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On the Cooccurrence of Demixing and Thermoreversible Gelation of Polymer Solutions. 2. Thermodynamic Background

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ABSTRACT: By the combination of different experimental methods (light scattering, vapor pressure measurements, and inverse gas chromatography), the Flory–Huggins interaction parameters χ were determined for poly(*n*-butyl methacrylate) (PBMA) plus the Θ-solvents 2-propanol and ethanol as a function of composition and temperature. The subdivision of χ into its enthalpy and entropy parts χ_H and χ_S reveals fundamental differences for the present systems as compared with normal Θ-solutions. For example, in the case of the system cyclohexane/poly(styrene), both of these contributions are positive and increase steadily with rising polymer content of the mixture. With the solutions of PBMA under investigation, however, one observes minima in χ_H and maxima in χ_S, where the former quantity remains positive at all compositions and temperatures, whereas the latter starts from slightly positive or negative values (depending on T) at low concentrations but becomes considerably negative with increasing polymer content.

Introduction

In the preceding paper,[1] a phenomenological investigation on the demixing and thermoreversible gelation of the system 2-propanol/poly(*n*-butyl methacrylate) (2-POH/PBMA) was described. According to that work, gelation occurs only in thermodynamically sufficiently poor solvents and should thus, at least with the present system, be bound to particular thermodynamic conditions. General attempts to correlate gelling ability and solvent power seem to be inconclusive so far.[2–7]

The aim of the present paper is to obtain as complete thermodynamic information as possible for solutions of PBMA in 2-POH and in ethanol (ETOH). To this end the Flory–Huggins interaction parameter χ was measured from infinitely dilute solutions up to the limit of the pure polymer as a function of temperature.

Experimental Section

Materials. The following poly(*n*-butyl methacrylate) (PBMA) samples were used: PBMA 8.9 ($M_w = 8900$); $U = (M_w/M_n) - 1 = 0.12$) for vapor pressure and light scattering measurements and PBMA 2050 ($M_w = 2\,050\,000$); $U = 0{,}23$) for inverse gas chromatography (IGC). The solvents were analytical grade. More details can be obtained from part 1.[1]

Procedure. Light Scattering Measurements. For the determination of χ_0, the Flory–Huggins parameter at infinite dilution of the polymer, LS measurements were performed on a commercially available FICA 50 instrument with special closed cells,[8] which allow measurements at temperatures close to the boiling point of the solvents under atmospheric pressure.

Because of the relatively low molecular weight of the polymer, only the data for the angle of 90° were evaluated according to

$$\frac{c}{i_{90}} = \frac{1}{M_w K} + \frac{2A_2 c}{K} \tag{1}$$

where c is the polymer concentration (mass/volume), i_{90} the galvanometer reading of the solution in excess of that of the pure solvent at the angle of 90°, and K a constant. A plot, typical for the present results, is shown in Figure 1. To obtain the second osmotic virial coefficient A_2 the constant K was determined from the intercept by means of the known molecular weight of the polymer. χ_0 values were then obtained according to

$$\chi_0 = \lim_{\varphi_2 \to 0} \chi = 0.5 - A_2 \rho_2^2 V_1 \tag{2}$$

where φ_2 is the volume fraction of the polymer of density ρ_2 and V_1 is the molar volume of the solvent.

Vapor pressure measurements were performed on an apparatus constructed in this laboratory[9,10] to obtain χ for weight fractions of the polymer ranging from 0.3 to 0.7. From the ratio of the equilibrium vapor pressure of the solvent above the solution p_1 to that above the pure solvent p_1^0 the Flory–Huggins parameter χ can be calculated according to

$$\ln \frac{p_1}{p_1^0} = \ln \varphi_1 + \left(1 - \frac{V_1}{V_2}\right)\varphi_2 + \chi\varphi_2^2 \tag{3}$$

where φ_1 and φ_2 are the volume fractions and V_1 and V_2 the molar volumes of solvent and polymer, respectively.

In order to measure p_1 and p_1^0, the flask containing the already partially degassed liquid was attached to the vapor pressure apparatus and frozen-in by means of cooling with liquid nitrogen slightly below its freezing point. Then the gas phase was pumped off until the vapor pressure had fallen below ca. 10 Pa. After that the vacuum line was disconnected, the solid melted, and the equilibrium pressure at room temperature registered. These freezing and melting cycles were repeated until the pressure was constant. The samples were then inserted into the thermostat, and (after adjustment of the completely evacuated pressure sensor head) the valve connecting the sample and the measuring device was opened so that the developing vapor pressure could be measured as a function of time. Figure 2 gives an example for data obtained in this manner. Due to inevitable leakage ($<10^{-2}$ mbar L s^{-1}) the pressure does not become constant, even after a long time; the equilibrium value was obtained by extrapolating the linear part of the dependence to zero time.

Inverse gas chromatography (IGC) was the method used to determine χ values in the limit of pure polymer ($w_2 \to 1$). The measurements were carried out with a modified Perkin-Elmer F 42 gas chromatograph as described before.[10] The column was prepared by coating 0.7 g of PBMA 2050 from methyl ethyl ketone solution onto Chromosorb WAW-DMCS (ca. 20 wt % loading) and packing the dried, coated support into a 0.75-m copper column of 4-mm inner diameter. The filled column was preconditioned over 1 day at 156 °C under N_2 flow. In order to determine the death time, a calibration with C_6–C_8 alkanes was performed.

V_g^0, the specific retention volumes (corrected to 0 °C), were calculated from

$$V_g^0 = (t_R/m_2)FJ_3^2(273.15/T_F)(p_F - p_w)/p_o \tag{4}$$

where t_R is the net retention time, F is the volumetric flow rate, T_F is the temperature of the flow meter, m_2 is the mass of the polymer in the stationary phase, p_o is the outlet pressure of the column, p_w is the vapor pressure of water at T_F, and p_F is the pressure of the carrier gas in the flow meter. The pressure gradient correction factor is given by

$$J_3^2 = 3/2[(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1] \tag{5}$$

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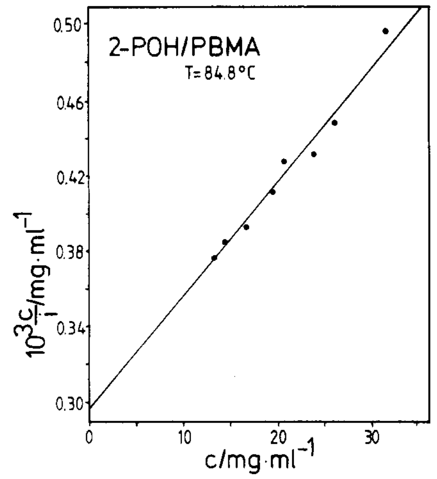

Figure 1. Typical light scattering data, exemplified for the system 2-propanol/poly(n-butyl methacrylate) 8.9 at 84.8 °C; i_{90} is the excess scattering of the solution over that of the solvent in arbitrary units observed at an angle of 90°.

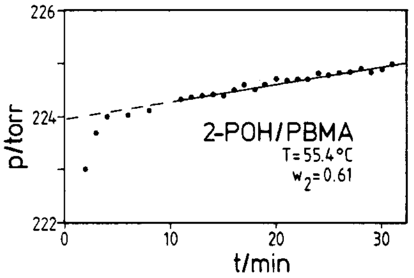

Figure 2. Typical example for the development of vapor pressures given for the system 2-propanol/poly(n-butyl methacrylate) 8.9 at a polymer concentration of 61 wt % and 55.4 °C; 1 Torr = 133.32 Pa.

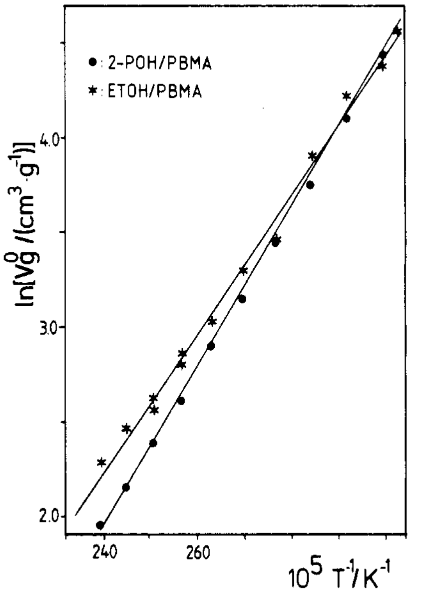

Figure 3. Temperature dependence of the specific retention volumes V_g^0 of inverse gas chromatography, corrected to 0 °C for PBMA 2050 and the solvents 2-propanol (●) and ethanol (✱).

where p_i is the column inlet pressure. Figure 3 gives the temperature dependence of V_g^0 for the two systems under investigation.

The Flory–Huggins interaction parameter χ_∞ can be calculated by

$$\lim_{w_2 \to 1} \chi = \chi_\infty = \ln\left(\gamma_{w_1}{}^{\infty} \frac{\rho_1}{\rho_2}\right) - 1 + \frac{M_1 \rho_2}{M_n \rho_1} \qquad (6)$$

Table I
Limiting Values of the Flory–Huggins Interaction Parameter χ_0 at Infinite Dilution for PBMA 8.9 in 2-Propanol and in Ethanol, As Obtained from Light Scattering Measurements.

2-propanol[a]		ethanol[b]	
T/°C	χ_0	T/°C	χ_0
27	0.492	40	0.509
41	0.463	50	0.493
56	0.432	60	0.484
71	0.406	70	0.480
86	0.399	80	0.477

[a] The accuracy is ca ±0.002 for 2-propanol, except for the highest temperature (±0.01). [b] The accuracy is ±0.01 for ethanol, except for the highest T (±0.02).

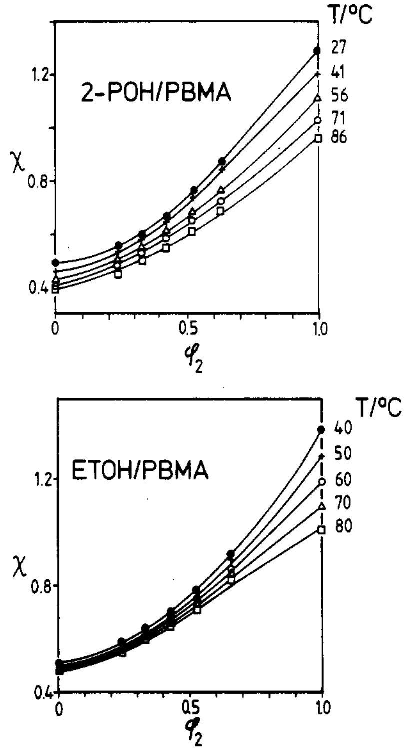

Figure 4. Flory–Huggins interaction parameter χ as a function of the volume fraction φ_2 of polymer for (a) 2-propanol/PBMA at the indicated temperatures; (b) ethanol/PBMA at the indicated temperatures. The data for infinite dilution were obtained by light scattering, the data in the limit of pure polymer by inverse gas chromatography, and all other stem from vapor pressure measurements.

(M_1 is the molecular weight of the solvent and M_n is the number-average molecular weight of the polymer) from the weight fraction based activity coefficient of the solvent at infinite dilution

$$\ln \gamma_{w_1}{}^{\infty} = \ln \frac{273.15R}{M_1 p_1{}^0 V_g{}^0} - \left[p_1{}^0 \frac{B_{11} - V_1{}^0}{RT} + p_0 \right]_3^4 \frac{2B_{13} - V_1}{RT} \qquad (7)$$

where B_{ij} are the corresponding second pressure virial coefficients[10] and the index 3 stands for the inert gas.

The vapor pressure $p_1{}^0$ of 2-propanol and ethanol at the column temperature T were calculated from Antoine's equation; the coefficients given in eq 8 and 9 were obtained by fitting of the present data.

$$\text{2-POH:} \quad \log (p_1/\text{Pa}) = 9.646 - \frac{1257}{188.7 + T/°\text{C}} \qquad (8)$$

$$\text{ETOH:} \quad \log (p_1/\text{Pa}) = 9.713 - \frac{1313}{200.8 + T/°\text{C}} \qquad (9)$$

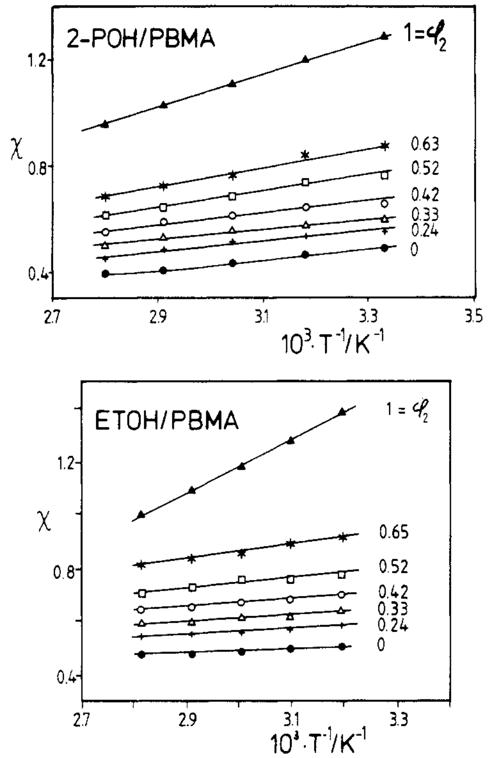

Figure 5. Flory–Huggins interaction parameter χ at the indicated volume fractions φ_2 of polymer as a function of the inverse temperature for the systems and data of Figure 4.

Results

Light Scattering. χ_0 values at infinite dilution, obtained from the second osmotic virial coefficients A_2 of the systems 2-POH/PBMA 8.9 and ETOH/PBMA 8.9 according to eq 2, are listed in Table I.

Inverse Gas Chromatography. By means of eq 4–9, the following χ_∞ values as a function of temperature were obtained for 2-POH/PBMA 2 050 (eq 10) and ETOH/PBMA 2050 (eq 11):

$$\text{2-POH:} \quad \chi_\infty = (-0.738 \pm 0.067) + (608 \pm 25)T^{-1}/\text{K}^{-1} \tag{10}$$

$$\text{ETOH:} \quad \chi_\infty = (-1.89 \pm 0.20) + (1026 \pm 73)T^{-1}/\text{K}^{-1} \tag{11}$$

From the temperature dependence of V_g^0, which can be represented by

$$\text{2-POH:} \quad \ln (V_g^0/\text{cm}^3\ \text{g}^{-1}) = -7.922 + 4110T^{-1}/\text{K}^{-1} \tag{12}$$

$$\text{ETOH:} \quad \ln (V_g^0/\text{cm}^3\ \text{g}^{-1}) = -6.441 \pm 3616T^{-1}/\text{K}^{-1} \tag{13}$$

ΔH_s, the molar heat of solution of the gaseous solvents is accessible according to

$$-R\,\frac{\partial \ln V_g^0}{\partial(1/T)} = \Delta H_s \tag{14}$$

The following values were obtained: −(34.17 ± 0.28) for 2-POH and −(30.07 ± 0.72) kJ/mol for ETOH.

Vapor Pressures and $\chi(\varphi_2;T)$. Figure 4 contains the χ values obtained with the different methods as they vary with φ_2, the volume fraction of the polymer, for 2-POH (Figure 4a) and ETOH (Figure 4b); for both solvents measurements were carried out at five temperatures, so that it is possible to obtain the enthalpy and the entropy part[12] of χ according to

$$\chi_H = \frac{\Delta H_1}{RT\varphi_2^2} = -T\left(\frac{\partial\chi}{\partial T}\right) \tag{15}$$

and

$$\chi_S = -\frac{\Delta S_1^R}{R\varphi_2^2} = \chi - \chi_H \tag{16}$$

where ΔH_1 is the enthalpy and ΔS_1^R the residual entropy of dilution. Figure 5 shows the evaluation of the data presented in Figure 4 according to the above equations. Straight lines are obtained in the case of ETOH within the entire T range (Figure 5b), whereas a slight curvature results for 2-POH at high dilution and high temperatures. The above evaluation makes it possible to break the concentration dependence of χ up into that of its enthalpy and its entropy constituents χ_H and χ_S. Figure 6, parts a and b, shows the results for the solvent 2-POH and the two extreme measuring temperatures; Figure 6, part c and d gives the corresponding data for ETOH. It should be noted that, according to the present experimental results, the entropy contributions do not depend on T. For comparison, the behavior of a standard system, namely that of cyclohexane/poly(styrene) (CH/PS), is given in Figure 7; the curves have been calculated from published data[13] for 30 °C.

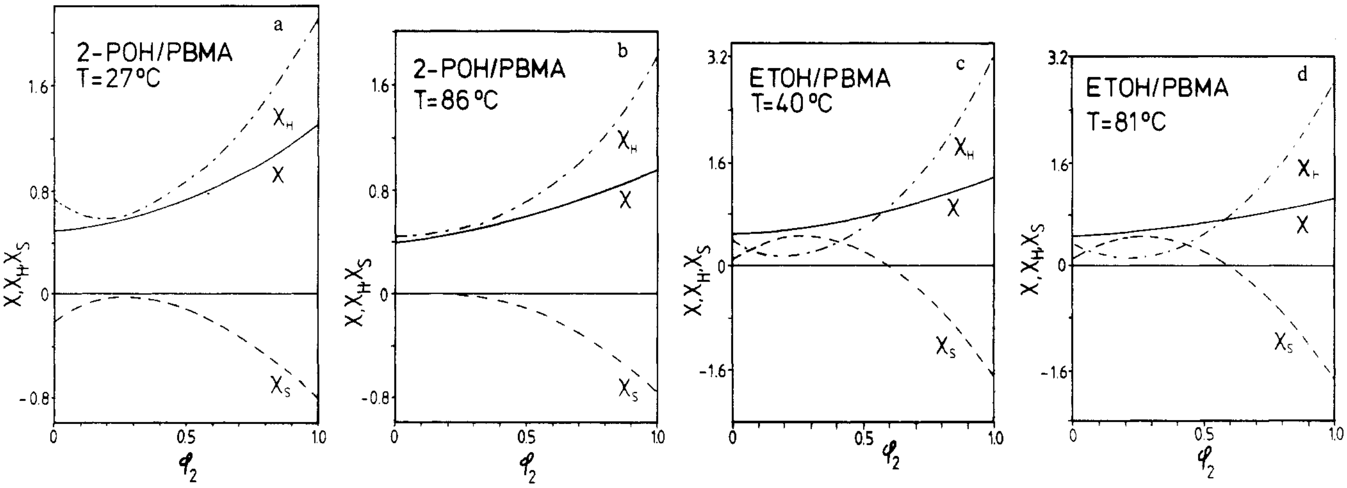

Figure 6. Concentration dependence of the Flory–Huggins interaction parameter χ, of its enthalpy χ_H, and its entropy part χ_S for the system 2-propanol /PBMA at (a) 27 °C and (b) 86 °C and of the system ethanol/PBMA at (c) 40 °C and (d) 81 °C.

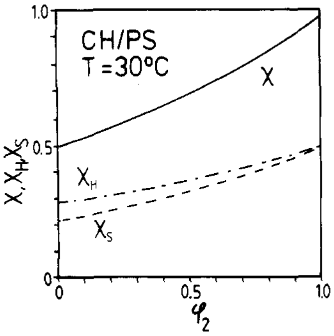

Figure 7. Concentration dependence of the Flory–Huggins interaction parameter χ, of its enthalpy part χ_H, and entropy part χ_S for the system cyclohexane/polystyrene at 30 °C, calculated from published data.[13]

Discussion

With both θ-solvents of PBMA, the concentration dependence of χ is more pronounced at the lower temperatures, as shown in Figure 4. Furthermore, the differences between the individual isotherms become more significant at higher polymer concentrations. These observations can be attributed to free volume effects which are more pronounced for high dilution and high temperatures.[10]

A comparison of the results observed for the gelling systems 2-POH/PBMA and ETOH/PBMA with those of the nongelling system CH/PS shows that the concentration dependence of χ in all three systems is similar, while the enthalpic and entropic contributions follow clearly different lines in the former two systems as compared with the latter. For CH/PS, χ_H and χ_S are always positive and increase slightly and monotonically with polymer concentration (Figure 7). For 2-POH/PBMA and ETOH/PBMA (Figure 6), on the other hand, only χ_H is positive, irrespective of composition, whereas χ_S assumes considerably negative values, particularly at high polymer concentrations. Furthermore, the concentration dependence of these parameters is more complicated than normal, showing pronounced minima in $\chi_H(\varphi_2)$ and maxima in $\chi_S(\varphi_2)$ at $0.1 < \varphi_2 < 0.3$ and the lower temperatures of present interest.

In order to rationalize the results shown in Figure 6 for the systems exhibiting the coocurrence of phase separation and thermoreversible gelation, three different concentration regimes are distinguished:

(i) In the high polymer concentration range suitable intercalations of butyl side groups allow a relatively ordered packing of polymer chains. The introduction of solvent molecules here would involve the breakage of highly ordered, energetically very favorable contacts between polymer segments and consequently result in large positive χ_H values and large negative χ_S values.

(ii) A transition region is centered around volume fractions of the polymer of ca. 0.2. Here the ordering of side groups still exists but in a looser way that allows the introduction of solvent molecules between these groups such that the hydrocarbon part of the solvent molecules can favorably interact; this insertion, which could be looked at as a "cointercalation", leads to lower χ_H and higher χ_S values. Examples for an analogous participation of solvent molecules in the structuring of polymer solutions have been reported for the gelation of atactic PS[14] and poly(acrylates).[15,16]

(iii) In the region of highly dilute polymer solutions the mutual orientation of contacting segments becomes almost random and the introduction of solvent molecules involves no particular ordering or disordering effects.

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Registry No. PBMA, 9003-63-8; 2-POH, 67-63-0; EtOH, 64-17-5.

References and Notes

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