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Polydioxolane in Aqueous Solutions. 1. Phase Diagram

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ABSTRACT: A polydioxolane sample (M_W = 50 000) was studied in aqueous solutions by differential scanning calorimetry, turbidimetry, and densimetry. Its phase diagram was constructed between −100 and +100 °C in the whole range of composition. The solubility domain is limited at higher temperature by the demixing curve (lower critical solution temperature (LCST) = 70 °C) and at lower temperature by the melting point of a hydrate (containing three water molecules per monomer unit), and this domain does not extend beyond a polymer content of 50% weightwise. The excess mixing volume is found to be negative and to go through a minimum at 45 °C. These findings are compared to those of PEOG in water: excess volumes are much lower than those of PEOG, and this is consistent with the much lower solubility deduced from the comparison of the phase diagrams of both polymers.

Introduction

Despite their increasing importance in industrial applications as well as in fundamental research, relatively little work has been devoted to the description of the properties of nonionic water-soluble polymers in aqueous solutions.

Polyacrylamide (PAM) and poly(ethylene oxide glycol) (PEOG) which are two of the most typical polymers of such type, exhibit completely different behaviors in dilute water solutions. The former behaves like a nonpolar polymer in an organic solvent above its θ point (upper critical solution temperature (UCST) = −8 °C): its macromolecular expansion and its second virial coefficient (A_2) are increasing functions of temperature.[1-3] The PEOG–water system on the other hand presents a "closed loop solubility diagram" with a LCST value around 100 °C:[4,5] therefore, in the range of temperature between 0 and 100 °C, its coil dimensions and A_2 decrease with increasing temperature. Such behavior discrepancies are attributed to their fundamental difference in nature:[6] the PEOG solubility below 100 °C is due to the strong hydration of the monomer units via hydrogen bonding between water molecules and oxygen of the ether functions, and its phase separation upon heating stems from the release of the hydration molecules. PAM which is very polar because of the presence of amide groups does not need any specific hydrogen bonding to be soluble. Many theorical attempts were made in order to explain the so-called closed loop diagrams and predict the binodal demixing curve: the first models were based upon highly directional bonds between water and polymer molecules (Ising model[7] or models based on mechanical statistics).[8] A more recent approach of solvation-induced reentrant phase separation from Tanaka[9] introduces into the Flory–Huggins theory[10] solvation equilibrium giving the fraction of "free" and "solvated" sites on the chain as a function of temperature. Blandamer et al.[11] and Kjellander et al.[12] explained the solubility of PEOG in water by a structural model where a simple polymer chain could be incorporated in an hexagonal water lattice. This model suggests that the difference of solubility in water of the different polyethers (poly(methylene oxide) (POM) insoluble and poly(propylene oxide) (PPO) soluble only for low molecular weights) is mainly due to the fact that only PEOG satisfies geometrical conditions to allow the formation of a continuous network of water molecules around the chain. For instance, the methyl groups in PPO are assumed to constitute sterical hindrance to the formation of water structure. However, there is some evidence that the amount of "bound" water is slightly modified by the introduction of PPO units (up to 50%) in PEOG–PPO copolymers.[14] Finally, the Saeki et al. approach,[5,13] which is derived from the Flory–Huggins theory and from the corresponding state principle of Prigogine,[15] shows that it is possible to explain a closed loop diagram without taking into account the solvation effects but by considering the peculiar thermodynamic properties of water. However this latter approach does not provide a satisfactory explanation for the behavior of PAM.

It should be kept in mind that an important characteristic of these poly(ether oxides) is their ability to crystallize in the bulk. The influence of such a property can influence the behavior of those polymers in a solvent, and different studies have dealt with the crystallization of PEOG at low temperature in the presence of water.[16-19] It has been generally found that PEOG forms a eutectic with three water molecules per monomer unit. Random PPO–PEOG copolymers and PPO of low molecular weight do not produce a crystalline eutectic,[16] which is not really surprising since neither of these polymers is crystalline. One can remark that no study ever tried to relate the behavior at low temperature and the solubility diagram at higher temperature.

Because of the lack of reliable experimental data on the whole phase diagrams and on the behavior of water-soluble polymers in aqueous solutions, we have undertaken a systematic series of studies aiming at understanding the relative role played by a simple hydrophobic–hydrophilic balance and by the more specific effects of the chain structure, its accessibility to water molecules binding, and its crystalline structure. For instance, a most surprising behavior is the insolubility of POM in water for which a prediction based upon the solubility parameter should lead to a better solubility than PEOG. Copolymers whose composition is continuously varying between that of POM and that of PEOG appear to be very good models to understand such complex problems.

The present paper deals with poly(1,3-dioxolane) which is a perfectly alternating copolymer made of units constitutive of POM and PEOG:

$$\text{PDXL: } [-CH_2-CH_2-O-CH_2-O-]_n$$

The structure of the different crystalline forms of this polymer was widely studied,[20-27] and some of its properties in organic solvents[28] are also known. Its behavior in water is until now completely unknown, and we will discuss the phase diagram established from differential scanning calorimetry and turbidimetry measurements. The strength

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Table I
Characterization of the Polydioxolane Sample Used

	solvent	M_w	polydispersity
SEC	water	28 000[a]	1.6[a]
	THF	53 000[b]	1.5[b]
LS	water	50 000	

[a] Using PEOG calibration. [b] Using universal calibration with the following viscosity law for PDXL in THF: $[\eta] = 0.017M_w^{0.73}$.[28]

of the interactions between the polymer and water is studied through densimetric investigations.

Experimental Section

Polymer Sample. The polydioxolane sample (PDXL) was prepared by cationic polymerization in methylene chloride at -25 °C using trifluoromethanesulfonic anhydride.[29] It was terminated with sodium methanolate, precipitated in methanol at -40 °C, then washed with cold methanol, and dried under vacuum at room temperature. We have also used for comparison a commercial sample of poly(ethylene oxide glycol) (PEOG) from Merck (weight average molecular weight 35 000).

The PDXL sample was characterized by light scattering (LS) and size exclusion chromatography (SEC), as shown in Table I. The weight average molecular weight values (M_W) obtained by LS in water and SEC in tetrahydrofuran (THF) are in good agreement. On the other hand, the value obtained by SEC in water using PEOG calibration is significantly lower, evidence of the smaller expansion of PDXL in water as compared to that of PEOG.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC 7 microcalorimeter equipped with a thermal analysis data station (TADS) was employed. The desired quantities of polymer sample and water were introduced into a sample pan, which was then tightly sealed. The pans were heated for 24 h at 80 °C and then kept for 1 week at room temperature, to ensure thorough homogenization. The weight of each pan was determined prior to taking any data in order to obtain the concentration of the system in grams per gram. Cooling and heating rates ranging between 2 and 10 °C/min were used. The temperature interval was either -50 to +70 °C or -80 to 0 °C, and the apparatus calibration was carried out with gallium and water.

Turbidimetry. For the more dilute solutions (polymer concentration $C_P < 0.25$ g/g), the cloud points T_t were measured with a Mettler FP81 apparatus. The solutions contained in cylindrical cells (1-mm i.d. and 79-mm length) were heated at a rate of 2 °C/min.

For the more concentrated solutions, the cloud points were determined by visual observations. The solutions contained in 10-mm-diameter tubes were thermostated at different temperatures.

Dilatometry. The density of the pure polymer sample was measured by classical dilatometry. The dilatometers have two parts: a reservoir of 1.7 mL and a capillary of 0.4-mm inner diameter and 400-mm length, connected by a spherical ground joint. The calibration of these dilatometers was made with mercury distilled under vacuum. The measurements were carried out with 500 mg of PDXL sample. The thermostat temperature (T) was controlled by a quartz thermometer. The stability is $\pm 2 \times 10^{-3}$ °C for 25 °C < T < 44 °C, and $\pm 10^{-2}$ °C for 45 °C < T < 70 °C. The reproducibility of the specific volume measurements is 6×10^{-4} mL/g.

The sample was submitted to several cycles of heating to 100 °C and cooling to room temperature in order to eliminate traces of air.

Densimetry. The density of aqueous polymer solutions was obtained with a Kratky densimeter DMA02 equipped with a cell constructed in our laboratory.[30]

Light Scattering. Light-scattering experiments were performed on an apparatus which was built in this laboratory[31] and is equipped with a laser working at 6320 Å, in a scattering-angle range between 30 and 150°. The refractive index increment was measured with a Brice Phoenix refractometer.

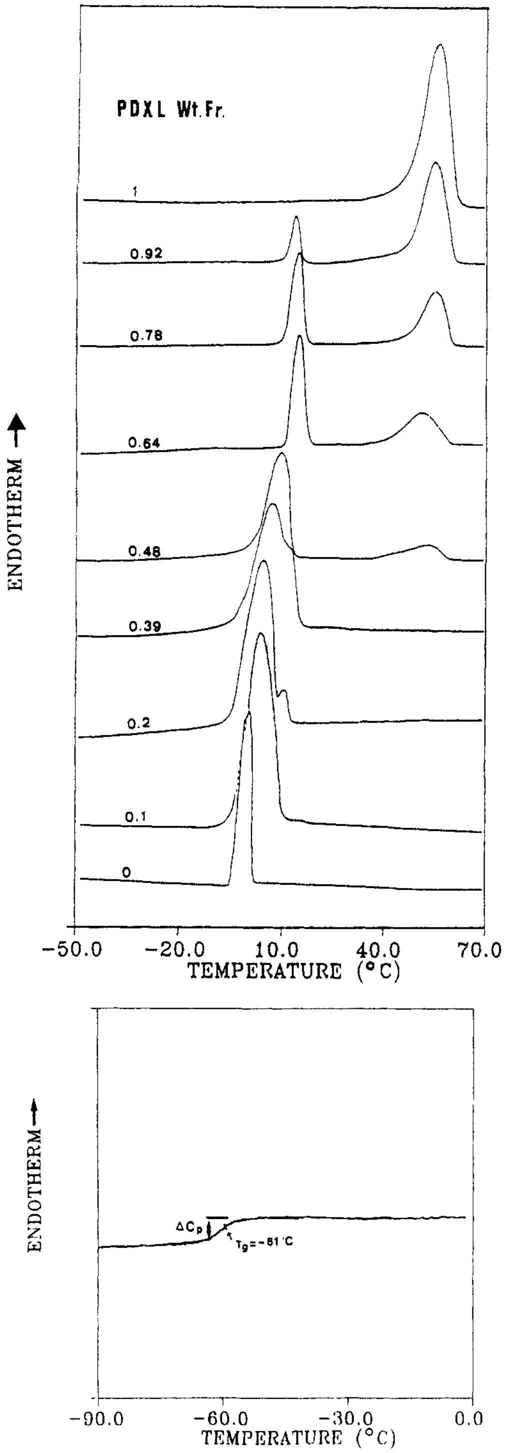

Figure 1. (a, Top) DSC traces obtained by heating PDXL-water systems at different polymer concentrations (expressed in g/g of solution). (b, Bottom) example of a DSC trace exhibiting a glass-rubber transition ($C_P = 0.92$ g/g).

Results and Discussion

DSC Experiments. The DSC measurements were performed for polymer concentrations (C_P) ranging from 0 to 1 g/g. Figure 1a gives some characteristic DSC traces obtained by heating water-PDXL systems of various compositions. Three melting endothermic peaks are observed around 55, 13, and 0 °C, respectively, and also at lower temperature an increase of the specific heat is observed which is characteristic of the glass-rubber transition (Figure 1b).

(i) For the pure polymer, one observes a peak at 55.1 °C, which corresponds to its fusion and which is in agreement with published data.[20] The degree of crystallinity (X_m)

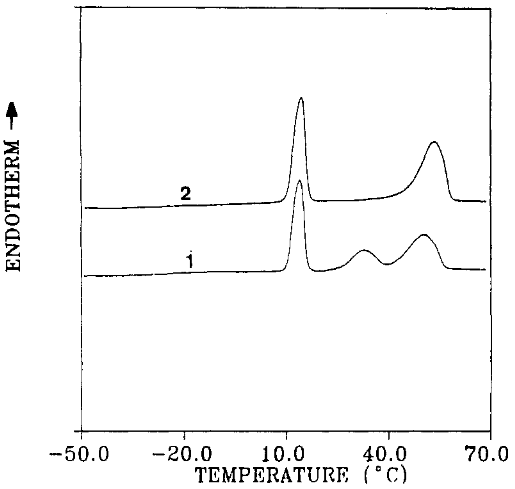

Figure 2. Comparison of DSC traces obtained with two different cooling rates (1, 10 °C/min, 2, 2 °C/min) before measurements were made upon heating.

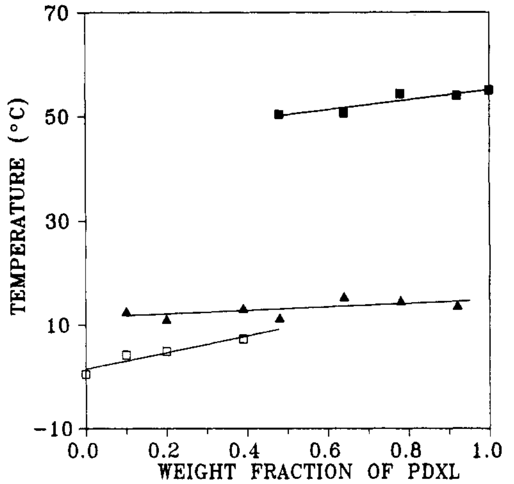

Figure 3. Melting temperature of the water (□), the hydrate (▲), and the polymer (■) versus polymer concentration.

can be calculated from the ratio between the measured melting enthalpy (107.5 J/g) and the melting enthalpy of crystalline PDXL (225.4 J/g).[21] A value of 47.5% was found. It was shown by Archambault et al.[25] that the proportion of crystalline material depends on the quenching conditions. X_m was found to vary from 33% to 50% when the quenching temperature (T_q) increased from 0 to 20 °C. There is then a discrepancy with our results, since in our case $T_q = -50$ °C.

This peak is also observed for systems where the concentration is higher than 0.48 g/g. It should be pointed out that the rate of cooling prior to the measurement (carried out by heating) is of paramount importance: Figure 2 shows the presence of two peaks when the cooling rate is 10 °C/min and the presence of only one when it is 2 °C/min. All further experiments were then carried out under the latter conditions. The maximum values of this peak (T_{mP}) are slightly shifted down to 50 °C for $C_P = 0.48$ g/g (see Figure 3). This behavior is quite different from PEOG which exhibits the usually strong decrease of the polymer fusion temperature by more than 40 °C within the same concentration range.[16-19] The polymer melting enthalpy (ΔH_{mP}) decreases with decreasing polymer concentration and for $C_P = 0.48$ g/g is close to 0 J/g (Figure 4).

(ii) The second peak is visible throughout the spectrum and its maximum (T_{mH}) is constant at 13 ± 2 °C. Its surface goes through a maximum around 0.55 g/g (Figures 3 and 4). This peak, located between the melting temperatures of polymer and water, may correspond to a very stable hydrate whose composition is constant throughout the whole composition domain.

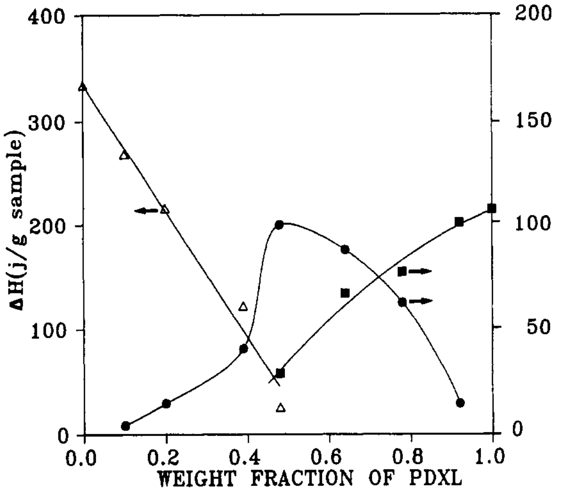

Figure 4. Melting enthalpy of the free water (ΔH_{mw}, ▲), the hydrate (ΔH_{me}, ●) and the polymer (ΔH_{mp}, ■) versus polymer concentration.

(iii) The third endothermic peak can be attributed without any ambiguity to the free water fusion. Its surface is a decreasing function of the polymer concentration. By deconvolution of this peak and that of the hydrate melting at 14 °C, we have obtained the melting enthalpy of water ΔH_{mW} which is plotted versus concentration in Figure 4. ΔH_{mW} reaches zero for $C_P = 0.55$ g/g. Then one can consider that above this concentration, no free water molecules remain present in the system. This threshold concentration corresponds to 3.36 mol of water/monomer unit, comparable to that found for water (3/1). On the other hand it corresponds only to 1.7 molecules of water/oxygen atom, which is half the value generally accepted for PEOG.[16-18,32] It looks as if an ethoxy group is hydrated the same way in both polymers while a methoxy group is not hydrated and remains free, therefore capable of participating in other interactions. Due to the partial superposition of the water melting peak with the previous one, it is rather difficult to obtain with great accuracy its maximum value T_{mW}; the deconvolution procedure nevertheless leads to the variation given in Figure 3 where T_{mW} is seen to slightly increase with polymer concentration.

Figures 5 and 6 display the dependences of the glass transition temperature T_g and the corresponding change in specific heat ΔC_P on the composition of the systems under study. At about $C_P = 0.6$ g/g T_g and ΔC_P pass through a minimum and a maximum, respectively. This composition is close to that of the maximum of the melting enthalpy of the hydrate. The same type of behavior was already described for PEOG in water.[17,19]

Turbidity Measurements. It is well-known that the solutions of water-soluble polymers exhibit particular solubility diagrams described as closed loop; PEOG is a typical example.[4,5] The more accessible demixing line is that which corresponds to the LCST (lower critical solution temperature), which is close to 100 °C for high molecular weight PEOG. Figure 7 displays a characteristic demixing curve that we have obtained with a PEOG sample of $M_W = 35\,000$. It exhibits the classical features with a minimum at the critical concentration 0.04 g/g in agreement with all published data. Beyond this minimum, the demixing temperature is an increasing function of the polymer concentration. The cloud point of a sample of $C_P = 0.6$ g/g lies above 150 °C, out of the temperature range

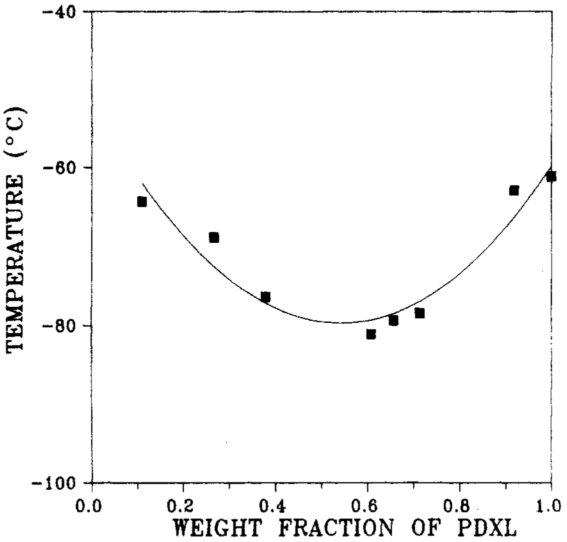

Figure 5. Temperature of the glass–rubber transition T_g versus polymer concentration.

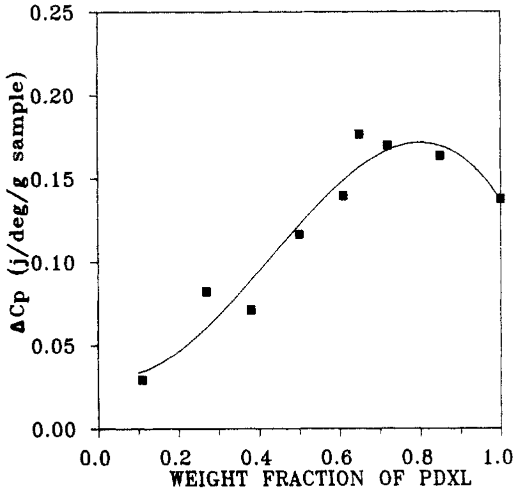

Figure 6. Specific heat increment ΔC_P at T_g versus polymer concentration.

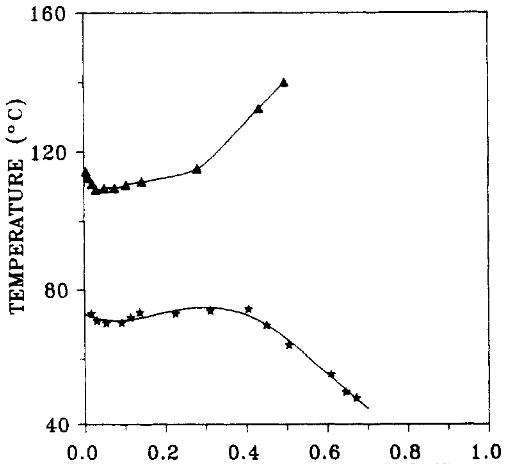

Figure 7. Demixing curve of the PDXL sample (★) obtained upon heating as compared to that of PEOG of the same molecular weight (▲).

of the apparatus. In Figure 7, the lower curve is relative to PDXL and exhibits a different shape: there is a first minimum at around the same C_P as for PEOG, but the demixing temperature reaches a kind of plateau for $0.2 < C_P < 0.4$ g/g and strongly decreases above 0.4 g/g. Moreover the critical temperature at $C_P = 0.04$ g/g is 69 °C, a value significantly lower than that of PEOG of the same molecular weight. These results evidently reflect not only the lower solubility of PDXL in water but also its non-classical behavior.

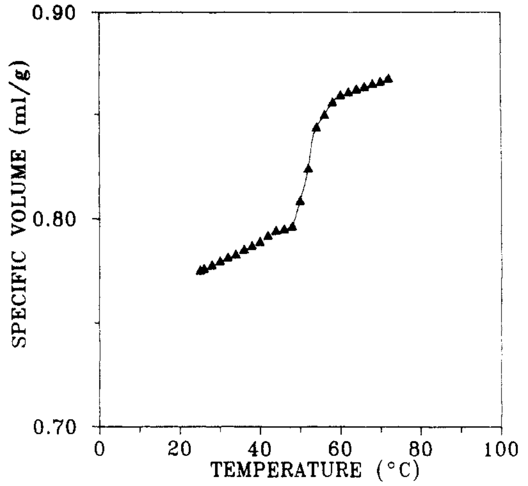

Figure 8. Specific volume of pure PDXL as a function of temperature.

It is very important to describe in detail the procedure used to obtain the demixing curves of Figure 7 if one wants to obtain reproducible results: the PDXL samples were homogenized in sealed glass tubes at 80 °C for 1 day and then cooled to room temperature; they were then completely transparent; they were kept at this temperature for less than 1 h, and then, they were heated until turbidity appeared; the cloud points were recorded and are plotted in Figure 7. The situation was different when $C_P > 0.5$ g/g: if the transparent solution was kept at room temperature for several days, the solution lost its fluidity and its transparence and took the typical appearance of a semicrystalline polymer; it was indeed shown by DSC that PDXL had crystallized. When this mixture was heated again, PDXL melted at 55 °C but the solution remained turbid as observed with a pristine solution (i.e. which was not aged at room temperature); upon cooling to room temperature this turbidity disappeared and the solution turned perfectly transparent again. This kind of reversible behavior was shown to take place over and over again. Therefore, when $C_P > 0.5$ g/g, the binodal curve is relative to a metastable state in which crystallization, corresponding to a more stable form, did not have time to occur. We will comment on this point again in the discussion.

Density Measurements. (i) Pure Polymer. In Figure 8, the temperature dependence of the specific volume is presented. The values were recorded only upon heating, at intervals of 2 °C, observing a 30-min stabilization period for each temperature of measurement. The transition corresponding to the polymer melting point occurs at 54 °C, in excellent agreement with the value obtained by DSC (55 °C). The specific volume of PDXL can be written as

$$v_{\mathrm{P_a}} = 0.813\,71 + 7.545 \times 10^{-4}T \qquad (1)$$

$$v_{\mathrm{P_c}} = 0.750\,71 + 9.713 \times 10^{-4}T \qquad (2)$$

for the melt and the semicrystalline states, respectively (T being expressed in °C). The corresponding values are slightly higher than those given by Archambault et al.[25] for a PDXL sample of lower molecular weight ($M_W = 6700$), but it must be pointed out that their measurements were made using a much higher heating rate (2 °C/min without a stabilization period) and the polymer sample was

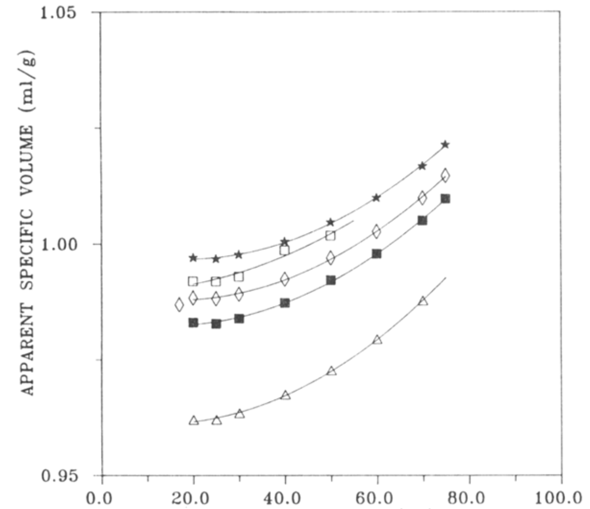

Figure 9. Apparent specific volume of PDXL in water as a function of temperature for different concentrations: $C_P = 0.025$ g/g (★), 0.05 g/g (□), 0.07 g/g (◇), 0.10 g/g (■), 0.20 g/g (△).

quenched at a lower temperature (0 °C) instead of 25 °C. Sasaki et al.[22] published a density value of PDXL equal to 1.29 g/mL at 25 °C, very close to our value of 1.2903 g/mL. We have calculated a degree of crystallinity of 47% at 25 °C from expression 1 and the density value of the pure crystal given in ref 22. This value is close to that obtained from DSC measurements though T_q was much higher in this case.

This value is close to those obtained by Archambault et al.[25] by densimetry at 25 °C and by us using DSC for $T_q = -50$ °C. Therefore, it seems that, at least for our sample, X_m is not as dependent upon T_q as observed by these authors but is more likely a function of the overall treatment of the sample prior to the measurements.

(ii) Aqueous Solutions. We have measured by densimetry the specific volumes of the solutions for $0 \le C_P \le 0.2$ g/g (Figure 9). These values increase normally with temperature. The apparent specific volume of the polymer in solution V_2 is calculated from the classical law:

$$V_2 = V_1 + \frac{V_{12} - V_1}{C_P} \tag{3}$$

V_1 and V_{12} are the specific volumes of the solvent and of the solution, respectively. For PDXL, we obtain $V_2 =$ 0.792 mL/g at 25 °C. For polymers, it is usual to discuss V_2 values in terms of V_{m2} partial molar volume ($V_{m2} = V_2 m_P$, m_P is the molecular weight of the monomer unit). We find a V_{m2} value of 58.6 mL/mol for PDXL at 25 °C. It is known that V_{m2} of a large number of molecules, including nonionic polymers, can be calculated from a simple law of additive partial molar volume group contributions.[33-36] By using for each constitutive group of PDXL the values given in ref 36 for aqueous solutions ($V_{CH} = 5.3$, $V_H = 10.7$ and $V_{-O-} = 4.1$ mL/mol), one finds $V_{m2} = 56.2$ mL/mol, a value which differs by −2.4 mL/mol from the experimental one. Discrepancies of the same sign were already observed between the calculated and experimental V_{m2} values in the case of PEOG and ethylene oxide–propylene oxide copolymers (PEO–PPO) by Louai et al.[14] These authors have proposed that the –O– contribution could be 4.8 instead of 4.1 mL/mol at 25 °C in water. By applying such a correction, the calculated value for PDXL becomes 57.6 mL/mol, which is closer to the experimental value. It must be pointed out that this usual additivity law does not take into account the specific solvation of the polymer according to its chemical structure.

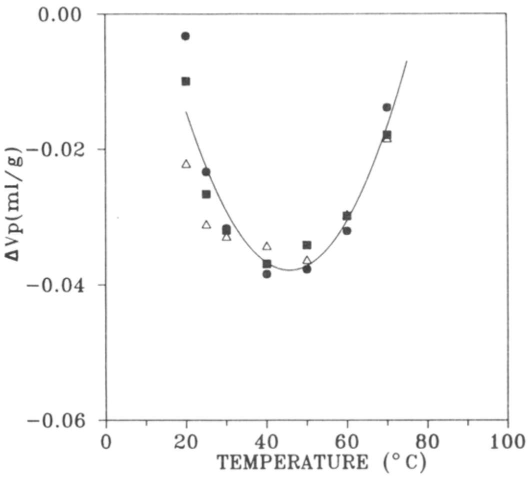

Figure 10. Excess mixing volume of PDXL in water versus temperature for different concentrations: $C_P = 0.07$ g/g (●), 0.10 g/g (■), 0.20 g/g (△).

It is more interesting to discuss the excess mixing volume which is expected to reflect such interactions. In Figure 10, the ΔV_P (mL/g) is plotted as a function of temperature for different polymer concentrations.

$$\Delta V_P = V_{Pa} - V_2 \tag{4}$$

is the difference between the specific volume of the pure polymer in the melt (relation 1) and its apparent specific volume in water at the same temperature. Here, we consider the melt as the reference state since DSC measurements show that no crystalline phase exists any more in the concentration range studied by densimetry.

ΔV_P is always negative in the whole temperature range. This means that the solubilization of PDXL in water corresponds to a loss of volume with respect to the volumes of the polymer and water before mixing. Such an effect is generally attributed for PEOG to the formation of hydrogen bonds between ether oxygens and water molecules, and the molar volume of the bound molecules is assumed to be lower than that of free water molecules.[37,38] Some authors have even proposed a structural model where PEOG could be incorporated in the hexagonal water lattice.[12,39] In fact for PEOG, the predicted molar excess volume is −18 mL/mol, while the experimental value does not exceed −4.4 mL/mol at 25 °C.

Figure 10 also shows that ΔV_P goes through a minimum at $T = 50$ °C. At this minimum ΔV_P corresponds to $\Delta V_{m2} = -2.96$ mL/mol, whose absolute value is much lower than that predicted by Kjellander et al.[12] and lower than that obtained for PEOG and for PEO–PPO copolymers at the same temperature. This indicates a lower effect of solvation or hydration for PDXL as compared to these polymers. Moreover, the shape of the variation of ΔV_P versus T seems to be quite general, since a minimum was already found for PEOG and for PEO–PPO copolymers,[14] with a minimum slightly shifted toward lower temperatures (25 °C) in the latter cases. In all three cases, ΔV_P tends to zero at higher temperature, when T reaches the critical demixing temperature, and also at lower temperature, when T approaches the melting temperature of the hydrate or of the free water in the case of PDXL or PEO–PPO copolymers, respectively.

Discussion

Phase Diagram. For the sake of clarity, we have plotted in Figure 11 three phase diagrams (PD). Part 1 corresponds to a schematized PD of the PEOG–water system deduced from different literature data.[16-19] Parts 2 and

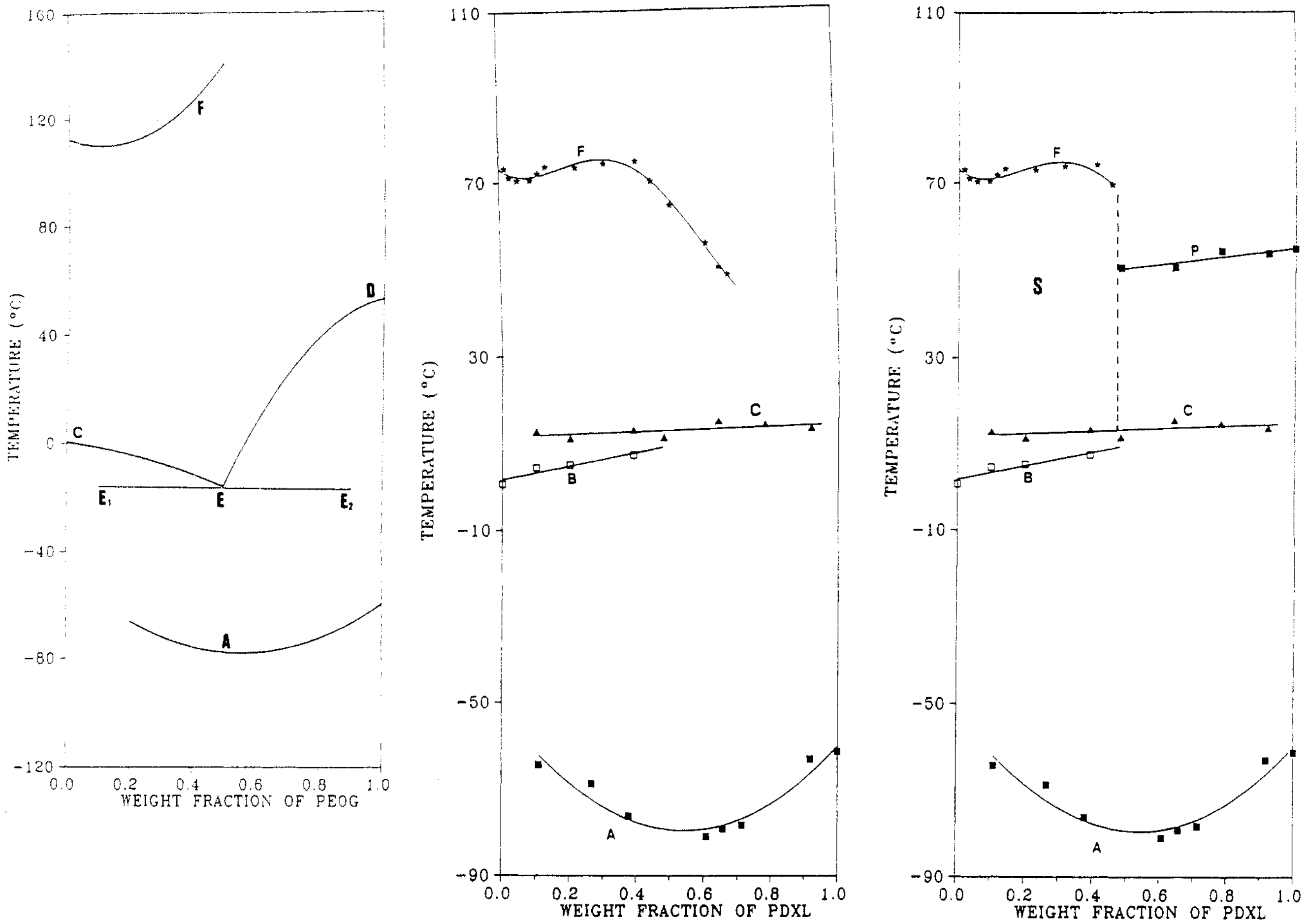

Figure 11. (1, Left) phase diagram of PEOG and water: line A, glass–rubber transition; line E_1EE_2, eutectic melting; line CE, water melting; line ED, polymer melting; F, demixing binodal curve. (2 and 3, Middle and right) phase diagrams of PDXL and water: line A, glass–rubber transition; line B, water melting; line C, hydrate melting; line F in 2, apparent demixing curve (see text); line F in 3, demixing curve for systems at equilibrium; line P in 3, polymer melting.

3 display two possible alternative PD for the PDXL–water system. We will discuss the main features of these two systems separately.

The PD of Figure 11-1 exhibits all the characteristics in the low temperature range of a system where crystallization occurs with formation of a eutectic and at higher temperature the binodal line is simply that expected from Flory–Huggins theory.

Lines CE and ED which represent the variation with composition of the melting points of water, T_{mW}, and polymer, T_{mP}, respectively, meet at point E which corresponds to a eutectic. The T_{mW} variation was well explained by Hager et al.[16] in terms of the Flory–Huggins theory applied to the calculation of the depression of the solvent melting point in a binary mixture.[40] Calculations and experiments are in good agreement by taking for the Flory interaction parameter between the PEOG and water the value $\chi_{12} = 0.05$, which corresponds to good solvent conditions. On the contrary, the decrease of T_{mP} (melting temperature of the polymer) by dilution is qualitatively well predicted through the same theoretical approach, although a downward curvature of T_{mP} versus C_P is observed while an upward curvature is predicted.[16] Moreover, there is some uncertainty concerning the true nature of this so-called eutectic: according to some authors[16,17] it is a true eutectic, i.e. made of intimately mixed water and polymer, whereas for others[18] it corresponds to a eutectic between a definite compound—or hydrate of two water molecules per monomer unit—and water. Besides, others propose that a mono- or trihydrate could exist depending on the polymer concentration.[19]

Parts 2 and 3 of Figure 11 represent two PDs of the PDXL–water system, which are the same at $C_P < 0.5$ g/g but which are strikingly different for $C_P > 0.5$ g/g, depending on the thermal treatment of the samples. In Figure 11-2, the PDXL–water mixtures were kept only for short periods of time at low temperature so that crystallization of PDXL did not take place. In this case, at higher temperature we only observe a cloud point, as given by line F. Figure 11-3 corresponds to solutions kept at low temperature long enough to allow PDXL crystallization to take place: in this case the melting point is observed around 55 °C (line P).

The PDs of Figures 11-3 and 11-1, which both correspond to conditions where PDXL and PEOG can crystallize, are remarkably different since the former one shows practically horizontal lines for each melting point. This suggests that the melting of the polymer (line P), of the hydrated polymer (line C), and of the free water present (line B) occurs in already almost demixed systems. Water has to be a poor solvent of both the polymer and its hydrate in this temperature range.

The theoretical approach used by Hager et al.[16] for PEOG allows one to account for this behavior: very small variations of T_{mW} and of T_{mP} are predicted when $\chi_{12} \gg 0.5$. This behavior is consistent with the Zimm plot of PDXL in water at 25 °C, which is shown in Figure 12: it exhibits a negative second virial coefficient and values of the radius of gyration unexpectedly high (500 Å) for such a value of the molecular weight and that increase with increasing concentration. These values as well as the curvature observed at low angle are evidences of an

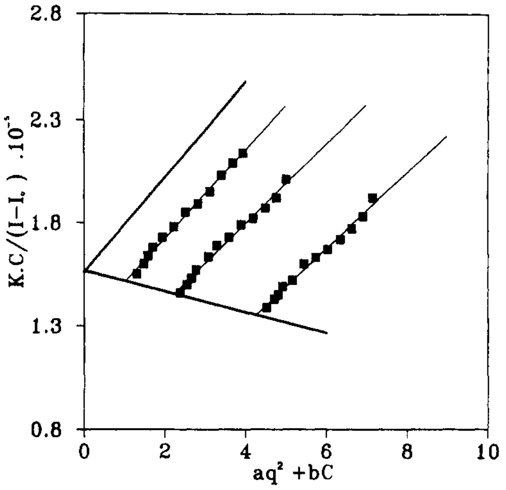

Figure 12. Zimm plot of dilute solutions of PDXL in water at 25 °C ($1 \times 10^{-3} < C_P < 4 \times 10^{-3}$ g/mL).

aggregation occurring above the melting point of the hydrate. Nevertheless, since the extrapolation to $C_P \rightarrow 0$ g/g is consistent with the SEC determination of M_W (cf. Table I), this aggregation effect disappears at high dilution. Such aggregation was already shown for PEOG in water[41-43] and even in some less polar systems such as polystyrene in various solvents.[44]

Another difference lies in the fact that the melting point of the hydrate is higher than that of water, which corresponds to a greater stability of this species as compared to that of the PEOG eutectic. This behavior is reminiscent of the polystyrene–CS_2 system already mentioned for which the presence of a complex was described by DSC and whose melting point is higher than that of CS_2.[45] In both cases this complex (or hydrate) can be considered as a definite compound which possesses a congruent melting point.

Then, if one considers that only the PD in Figure 11-3 is characteristic of a stable state, the domain of solubility of PDXL in water is very limited in both concentration and temperature since a solution exists only in domain S. The shape of the binodal demixing curve at high temperature (which exists only at $C_P < 0.5$ g/g) is not expected from a simple application of the Flory–Huggins theory with a value of χ_{12} independent of the system composition, since an increase of the cloud point with C_P is predicted for C_P higher than the critical concentration. This opposite behavior may be explained by an increase of χ_{12} with C_P, which would be consistent with the nonmiscibility of the polymer and of the hydrate. Such a variation of χ_{12} at higher C_P was already observed for PEOG in water, though to a smaller extent than for PDXL.[37]

Finally, the domain of true molecular solution of PDXL in water remains to be determined by accurate light-scattering measurements.

Binding of Water. At low temperature, DSC experiments clearly show that some of the water is bound to the polymer. The variations of the melting enthalpy of water ΔH_W (which reaches zero at $C_P = 0.55$ g/g) and that of the hydrate (which goes through a maximum for $0.5 \leq C_P \leq 0.6$ g/g) allow us to evaluate the probable stoichiometry of the PDXL hydrate. These results are consistent with a hydrate containing three water molecules per monomer unit. More accurate experiments ought to be carried out in order to better determine this stoichiometry.

It is well-known that when polymers are dissolved in a solvent with strong interactions through hydrogen bonding, the excess mixing volume is strongly negative due to the lower molar volume of bound water molecules with respect to those in the bulk. At the same temperature, the absolute value of ΔV_P for PDXL in water is smaller than that obtained for PEOG. This means that for PDXL, the interactions are weaker. This is consistent with the fact that, though three molecules of water are bound to a monomeric unit in both polymers (PDXL and PEOG), it corresponds to one atom of oxygen in the case of PEOG and to two oxygen atoms in the case of PDXL, as found by DSC.

Densimetry experiments reveal an interesting variation of the partial specific volume of PDXL in water with temperature. It corresponds to a minimum of the excess volume at $T = 45$ °C. This minimum was already observed for PEOG and PPO–PEOG copolymers[14] but for a lower value of temperature ($T = 20$ °C) and seems therefore to be a quite general phenomenon.

Although few data are available in the literature concerning this type of measurements, a decrease of the absolute value of ΔV_P with increasing temperature is expected due to the progressive release of water molecules by the polymer. The occurrence of such a minimum may be explained by two antagonistic effects: the first effect concerns the decrease of the average number of molecules bound per unit with increasing temperature while the second effect that is suggested is the increase of the difference in molar volumes between the free and the bound water molecules when the temperature increases. In other words, the molar volumes of free and bound water are the same, just prior to the hydrate crystallization.

Conclusion

Polydioxolane exhibits a structure which is intermediate between those of poly(methylene oxide) and poly(ethylene oxide). Therefore, its properties in water are quite interesting since PMO is totally insoluble and PEOG is miscible. We present the phase diagram of PDXL–water, and we compare it to that of PEOG which was extensively studied by others. They are quite different: the PEOG diagram exhibits some characteristics that are usually described as the formation of a eutectic and a binodal curve which is a classical LCST curve so that the domain of miscibility of PEOG and water extends over the whole range of composition. On the other hand PDXL forms a definite compound with water (a hydrate corresponding to three water molecules per monomer unit) that melts around 15 °C. The most dramatic difference is the limited solubility of PDXL in the lower range of concentration. We are presently investigating the domain of true molecular dispersion in water as well as the structure of the hydrate formed.

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