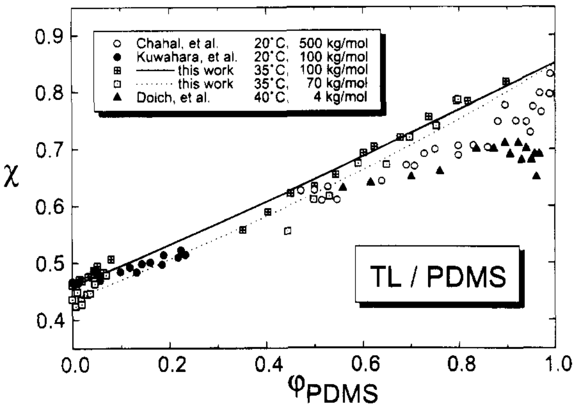

Figure 8. Comparison of all information on $\chi(\varphi_2)$ for the system toluene/poly(dimethylsiloxane) found in the literature[14-16] with the present results.

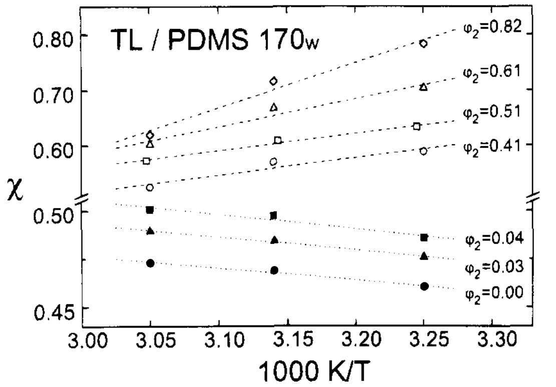

Figure 9. Evaluation of the temperature dependence of χ for the system toluene/poly(dimethylsiloxane) 170w at different concentrations according to eq 7.

one considers the differences in the methods applied, in temperature and in the chain length of the polymers.

Temperature Dependence. In order to separate χ into χ_H, its enthalpy part, and χ_S, its entropy part, according to

$$\chi_H = \frac{\Delta \overline{H}_1}{RT{\varphi_2}^2} = \frac{1}{T}\left(\frac{\partial \chi}{\partial 1/T}\right) \tag{7}$$

and

$$\chi_S = \chi - \chi_H = -\frac{\Delta \overline{S}_1^R}{R{\varphi_2}^2} \tag{8}$$

χ is plotted as a function of $1/T$ for constant composition of the mixture, as shown in Figure 9 for one example.

From the above diagram it becomes immediately obvious that the heat of dilution for the system TL/PDMS 170w changes sign from exothermal at low φ_2 to endothermal at high φ_2. Similar behavior has already been reported[17] for the system *tert*-butyl acetate/poly(styrene). From a plot of χ_H and of χ_S as a function of composition (Figure 10) one can see that the heat of dilution passes through zero at the characteristic concentration $\varphi_2^{\text{atherm}}$, whereas the entropy of dilution becomes purely combinatorial at the higher characteristic concentration φ_2^{comb}, the entropic driving forces being larger than combinatorial for $\varphi_2 > \varphi_2^{\text{comb}}$ and less than combinatorial for $\varphi_2 < \varphi_2^{\text{comb}}$.

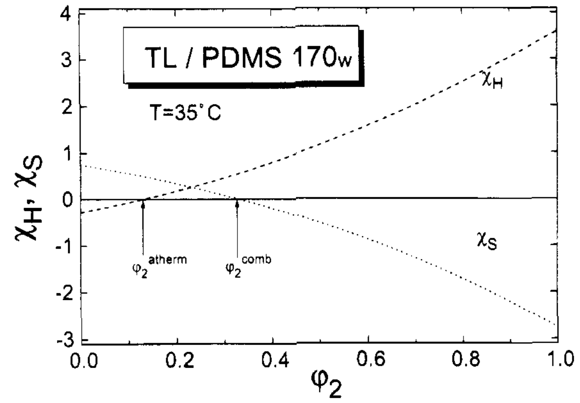

Figure 10. Dependence of χ_H and χ_S (eqs 7 and 8), the enthalpy and the entropy constituents of χ, on the volume fraction of the polymer for the system toluene/poly(dimethylsiloxane) 170w. The volume fractions at which the mixture behaves athermally and combinatorially, respectively, are indicated.

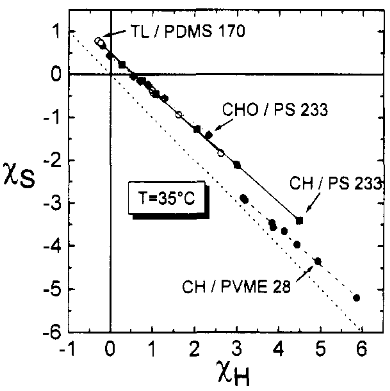

Figure 11. Interdependence of χ_H and χ_S (eqs 7 and 8) at 35 °C for the systems toluene/poly(dimethylsiloxane) 170w, cyclohexane/poly(vinyl methyl ether) 28w, cyclohexane/poly(styrene) 233[1] and cyclohexanone/poly(styrene) 233.[2]

A further interesting feature of the above subdivision of χ is a linear interdependence of χ_H and χ_S which was recently observed with the system cyclohexanone/poly(styrene).[2] This result is included in Figure 11 which demonstrates that linear interrelations also hold true for the polymer solutions under investigation. A theoretical discussion of the reasons for simultaneous changes in enthalpy and in entropy has already been presented.[18]

According to presently available limited information, it appears as if the length of the lines in this diagram are correlated with the position of their starting point for infinitely dilute solutions. The lower the corresponding χ_H (which normally implies the better the solvent) the smaller is the range of χ_H that is covered as one proceeds to the pure polymer. The parallel shift of the line for CH/PVME 28 is probably due to the low molecular weight of this polymer as compared with the rest. With this example it should also be noted that it gives the results of vapor pressure measurements only, i.e. does not include the dilute regime for which no information is presently available.

Chain Length Dependence. The results shown in Figures 12 and 13 give evidence that previously reported effects of chain length in the region of high polymer concentrations[2] are not only specific to poly(*butyl* methacrylate) but may also be observed with familiar polymers like PDMS or PVME. For the sake of clarity the curves (already shown in Figures 2 and 3 for PDMS and

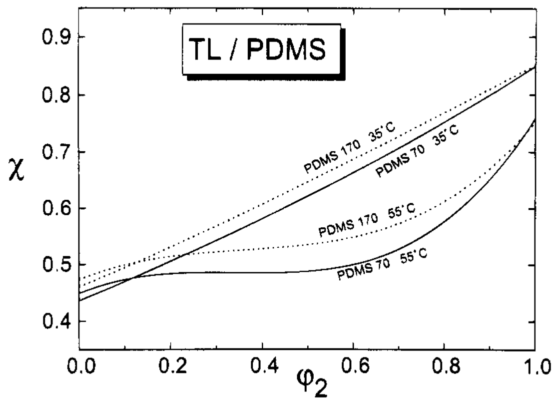

Figure 12. Concentration dependence of χ for two representatives of the system toluene/poly(dimethylsiloxane) at 35 and 55 °C, respectively, calculated according to eq 5 by means of the parameters given in Table 2.

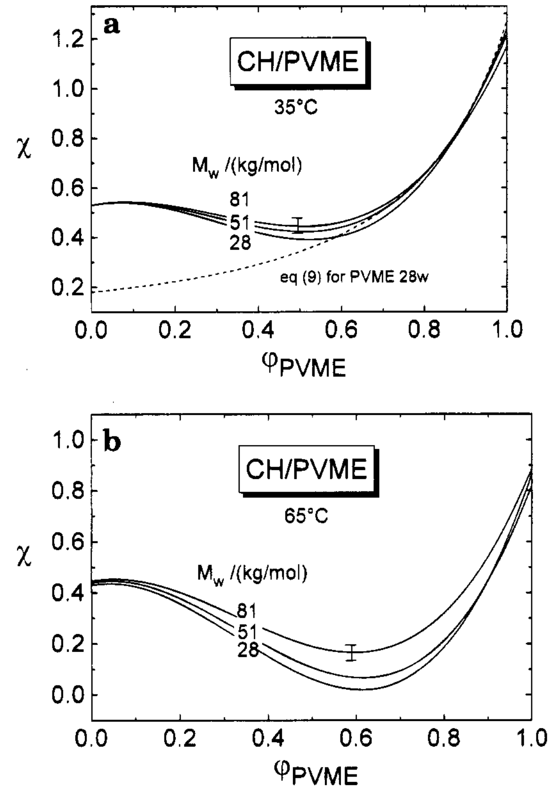

Figure 13. Concentration dependence of χ for three representatives of the system cyclohexane/poly(vinyl methyl ether) at 35 (part a) and at 65 °C (part b) calculated according to eq 5 by means of the parameters given in Table 2.

in Figures 5–7 for PVME) are given without data points.

The most prominent features of the above diagram are the following: Even for volume fractions of polymer well beyond 0.5, chains of different lengths behave differently and the effects are beyond experimental error. Whether the curves at constant T for different molecular weights meet at $\varphi_2 \rightarrow 1$ (as indicated in Figure 12) is uncertain owing to the lack of data for $\chi_\infty(M)$. In accord with the inversion of the enthalpies of dilution upon the variation of φ_2 and with the large values of χ_H for high polymer content, $\chi(\varphi_2)$ exhibits a point of inflection for both polymer samples if T is sufficiently large. According to the present results the effects of varying chain lengths increase with rising temperature.

How the individuality of chains differing in length can be felt in χ for the system CH/PVME is shown in Figure 13a,b for two temperatures. The general features are very similar to those discussed above. This time the point of inflection in $\chi(\varphi_2)$ is already observed at the lower temperature (which is ca. 15 deg below Θ). Again the effects become larger as T is raised; the curves for the different molecular weights drift apart and the minimum in χ becomes more pronounced.

A conclusive theoretical explanation of the present observations is still lacking; a description in terms of end group effects, however, appears very unlikely in view of the general experience. Tentatively, the influences of M on χ in the concentrated regime are attributed to changes in the dimensions of polymer coils with composition,[19] which—according to experimental evidence[20] and theoretical considerations[21]—should not be restricted to the dilute regime but should persist up to large φ_2 values. At the moment it is being tested whether the new approach[19] formulated for dilute solutions (considering χ to be composed of two contributions—one measuring the effects of dilution at fixed dimension and the other the subsequent effects of relaxation into the equilibrium state) can be used to understand the present results.

It is interesting to note that it is once more possible to represent the χ data located within the region of sufficiently high polymer content very well by means of the relation of Koningsveld and Kleintjens[22]

$$\chi = \alpha + \frac{\beta(1-\gamma)}{(1-\gamma\varphi_2)^2} \tag{9}$$

in which α, β, and γ are constants for a given system and temperature. Like with the previously studied low molecular weight representatives of the system cyclohexanone/poly(n-butyl methacrylate),[2] however, this equation no longer holds true at high dilution, as demonstrated by the broken line in Figure 13a.

Conclusion

Concentration dependent interaction parameters in the region of moderate to high polymer concentrations have become much more readily available by combining a head-space sampler with a common gas chromatograph. Complementing these data with the results of standard methods yielding χ at high dilution (light scattering/osmometry) or near the polymer melt (inverse gas chromatography) gives access to the variation of χ over the entire range from the pure solvent to the pure melt. Even on the basis of the limited information collected in the manner described, it appears mandatory to search for a deeper understanding of the concentration dependence of the Flory–Huggins parameter. It is obvious that additional experimental evidence would be highly desirable for that purpose. Further measurements and theoretical calculations are therefore under way.

Acknowledgment. H.-M.P. gratefully acknowledges a stipend of the "Konrad-Adenauer-Stiftung", Bonn, Germany.

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