Transient phase diagram of ternary polyetherimide solutions: effect of polymer association

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Effects of chain association on the demixing behaviour of ternary solutions containing a polyetherimide in a solvent–non-solvent mixture are investigated. Time evolution of the temperature of demixing of the solutions is observed over 1 month. It is ascribed to a slow dissociation process involving charge transfer and hydrogen bonding complexes in the system. The observed demixing curves are characterized by high values of the precipitation threshold. A model based on the Flory–Huggins theory of polymer solutions is developed to explain this effect, and an intermolecular association parameter is introduced into the discussion. Fairly good agreement is obtained between calculated and experimentally found demixing curves. The fraction of associated electron donor or acceptor groups of a polymer chain is predicted by the model.

(Keywords: membrane; polyetherimide; phase diagram; charge transfer complexes)

INTRODUCTION

Chain association is currently observed in aromatic polyimides in solution or in the solid state[1–3]. For instance, the existence of charge transfer complexes between monomeric units is known to induce the formation of intermolecular aggregates in these systems. The purpose of this paper is to study the effect of chain association on the demixing phenomenon which takes place in ternary solutions containing polyetherimide (PEI) in a solvent–non-solvent mixture. More precisely, this study is focused on the one hand on the time evolution of the temperature of demixing of ternary PEI solutions, and on the other hand, on the phase separation observed in freshly made systems. The latter point is of particular interest, since PEI solutions are used to make asymmetric membranes. These membranes result from a phase inversion process where demixing is induced by immersion of a film of PEI solution in a non-solvent bath. It is known that membrane morphologies depend on the physical phenomena involved during their formation[4–6]. Up to now, little attention has been paid to association effects as playing a determining role in the formation of asymmetric polymeric membranes. However, it will be seen in this paper that these effects drastically affect the demixing process of ternary solutions. Consequently, intermolecular association is expected to have a significant influence on the structural properties of the final membrane.

In a viscometric study reported elsewhere[7], evidence was given for the existence of chain aggregation in solution of PEI in a binary solvent (*N*-methylpyrrolidone(NMP)–water). It was suggested that the formation of intermolecular charge transfer complexes (CTC) was involved in the association process; electron donor and electron acceptor groups were supposed to be, respectively, the phenyl and the phthalimide moieties of the monomeric unit.

In this work, association effects clearly reveal the existence of slow kinetics in an association–dissociation process in PEI solutions. Thermodynamical properties of freshly made solutions are discussed by assuming the presence of chain aggregates. In this paper the sample preparation method, the thermal analysis procedure and the turbidimetry experimental set-up are described and the stability of solutions is briefly examined as a function of the age of the systems. Then, variations of the glass transition temperature (T_g) of PEI–NMP and PEI–NMP–water solutions are reported as a function of the polymer concentration. Phase diagrams of ternary solutions are also studied. They are plotted using a pseudo binary representation and the results are discussed on the basis of Flory–Huggins theory.

EXPERIMENTAL

Sample preparation

The polymer Ultem 1000 was obtained from General Electric. Its structure is shown in *Figure 1*. Its molecular weight is $M_n = 10\,000$ with a polydispersity index of 1.6. It was dried at 150°C for 4 h prior to use. NMP was dried over a 3 Å molecular sieve.

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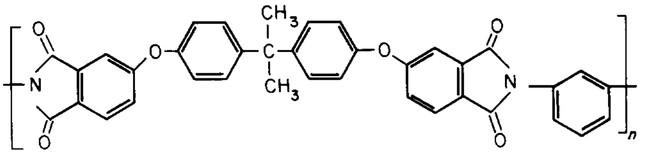

Figure 1 Monomer unit

Homogeneity of the solutions was controlled visually. In ternary systems where demixing could be observed, solutions were considered to be homogeneous when the phase separation induced upon cooling took place uniformly over the whole sample volume.

Solutions used to perform d.s.c. measurements were obtained by stirring gently and continuously the polymer in pure NMP or in a binary solution of NMP–water over 24 h at room temperature. The mixtures were then heated at 60°C until homogenization was achieved. Five binary solutions were prepared which contained, respectively, 0.5, 1, 2, 3 and 4% w/w of water.

Ternary systems used to perform turbidimetry experiments were obtained first by preparing binary solutions with 4, 5, 5.5 or 6% w/w of water in NMP and then by mixing the polymer in the binary solution. Each of the resulting three-component mixtures was warmed and shaken until homogeneity was achieved, depending on the particular system: systems prepared with a binary solution containing 5.5 and 6% of water were kept for 2 days at a temperature of 70°C; samples prepared with a binary solution containing 4 and 5% of water were homogenized using two different procedures, depending on the polymer concentration. Systems whose polymer concentration was $<12\%$ w/w were kept for 2 days at a temperature of 50°C whereas more concentrated systems were kept for 5 days at 50°C.

The highest polymer concentration obtained in a ternary system was 30% w/w. In the binary solution containing 6% of water, the most concentrated solution which could be prepared contained 12% w/w of polymer. Beyond these concentrations, no complete homogenization was obtained using this method of preparation.

Thermal analyses

Each sample (100 mg) was carefully weighed and was sealed into aluminium pans under a dry nitrogen atmosphere. The samples were kept for 7 days at 60°C in order to ensure the same thermal history for all the samples. A weight control was done after this heat treatment to check that no solvent had evaporated. The solutions of polymer concentration equal to 80% w/w and 90% w/w were prepared by controlled evaporation of NMP from a polymer solution concentrated to 25% w/w.

Thermal analyses were conducted using a Mettler TA 3000 differential thermal analyser equipped with a differential scanning calorimeter cell (DSC 30). D.s.c. analyses were obtained at a cooling rate of 10 K min^{-1} under a flowing argon atmosphere. Indium was used for calibration. The T_g was determined at the onset of the transition region on the cooling curves.

Turbidimetry experiments

Demixed concentrated solutions ($>16\%$ w/w) were formed of microdomains of a dilute polymer phase, embedded in a polymer concentrated phase, and were turbid. Cloud points were determined by the detection of the onset of turbidity; it was observed visually upon cooling the ternary solutions. The device used for these experiments is shown in *Figure 2*. Two cylindrical holes were bored into the bulk copper cylinder. A heating copper wire and narrow copper tubing through which a flow of cold nitrogen circulated were coiled about the bulk cylinder in order to ensure temperature regulation. The tube containing the solution was set in the large cylindrical hole. A thermocouple was set in the small hole in contact with the tube. The temperature was lowered stepwise by single degrees. The sample was kept for 15 min at each temperature. The laser which was used initially to measure the optical absorptions was given up because the laser beam induced a local phase separation on its trajectory.

TRANSIENT BEHAVIOUR OF SOLUTIONS

Solutions of PEI in pure NMP solutions and in binary water–NMP solutions were prepared over several days by the procedure described in the previous section. Experiments started with fresh solutions. The time evolution of the samples which is observed after homogenization is considered to depend on the initial state of the solutions resulting from the preparation procedure.

Stability of the binary solutions

Prior to the study of the ageing process of ternary solutions, the time behaviour of PEI in a simple solvent is examined. It was chosen to study two solutions containing, respectively, 16% w/w and 30% w/w of polymer in NMP. The time behaviour of the systems was observed using thermal analysis: the measured parameter was the T_g. When homogenization was achieved, the T_g for each sample was measured. Then, for each system, part of the system was kept at room temperature while the other part was heated to 60°C. The T_g of both solutions measured after 1 month did not differ from that for freshly made solutions.

Phase separation in ternary solutions

The situation of ternary solutions is very different to that of binary solutions: a demixing process is observed in ternary solutions upon decreasing temperature. It was found that the demixing temperature of each sample varied with the age of the system. For instance, the phase separation temperature of a solution containing

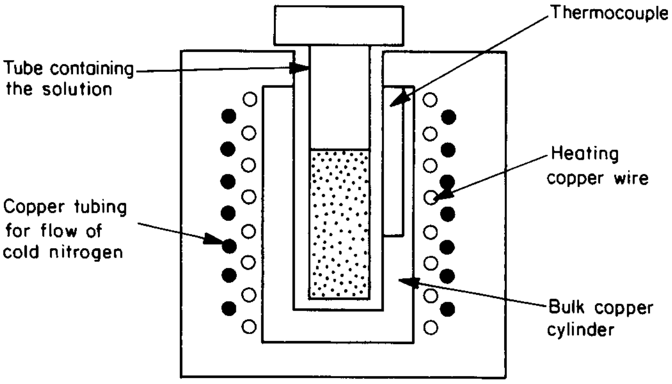

Figure 2 Experimental device for turbidimetry experiments

12% w/w of polymer in a binary solution of NMP and 6% w/w water, measured just after its preparation, was 67°C. Then the sample was heated to 75°C. A decrease in the phase separation temperature was first noted at a temperature of 52°C, followed, after a few days by another measurement which yielded a phase separation temperature of 45°C. After 1 month, the system remained homogeneous at all temperatures.

The time behaviour of the solutions was observed from the evolution of their demixing temperatures. First, the temperature of demixing, $T_d^i(\phi)$, was determined for all the freshly made solutions. After these measurements, the systems were kept at a temperature higher than their respective demixing temperature. A few days later, the temperatures of phase separation were measured again; they were found to be lower than the initial $T_d^i(\phi)$ values. They became increasingly lower as the time of storage of the samples at high temperature increased.

After 1 month the samples were slowly cooled until the systems reached the glassy state. The clearness of the solutions did not change: no demixing phenomenon could be observed.

Ternary solutions of PEI are dependent on time. The following qualitative description can be proposed to explain this behaviour. In the solid state CTC are formed between the polymer chains. When the system is put into solution, a slow dissociation of the CTC takes place. This can be due to the strong increase of conformational entropy resulting from the dilution process. The presence of hydrogen bonds between the carbonyl groups of the monomers and water molecules may also play a role. The kinetics of dissociation is expected to depend on the water content present in the ternary solutions since either the entropy and the energy of the systems are modified by water addition.

GLASS TRANSITION TEMPERATURES OF THE SOLUTIONS

Values of the T_gs were determined for PEI–NMP solutions and ternary PEI–NMP–water solutions at several PEI concentrations. A typical thermogram obtained for a PEI–NMP solution of polymer concentration of 40% w/w is shown in *Figure 3*.

Crystallization is not detected on the thermogram of the bulk PEI. The polymer is in the amorphous state. Its T_g was found to be 491 K.

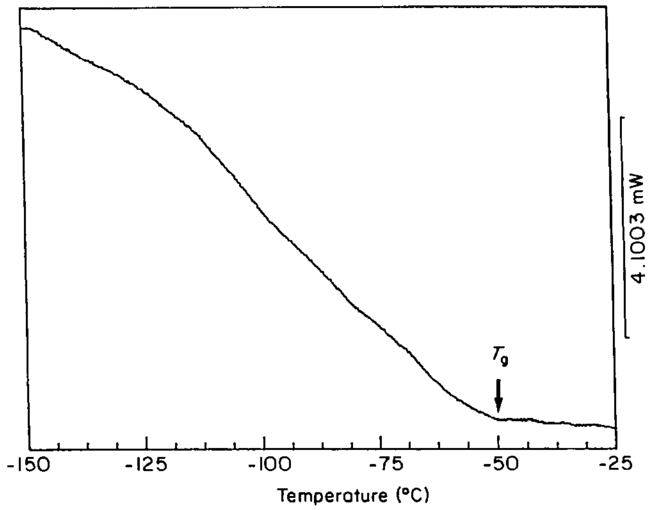

Figure 3 Thermogram of a PEI–NMP solution (c = 40% w/w)

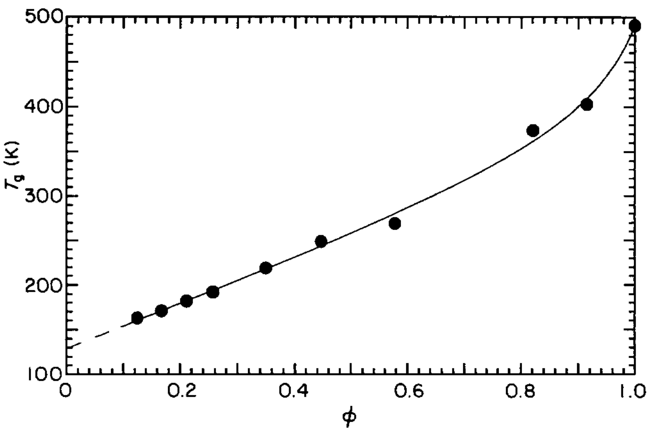

Figure 4 Variation of the glass transition temperature (T_g) as a function of the polymer volume fraction (ϕ) in PEI–NMP solutions

PEI–NMP solutions

Variations of the T_g are shown in *Figure 4* as a function of the polymer volume fraction, ϕ. It is worth noting that the T_g of solutions used for the preparation of membranes (polymer concentration in the range of 15–30% w/w) is far below the room temperature. The depression of T_g with polymer concentration is induced by the increase of the fractional free volume resulting from the addition of the diluent. The observed curve was fitted according to the semi-empirical equation[8] which describes the dependence of T_g on composition:

$$T_g = \frac{(1-\phi)T_g^s\alpha_f^s + \phi\alpha_f^p T_g^p + K\phi(1-\phi)}{(1-\phi)\alpha_f^s + \phi\alpha_f^p} \qquad (1)$$

where α_f^s and α_f^p are the thermal expansion coefficients of the free volume of the solvent and of the polymer, T_g^s and T_g^p are the T_gs of the solvent and the bulk polymer and K reflects the interactions between the polymer and the solvent; K is usually negative and of the order of 10^{-2}.

The T_g^s can be easily extrapolated from the curve represented in *Figure 4* to a value of 129 K. The values for α_f^p/α_f^s and α_f^s/K found for the best fit were 0.098 and -4.72×10^{-3}, respectively; the fit was obtained by the least mean squares method. The order of magnitude of these ratios is reasonable as the thermal expansion coefficients of polymers and solvents are generally, respectively, of the order of 10^{-4} and 10^{-3} K^{-1}.

Increase in T$_g$ *upon water addition*

The behaviour of the mixed solvent NMP–water was examined for a system containing 3.6% w/w of water in NMP by first cooling and then reheating the sample. The observed thermograms exhibited only one melting endothermic peak at a temperature of −28°C, corresponding to a displacement of the melting temperature of pure NMP which is equal to −19°C. The binary solvent is homogeneous in this range of water concentration, since a single melting temperature was observed. A weak exothermic peak was found at −80°C; this may be assumed to result from a modification of the structure of the solid system.

Figure 5 illustrates the effect of water concentration on the curves representing variations of T_gs upon polymer

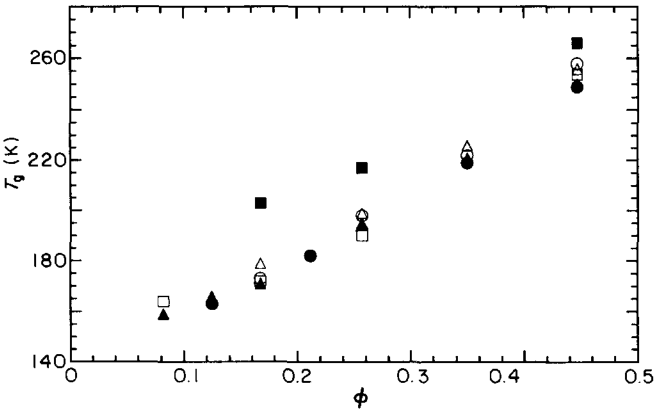

Figure 5 Variation of the glass transition temperature (T_g) as a function of the polymer volume fraction (ϕ) in PEI–NMP–water solutions. Water content: (●) 0%; (□) 0.5%; (▲) 1%; (○) 2%; (△) 3%; (■) 4%

concentration. Water addition has a weak effect on the T_g values in the concentration range investigated. A small increase in the T_g is observed for the system which has 4% water content in the binary solvent. It shows that the addition of fractional free volume induced by the presence of the diluent is smaller when water is introduced in the NMP than in the absence of water: the molecular mobility of the solvent is decreased upon water addition. Since these effects are small they cannot be responsible for the original form of the phase diagram described in the next section.

POLYMER ASSOCIATION: EFFECTS ON DEMIXING

All results concerning the phase separation occurring in ternary solutions were obtained with freshly made solutions. A model is proposed to describe the demixing mechanisms occurring in the presence of polymer association.

Phase diagrams in pseudo binary representation

The temperature of phase separation of the ternary solutions is plotted *versus* the polymer concentration for given compositions of the binary solvent (*Figures 9–12*). As solvent- non-solvent ratios are not necessarily the same in the two phases, the cloud point curves thus obtained are not exactly comparable to the ones observed for binary solutions. More precisely, the maximum of the curve represents the precipitation threshold and not the critical point, as is the case in binary systems. The compositions of the two phases in equilibrium at the precipitation threshold are not identical, in contrast to what is observed at the critical point. The polymer concentration at the precipitation threshold is generally greater than the concentration of the critical point.

However, the use of a phase diagram of ternary solutions is not easy. It involves the interaction parameters between polymer and solvent, between polymer and non-solvent and between solvent and non-solvent; none of which are known for the systems studied here. Therefore, in order to be able to treat the effects of intermolecular association on the phase separation process in a quantitative way, we deal with the binary solvent NMP–water as if it was a single solvent.

The striking feature in the phase separation curves plotted in a pseudo binary representation is that no maximum is reached over the whole explored range of polymer concentrations, i.e. up to 35% w/w. In polymeric systems currently used for the preparation of asymmetric membranes[9,10], the experimental values of the critical concentration in ternary diagrams are generally <10% w/w. However, the part of the binodal curve associated with polymer concentrations >10%w/w is seldom investigated in such systems due to the difficulties in obtaining homogeneous solutions.

A recent experimental study[10] concerning the systems studied here confirms that the critical concentration is <10% w/w. In this work, observations showed that the concentration of the precipitation threshold is >35% w/w. The difference between this value and the concentration of the critical point seems exceptionally large.

Gibbs free energy and intermolecular association

In this study, it is proposed to describe the polymer association effects induced by the formation of CTC between phenyl and imide rings of monomeric units as a chemical equilibrium between free and associated rings. The structural unit of PEI contains eight skeletal bonds. Among the eight corresponding groups, only five are susceptible to belong to a CTC: these are the two imide moieties and the three phenyl moieties. Due to steric hindrance considerations, it is likely that the five groups cannot be associated simultaneously. The fraction of groups involved at a given time in a CTC, θ, is therefore <5/8.

The formation of a CTC is described by the equilibrium:

$$\mathrm{a} + \mathrm{d} \rightleftharpoons \mathrm{ad}$$

where a is an acceptor group, d is a donor group and ad is the CTC formed between a and d. In the following, no distinction will be made between electron acceptor groups, electron donor groups or neutral groups of the structural unit. The latter equilibrium will be simply written as

$$\mathrm{g} + \mathrm{g} \rightleftharpoons \mathrm{gg}$$

where g represents any group among the eight belonging to the structural unit.

An equilibrium constant K_c is characteristic of the values of the concentration of associated groups, c_a, and of the concentration of free bonds, c_d. However, equilibrium is not reached in solutions examined immediately after their preparation. In the model proposed here, one defines at any time a variable $\rho_c(t)$ characteristic of the system; it is a slow function of time and is equal to the ratio c_a/c_d^2 measured at a given time, t. The limit $\rho_c(\infty)$ is the equilibrium constant K_c. As the kinetics of the dissociation process is very long, one considers that $\rho_c(t)$ is constant during a turbidimetry measurement.

The fraction of associated groups, θ, is readily derived from the expression of $\rho_c(t)$:

$$\rho_c = \frac{c_a}{c_d^2} = \frac{V\frac{\theta m}{2}}{(1-\theta)^2 m^2} = \frac{\theta \omega}{2(1-\theta)^2 \phi} \qquad (2)$$

where m is the total number of groups (donor, acceptor or neutral) in the system, ω is the molecular volume of one group, V is the volume of the solution and ϕ denotes the polymer volume fraction. By solving equation (2) and by noting $K = \rho_c \omega^{-1}$ one finds for θ:

$$\theta = \frac{1}{2K}\left(\frac{1}{2\phi} + 2K - \sqrt{\frac{1/4\phi + 2K}{\phi}}\right) \quad (3)$$

According to this formula, the numerical value of θ increases when ϕ or K increases.

This model relies on an hypothesis analogous to the one made in the description of polymer gels proposed by Flory[11]. In this theory, the translational entropy of the chains, $\phi/N \ln \phi$, is not present in the free energy since the chains are attached together. In the proposed model it is considered that associated groups do not contribute to the entropic term of the Gibbs free energy. More precisely, these groups are totally excluded from the calculation of the number of arrangements possible in solution. The calculation of the configurational entropy involves the number of monomers per polymer chain. As associated monomers are not taken into account in this calculation, the resulting value of the entropy is the same as that obtained for a shorter chain: the effective length of the polymer chains decreases. The enthalpic term which reflects polymer–solvent interactions retains the value it has in the Flory–Huggins theory.

In the following discussion, the approximation in which the binary solvent is taken as a single solvent is made so that the solutions are considered as pseudo binary solutions. Let s be the number of solvent molecules, ω denotes the molecular volume of the groups and of the molecules of solvent, N denotes the number of groups per polymer chain and χ is the apparent interaction parameter between the binary solvent and the polymer. The Gibbs free energy of the system is:

$$\Delta G = kT\left\{s \log\left[\frac{s}{s + (1-\theta)m}\right] + \frac{m}{N}\log\left[\frac{(1-\theta)m}{s + (1-\theta)m}\right] + \chi\frac{sm}{s+m}\right\} \quad (4)$$

The free enthalpy per site can be written as a function of ϕ:

$$\Delta G_{\text{site}} = kT\left\{(1-\phi)\log\left[\frac{(1-\phi)}{1-\theta\phi}\right] + \frac{\phi}{N}\log\left[\frac{(1-\theta)\phi}{1-\theta\phi}\right] + \chi\phi(1-\phi)\right\} \quad (4')$$

The entropic term

$$\Delta S = -k\left\{(1-\phi)\log\left[\frac{(1-\phi)}{1-\theta\phi}\right] + \frac{\phi}{N}\log\left[\frac{(1-\theta)\phi}{1-\theta\phi}\right]\right\} \quad (5)$$

decreases with θ when θ is $< 1 - 1/N$. When the ratio of aggregated groups increases, the entropy of mixing of the solution decreases. The variation of ΔG as a function of ϕ and K is represented in *Figure 6* for $\chi = 0$ and 0.4.

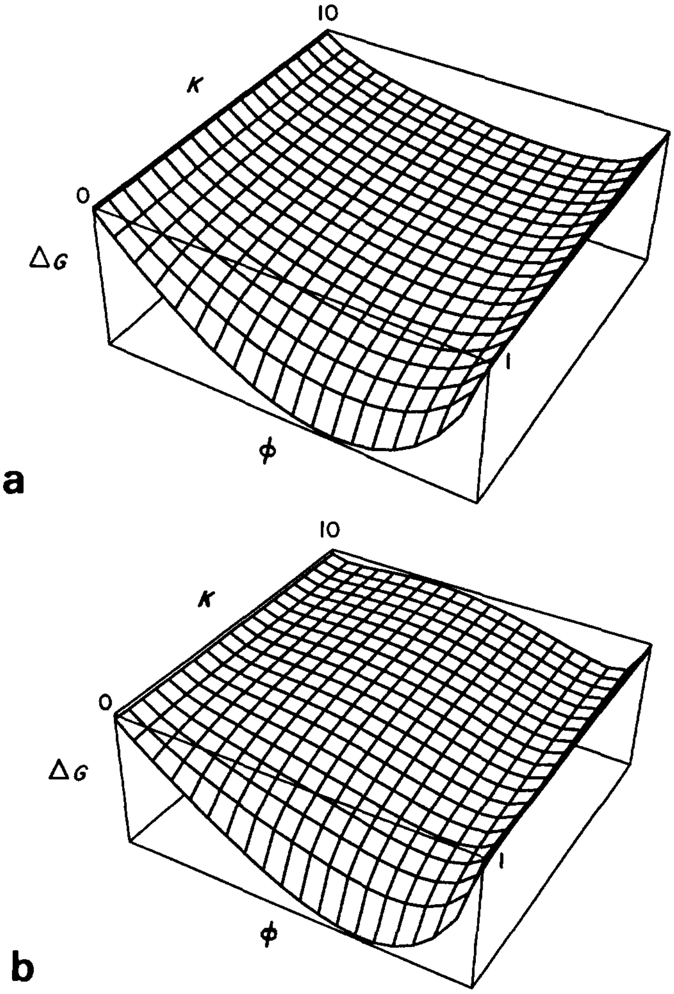

Figure 6 Variation of the Gibbs free enthalpy (ΔG) as a function of the polymer volume fraction (ϕ) and the association parameter (K): (a) $\chi = 0$; (b) $\chi = 0.4$

Polymer concentration at the critical point

In order to further characterize the effect of association on demixing, variations of the polymer volume fraction at the critical point have been investigated as a function of the association constant and of the polymer–solvent interaction parameter. At the critical point, the first and second partial derivatives of the chemical potential with reference to ϕ are equal to zero. Let us first calculate the chemical potential of the solvent, μ_1:

$$\mu_1 = \frac{\partial \Delta G}{\partial s} = kT\left\{\log\left[\frac{s}{s+(1-\theta)m}\right] + \frac{m}{s+(1-\theta)m} \times \left(1-\theta+s\frac{\partial\theta}{\partial s}\right)\left[1-\frac{1}{N(1-\theta)}\right] + \chi\frac{m^2}{(m+s)^2}\right\} \quad (6)$$

which can be written as a function of ϕ:

$$\mu_1 = kT\left\{\log\left(\frac{1-\phi}{1-\theta\phi}\right) + \frac{\phi}{(1-\theta)\phi}\left(1-\theta+s\frac{\partial\theta}{\partial s}\right) \times \left[1-\frac{1}{N(1-\theta)}\right] + \chi\phi^2\right\} \quad (7)$$

where

$$s\frac{\partial\theta}{\partial s} = \frac{1-\phi}{4K\phi}\left[1-\left(\frac{1}{2\phi}+2K\right)\sqrt{\frac{\phi}{1/4\phi+2K}}\right] \quad (8)$$

and θ is given by equation (3).

The expressions for the first and second derivatives of μ_1 with respect to ϕ are complicated. The curve which satisfies the system for the following two equations

$$\frac{\partial\mu_1(\chi,K,\phi)}{\partial\phi}=0 \quad\text{and}\quad \frac{\partial^2\mu_1(\chi,K,\phi)}{\partial\phi^2}=0 \qquad (9)$$

in three-dimensional space (χ, K, ϕ) is not easily established, because of the very long expression for the second derivative. However, in equation (9), the terms involving χ are very simple; they are respectively $2\chi\phi$ and 2χ. Therefore, using equation (9), the two curves representing the variations of χ as a function of ϕ are drawn for fixed values of K. Their intersection determines the critical point (*Figure 7*). The curve representing the variations of ϕ_c in space (χ, K, ϕ) is constructed point by point (*Figure 8*). It is found that ϕ_c increases with K whereas χ_c first increases and then decreases with K. As it could be predicted from *Figure 6*, when association effects exist the entropy of mixing of the solution is strongly reduced; demixing takes place unless polymer–solvent interactions are strong; demixing is observed in systems characterized by small values of χ.

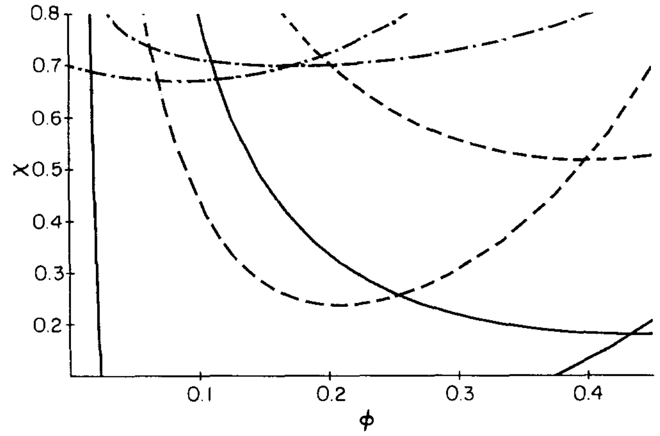

Figure 7 Graphical determination of the critical polymer volume fraction: variation of χ as a function of ϕ, according to equation (9) (see text). Values of K: (—·) 0.1; (– –) 1; (—) 10

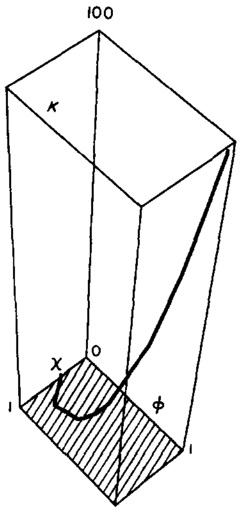

Figure 8 Variation of the association constant (K) as a function of the critical polymer volume fraction (ϕ) and the critical polymer solvent interaction parameter (χ)

Binodal curve

The two demixed phases are in equilibrium with one another when the chemical potentials of the two phases are equal, that is

$$\mu_1(\phi_d, K, \chi)=\mu_1(\phi_r, K, \chi) \qquad (10a)$$

$$\mu_2(\phi_d, K, \chi)=\mu_2(\phi_r, K, \chi) \qquad (10b)$$

where μ_2 is the chemical potential of the polymer, ϕ_r and ϕ_d are, respectively, the polymer volume fractions in the concentrated and in the dilute phase; μ_1 was calculated earlier. The expression for μ_2 is:

$$\mu_2=\frac{\partial\Delta G}{\partial(m/N)}=kT\left\{\log\left[\frac{(1-\theta)\phi}{1-\theta\phi}\right]-N\frac{(1-\phi)}{(1-\theta\phi)}\times\left[1-\frac{1}{(1-\theta)N}\right]\left(1-\theta-m\frac{\partial\theta}{\partial m}\right)+\chi N(1-\phi)^2\right\} \qquad (11)$$

with

$$m\frac{\partial\theta}{\partial m}=\frac{(1-\phi)}{4K\phi}\left[-1+K\sqrt{\frac{\phi}{1/4\phi+2K}}\left(2+\frac{1}{2K\phi}\right)\right] \qquad (12)$$

By substituting in equation (10b) the expression for χ found in equation (10a) and using equation (11), we obtain a final expression $F(K,\phi_r,\phi_d)=0$. F is solved for fixed values of K. Corresponding values for χ are computed. Binodal curves are then drawn in a χ *versus* ϕ representation for various values of K. More interesting is the T *versus* ϕ representation of the phase diagram. The conversion of χ to the temperature is done by using a linear function of $1/T$:

$$\chi-\tfrac{1}{2}=\psi(\Theta/T-1) \qquad (13)$$

where Θ is the theta temperature and ψ is the entropy parameter; ψ is usually positive, of the order of unity.

It was then possible to draw the calculated binodal curves and to find a fit for the experimental phase diagrams. The parameters for the fit were Θ, ψ and K. Binodal curves were drawn for several Θ and ψ values and for various values of K. They were constructed point by point because no explicit analytical function was found for the theoretical binodal curves. The parameter ψ controls the gradient of the curve; Θ and ψ determine the temperature domain of the binodal curve; K governs the shift of concentration of the critical point and the curvature of the binodal. Considering that the range of concentration experimentally explored was small, it did not appear relevant to propose only one set of values for the fit parameters (Θ, ψ, K) for each experimental curve. Several fits are proposed in *Figures 9–12* for experimental curves obtained on systems prepared with 4, 5, 5.5 and 6% w/w of water in NMP.

Several main trends emerge from these fits:

1. The Θ temperature does not change significantly upon variation of the concentration of water in the solution. Its value is in the range of 400 K depending on the value of K chosen for the fit.
2. The value of K is ~0.2. It does not vary significantly with temperature or with the water content in NMP. The variation of the fraction of imide and phenyl groups involved at a given time in an aggregate can be deduced for various values of K. Since five out of

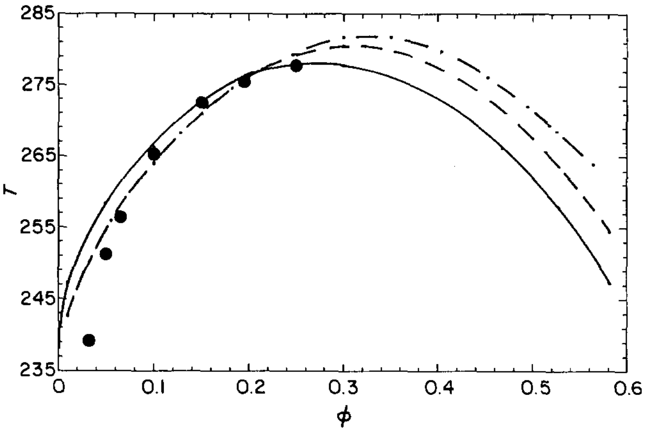

Figure 9 Experimental cloud points curves (●) and proposed fits in a PEI–NMP solution with 4% w/w of water added: (——) $K = 0.2$, $\Theta = 410$ K, $\psi = 0.45$; (– –) $K = 0.25$, $\Theta = 395$ K, $\psi = 0.5$; (—·) $K = 0.3$, $\Theta = 365$ K, $\psi = 0.65$

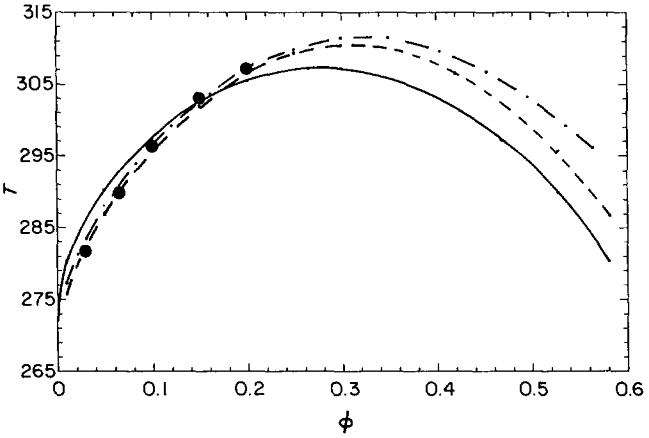

Figure 10 Experimental cloud points curves (●) and proposed fits in a PEI–NMP solution with 5% w/w of water added: (——) $K = 0.2$, $\Theta = 410$ K, $\psi = 0.64$; (– –) $K = 0.25$, $\Theta = 405$ K, $\psi = 0.67$; (—·) $K = 0.3$, $\Theta = 378$ K, $\psi = 0.9$

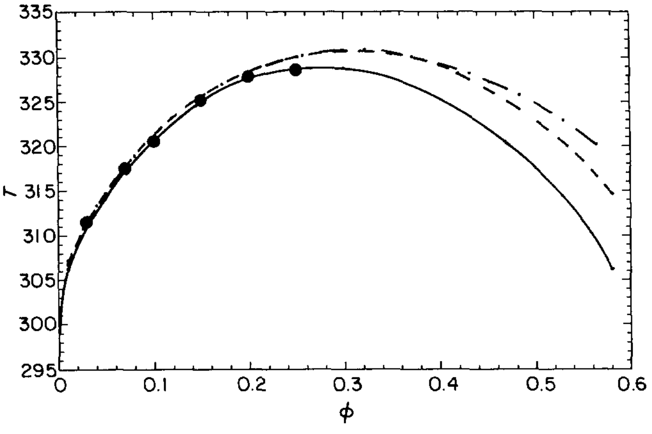

Figure 11 Experimental cloud points curves (●) and proposed fits in a PEI–NMP solution with 5.5% w/w of water added: (——) $K = 0.2$, $\Theta = 407$ K, $\psi = 0.9$; (– –) $K = 0.25$, $\Theta = 387$ K, $\psi = 1.2$; (—·) $K = 0.3$, $\Theta = 370$ K, $\psi = 1.6$

eight of the groups of the structural unit can be involved in interaction, the fraction of imide and phenyl groups in interaction is $8\theta/5$. This is shown in *Figure 13* for $K = 0.2$ and 0.3. In both cases, the proportion of associated groups in solution is significant.

The main question which arises from the study of these systems concerns the mechanism of association between the polymer chains. It would be interesting to know whether or not a collective effect is involved in the mechanism of CTC formation; this could lead to the existence of a distribution of CTC along the chain backbone and could induce a partial ordering of the chains.

3. The term $k\psi\phi^2$ is the entropic contribution to the chemical potential of the solvent due to monomer–solvent interactions; it represents a supplementary term to the chemical potential of the ideal mixture, which is $-kT\phi/M$ in dilute solutions; ψ increases when the content of water increases in the diluent. This behaviour reveals that the entropy of the solution deviates more strongly from ideality when water is added to the system. This indicates that organized structures are formed in the solutions; they are very likely formed of polymer aggregates whose cohesion is insured by CTC, and of NMP molecules in interaction with water, due to possible preferential attraction of NMP to water.

CONCLUSIONS

Association effects play an important role in polymer solution properties. We attempted to deal with this problem from the observation of the time evolution of

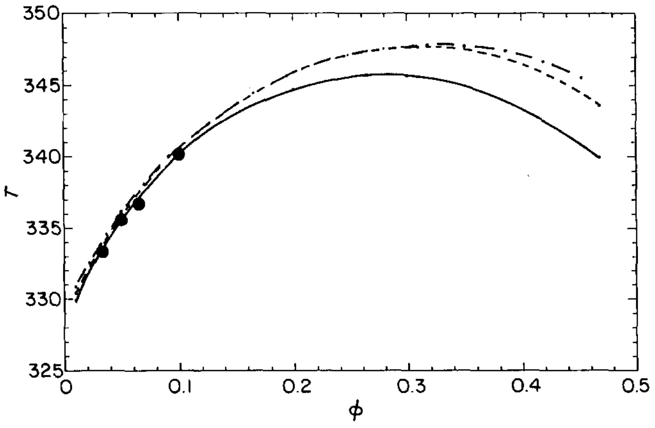

Figure 12 Experimental cloud points curves (●) and proposed fits in a PEI–NMP solution with 6% w/w of water added: (——) $K = 0.2$, $\Theta = 395$ K, $\psi = 1.5$; (– –) $K = 0.25$, $\Theta = 385$ K, $\psi = 1.9$; (—·) $K = 0.3$, $\Theta = 375$ K, $\psi = 2.45$

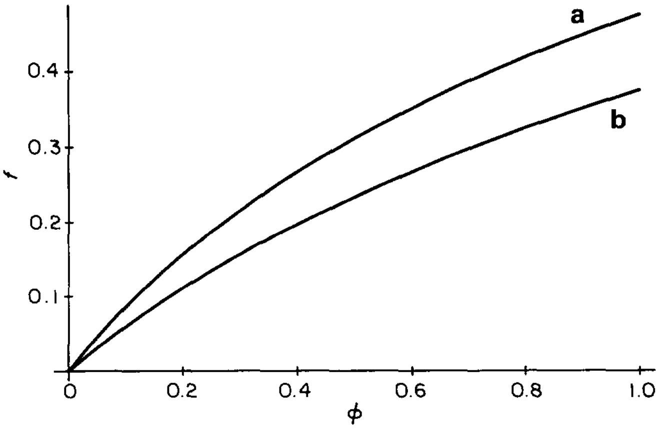

Figure 13 Variations of the fraction (f) of associated donor or acceptor groups as a function of the polymer volume fraction (ϕ), as predicted by equation (3): (a) $K = 0.3$; (b) $K = 0.2$

PEI solutions and from the description of their transient demixing behaviour. Time evolution of ternary PEI–NMP–water solutions was observed over 1 month: the demixing temperature of the systems was found to decrease with ageing, the systems remaining homogeneous after 1 month.

Phase diagrams of freshly made solutions were found to exhibit very specific features. These are not due to an effect which could be associated with the glass transition, since the values of the T_gs of the solutions were found to be far below the room temperature at which the demixing experiments were performed.

In order to describe the original phase diagram observed for these systems, a model based on the Flory–Huggins theory for polymer solutions was developed where a polymer association effect was introduced. Although strong approximations were done – in particular, the binary solvent was taken as a single solvent – it was found that this model correctly described the form of the cloud point curve. More precisely, it gave theoretical support to explain the shift of the precipitation threshold towards greater values of polymer concentration. Important entropic deviations from ideal solutions were predicted upon water addition. This corroborated the hypothesis that the polymer solution is organized due to an association effect.

The procedure of formation of asymmetric membranes made from PEI solutions involves phase separation induced by immersion of the solution in a non-solvent bath. The results of the present study show that when the non-solvent penetrates into the solution, the resulting ternary solution is far from its equilibrium state. The demixing which results from this immersion depends on the transient state which characterizes the system at a given time. Therefore, it is expected that association effects play a very active role in the mechanisms of membrane formation and are involved in determining the pore structure of the final membrane.

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