Nuclear magnetic resonance approach to the characterization of the phase diagram of polyacrylonitrile in ternary solutions

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(Received 3 March 1993; revised 21 July 1993)

This work deals with the properties of the temperature–concentration phase diagram of ternary polyacrylonitrile solutions that were mainly observed from the transverse magnetic relaxation of protons attached to polymer chains, used to disclose the presence of solid-state domains. The binary solvent was a mixture of dimethylformamide (DMF) and water; the molar fraction of monomeric units was varied from 0 to 0.5, while the relative molar fractions of DMF and water were 1:1 or 2:1. The solvent quality was found to decrease upon addition of water. A curve (liquidus) that relates the temperature of formation of solid-state domains to the initial polymer concentration in solution was drawn from nuclear magnetic resonance (n.m.r.). The demixing part of the liquidus, determined as a plateau from n.m.r., was identified on observing a cloud-point curve. The main feature of the phase diagram concerns the specific behaviour of solutions observed whenever the concentration of disordered segments becomes lower than half the initial polymer concentration.

(Keywords: polyacrylonitrile; ternary solutions; n.m.r. characterization)

INTRODUCTION

This work deals with the characterization of the ordering effect of polyacrylonitrile (PAN) chains: it is usually considered that partial crystallization may occur in pure PAN[1,2]. However, the high melting temperature T_m° of the pure polymer is not easily measured; it has been estimated only from the melting-point depression induced upon addition of a good solvent: $T_m^\circ = 317\,K$[3]. Furthermore, crystallites are not easily characterized from X-ray diffraction. Ordered domains are described as hexagonal packings of rigid segments; these result from helical structures. The lateral order within crystallites is observed without any ambiguity, while the length of rigid segments is not uniform; no periodicity has been disclosed along the *c* axis[4]. Consequently, no regular crystallization can be evoked for pure PAN.

The purpose of this work was to characterize the ordering property of PAN chains, observed in solution in a binary solvent, in order to attempt to disclose the real nature of ordered domains. The addition of solvent was mainly used to lower conveniently the temperature interval of observation of the ordering process of PAN chains. It was also supposed that the definition of the polymeric order that occurs within domains would be possibly better in solution than in pure PAN. The binary solvent consisted of dimethylformamide (DMF) and water; DMF is a good solvent of pure polymer. Furthermore, water molecules play a particular role with respect to PAN ordering, since it has been shown that the addition of water under high pressure induces a melting-point depression, although water is not a good solvent of PAN[5]. The polymer and the binary solvent form a ternary mixture in which both crystallization and liquid–liquid phase separation may occur; however, the exact equilibrium phase behaviour of the mixture is still unknown. N.m.r. was applied to the determination of both the temperature of polymer ordering and the melting point; it was also used to measure conveniently the extent of polymeric order in solutions, observed under appropriate conditions.

Experimental conditions are described in the next section, followed by a discussion of the results of calorimetric measurements. The principle of the n.m.r. approach is then presented, and the temperature–concentration ordering curve determined. A qualitative description of the melting-point depression is given in the penultimate section. All results are discussed in the final section.

EXPERIMENTAL

Materials

Atactic polyacrylonitrile samples were supplied by Rhône-Poulenc; the acrylonitrile–sodium methallylsulfonate copolymer (AN69) was supplied by Hospal Industry.

Deuterated solvents used to perform n.m.r. experiments were: DMF ($D = 99.5\%$), glycerol ($D = 98\%$) and water ($D = 99.95\%$); solvents were bought from Aldrich-Chimie. For turbidimetry measurements, protonated solvents were purchased from Prolabo.

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Preparation of solutions

All concentrations are given as molar fractions of monomeric units. A small amount of PAN or AN69 (25 mg) was first introduced into the n.m.r. tube; an appropriate amount of solvent was then added in order to adjust the polymer concentration to a given value. Molar fractions up to 0.40 were obtained. N.m.r. tubes were sealed under a nitrogen atmosphere. Samples were heated up to 140°C and stirred to expedite their preparation. After waiting for 15 min, solutions were homogeneous and were slowly cooled down to room temperature. Resulting solutions were slightly yellow in colour. The coloration of PAN solutions upon heating is a well known property[6]. The nature of the bound chromophore is still undetermined[7].

N.m.r. measurements

The free induction decay of the proton magnetization, observed over a time interval equal to 100 μs, was used to characterize the spin-system response. The residual proton signals due to the probe and to the tube were subtracted from the relaxation function of the solutions.

Turbidimetry measurements

Demixing of PAN and AN69 solutions was observed by using laboratory-made equipment. The sample was put in a device whose temperature was controlled. The transmitted intensity of the laser beam (He–Ne, $\lambda = 0.632\,\mu$m) was measured by using a photodiode. Typical results of measurements of light intensity are reported in *Figure 1*. Monomeric molar fractions were equal to 0.01 or 0.09.

PARTIAL ORDERING OF PAN SEGMENTS

X-ray observations

Early X-ray measurements performed on PAN have shown that hexagonal packings of rigid segments that form crystallites in the pure polymer are characterized by a mean lateral size about equal to 80 Å[8]. The mesh size within the hexagonal packing is defined by $a = 9.18$ and $b = 5.30$ Å; no periodicity has been disclosed along the third direction[4]. The average number of segments that participate in the formation of one crystallite is about 12, and orientations of the crystallites are randomly distributed throughout the polymer sample. The crystallinity estimated from X-ray measurements is about 30%.

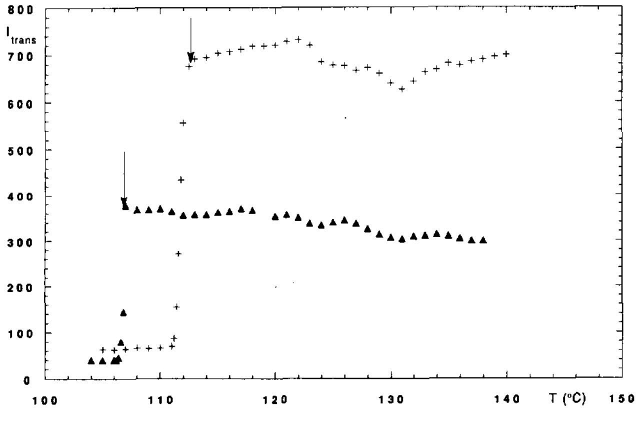

Figure 1 Observation of the cloud point in PAN solutions (monomeric molar fractions are 0.01 (+) and 0.09 (▲))

In this work, X-ray patterns were recorded from PAN solutions, at room temperature; they did not reveal any feature about the ordering of PAN chains in solutions corresponding to polymer molar fractions equal to 0.2 or 0.3.

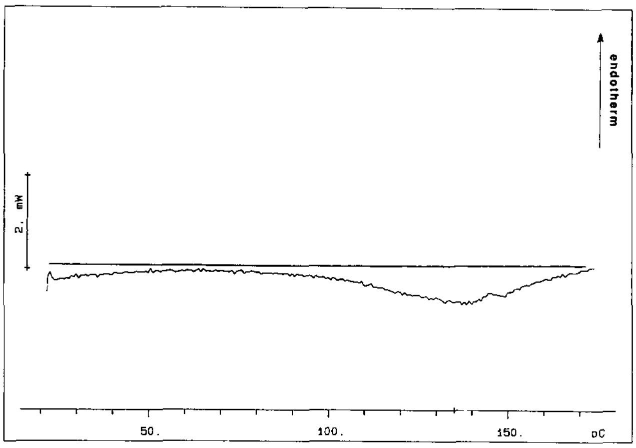

Figure 2 Thermogram recorded from a PAN solution (monomeric molar fraction is 0.30)

Calorimetric observations

The ordering transition of PAN in solution was identified on heating by d.s.c. measurements. Polyacrylonitrile solutions were prepared using a binary solvent (equal molar fractions of water and DMF); two (initial) polymer molar fractions were considered ($\phi_p^i = 0.20$ or 0.30). Solutions were rapidly cooled down to 293 K; then, the temperature was raised at a heating rate equal to 10 K min^{-1}. A typical result is shown in *Figure 2*. The melting point T_m was determined as the temperature of the minimum of the melting endotherm: $T_m = 138$°C for $\phi_p^i = 0.3$. This determination was in accordance with n.m.r. observations reported in a later section. A striking feature is clearly perceived from *Figure 2*: the width of the melting endotherm is found to spread over more than 80°C. This result is in marked contrast to observations of the narrow peaks that usually characterize the melting process of most linear polymers. The narrowness of melting endotherms that are normally observed is interpreted by assuming that a growth process of crystallites occurs on heating; thus, the surface enthalpy contribution to the free enthalpy of melting of ordered domains is reduced. Consequently, the melting temperature of each domain tends to be closer to the melting temperature of the polymer in bulk[9]. Anticipating the discussion about n.m.r. results given later, the broad melting endotherm reported in *Figure 2* implies that the ordering of PAN chains in solution occurs as a multi-step process: the simplest extension is a two-step process. The first step would be a coil–helix transition that appears within chains; such a transition corresponds to an equilibrium between helical parts and coil segments in one chain. For a biopolymer, for instance, the helix–coil endotherm is known to spread over about 30°C for a given chain length[10]. The second step would correspond to the formation of the lateral order that has been observed in the pure polymer, from X-ray measurements. Then, the broad melting endotherm would reveal the existence of a wide distribution of sizes of ordered segments. The total enthalpy of melting ΔH_m was found to be equal to 5.2 kJ mol^{-1}; no significant variation of

ΔH_m was detected by changing the polymer concentration from 0.20 to 0.30.

PRINCIPLE OF THE N.M.R. APPROACH

The n.m.r. approach was based on the discrimination of the transverse relaxation of protons linked to segments located in a solid-state region, whether they are ordered or not, from that of protons attached to segments still in a coil state. For the sake of simplicity, all segments embedded in a solid state will be called ordered segments throughout this work. This experimental n.m.r. approach has already been applied to observations of the kinetics of crystallization of polydimethylsiloxane[11].

Observing PAN chains in a deuterated binary solvent (DMF and water) and at temperatures lower than 130°C, the relaxation curve of the transverse magnetization of protons $M_x(t)$ was shown, without any ambiguity, to consist of two components $M_x^c(t)$ and $M_x^a(t)$. The presence of two components is illustrated in *Figure 3a*, where the two behaviours of the relaxatin function are well distinguished from each other within the temperature range from 25 to 125°C; the monomeric molar fraction was equal to 0.18. The $M_x^c(t)$ function was found to spread over about 30 μs; this is specific to solid-state n.m.r. Long components of relaxation curves, observed at temperatures lower than 140°C, are shown in *Figure 3b*. The non-exponential $M_x^a(t)$ component was found to spread over about 300 ms; this is specific to proton magnetic relaxation in the liquid state. Consequently, the $M_x^c(t)$ component was assigned to ordered monomeric units while the $M_x^a(t)$ component was supposed to represent chain segments joining ordered domains. Above 125°C, no ordering effect was observed and a single-component relaxation curve was recorded. It is worth noting that non-ordered segments are in a more and more dilute solution during the formation of segmental order; therefore, segmental motions must be faster and faster. Consequently, the corresponding $M_x^a(t)$ component must be described by a longer and longer time function, although the temperature is lowered; this effect is actually well illustrated in *Figure 3b*.

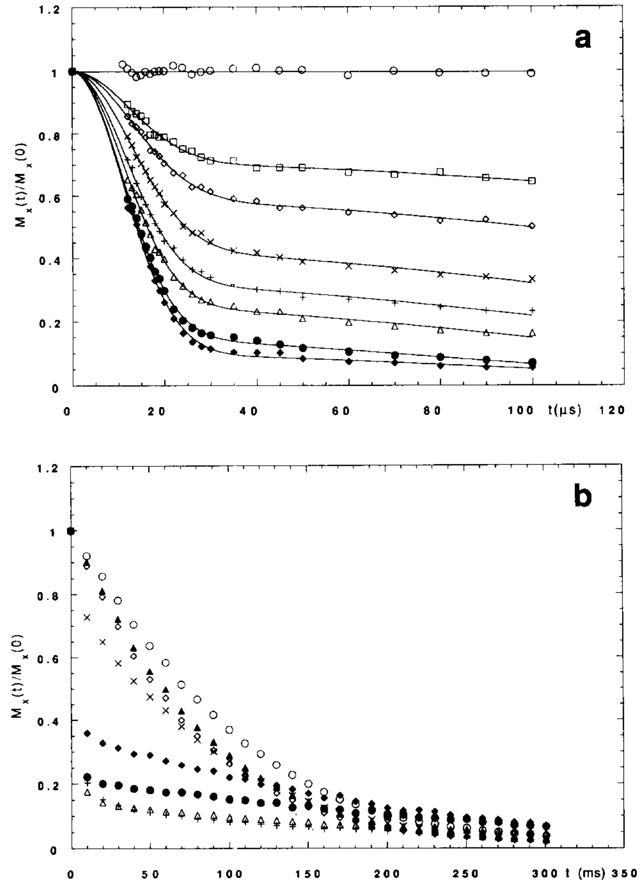

Figure 3 Proton transverse relaxation functions recorded from PAN solutions (monomeric fraction is 0.245). (a) Observation over a short timescale. Sample temperatures (°C) are: 25 (◆), 40 (●), 70 (△), 90 (+), 110 (×), 120 (◇), 125 (□), 130 (○). (b) Observation over a long timescale. Sample temperatures (°C) are: 40 (◆), 60 (●), 80 (△), 100 (+), 110 (×), 115 (◇), 120 (▲), 140 (○)

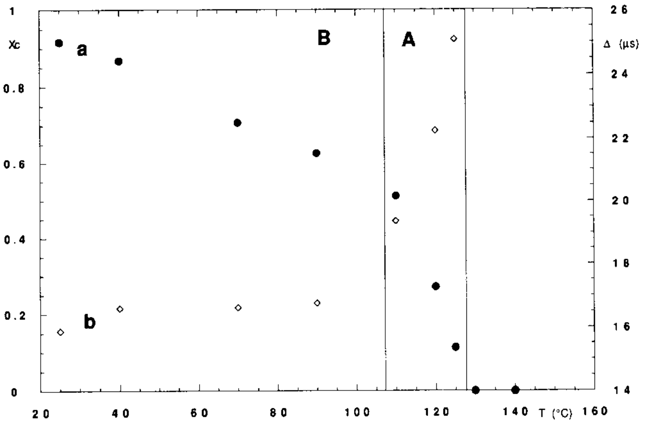

Figure 4 Curve a: extent of segmental ordering X_c observed as a function of temperature for a constant monomeric molar fraction (0.245). Curve b: relaxation time Δ measured as a function of temperature. Two behaviours are evidenced from temperature variations

Let X_c denote the extent of segmental ordering; typical relaxation curves reported in *Figure 3a* show that the experimental value of the fraction of ordered segments is easily derived from the relative amplitude of $M_x^c(t)$ corresponding to ordered segments; $M_x^c(t)$ was described as a Gaussian function characterized by a time constant Δ.

ORDERING PROCESS

The ordering process was observed in polyacrylonitrile in solution in a binary solvent (equal molar fractions of water and DMF). This process was found to occur during a time interval shorter than the time interval required to reach thermal equilibrium of the polymeric system, after introducing the n.m.r. probe in the spectrometer.

Ordering temperature

The temperature of the polymeric solution was progressively lowered step-by-step from the initial temperature $T_i = 140$°C, until a two-component relaxation function was detected without any ambiguity. Then, the temperature was again lowered step-by-step ($\Delta T \simeq 10$°C) and the X_c fraction of protons in the ordered phase was determined for each temperature. A typical variation of $X_c(T)$ is illustrated in *Figure 4* (curve a) for an initial monomeric molar fraction $\phi_p^i = 0.245$. The ordering temperature T_c was defined as the intersection of the $X_c(T)$ curve with the temperature axis; no significant change of the relaxation function was detected at $T = T_c$. Variations of the time constant Δ corresponding to the Gaussian function associated with the fast $M_x^c(t)$ component of the relaxation function are also reported in

Figure 4 (curve b). Two domains are clearly perceived in *Figure 4*. In domain A, there is a strong variation of X_c over a short temperature interval, while in domain B the variation of X_c spreads over about 100°C. The crossover point is defined by $X_c \simeq 0.5$ and $T = 10°C$.

Ordering curve

Construction of a partial phase diagram was attempted, first, by drawing a curve (the liquidus) that relates the ordering temperature T_c to the monomeric molar fraction in the liquid state, and, secondly, by drawing a curve (the solidus) that relates the temperature T_c to the monomeric molar fraction in the solid state. Before drawing these two curves, it was necessary to prove that water molecules of the binary solvent were completely expelled from the ordered state. This property was shown by recording relaxation functions of PAN chains in solution either in deuterated water and DMF or in protonated water and deuterated DMF. The monomeric molar fraction was $\phi_p^i = 0.25$. Variations of the relative number of protons X_r in the solid state with respect to the total number of protons in water and in the disordered polymer are shown as a function of T_c in *Figure 5* (curve a). Curve a′ ($X_c'(t)$) was drawn from curve a by assuming that all water molecules are expelled from the ordered state. Then, curve a′ was compared with curbe b ($X_c(t)$) drawn from relaxation curves observed from PAN chains in solution in a completely deuterated binary solvent. Curves a′ and b were found to be coincident with each other within experimental uncertainty. Therefore, the ordered state corresponds to pure polymer and the solidus (S) is a straight line, parallel to the temperature axis and drawn for the monomeric molar fraction equal to 1 (*Figure 6a*).

The ordering curve (liquidus) was drawn experimentally in the following two ways:

(i) Several initial polymer fractions were observed; for each concentration, the ordering temperature was determined from the intersection of the corresponding $X_c(T)$ curve with the temperature axis. The temperature T_c is reported as a function of the initial monomeric unit fraction ϕ_p^i in *Figure 6a* (filled symbols). An empirical curve was drawn through the experimental points obtained in this way. Two domains are perceived from *Figure 6a*: in domain I, defined by $\phi_p^i \gtrsim 0.10$, a small decrease of the ordering temperature is observed when the polymer molar fraction is lowered. A plateau can be drawn in domain II ($\phi_p^a < 0.10$).

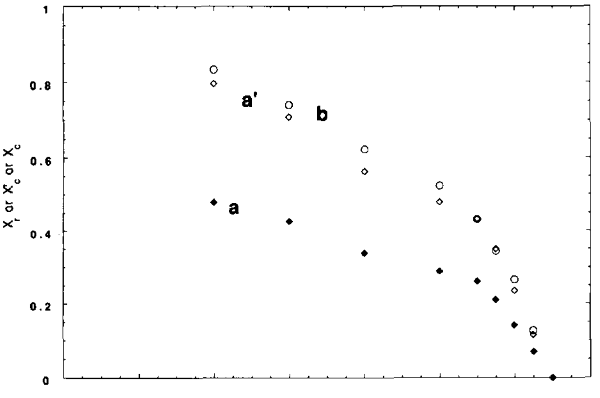

Figure 5 Curve a: extent of segmental ordering X_r observed by taking water protons into account. Curve a′: extent of segmental ordering X_c' calculated by eliminating water protons. Curve b: extent of segmental ordering X_c observed in the presence of deuterated water

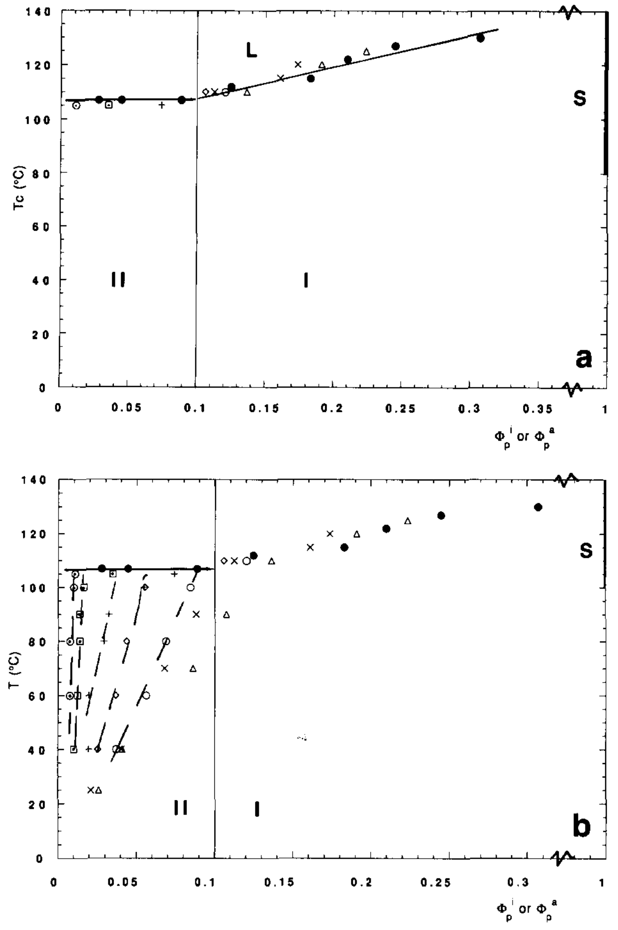

Figure 6 (a) Ordering temperatures determined from several initial PAN concentrations, ϕ_p^i (●). A continuous curve (L) was empirically drawn through experimental points. Two thermodynamic domains I and II are disclosed. The solidus (S) is also reported on the diagram. Open points correspond to the concentration of non-ordered polymer, ϕ_p^a, determined at a given temperature, by keeping the polymer concentration constant. Initial monomeric molar fractions are: 0.245 (△), 0.21 (×), 0.18 (○), 0.12 (◇), 0.09 (+), 0.045 (□), 0.03 (⊙). (b) Ordering temperatures related to different concentrations of non-ordered PAN, ϕ_p^a, are reported to give evidence for two behaviours of polymer solutions.

(ii) In the second approach to determining the ordering curve, the monomeric molar fraction was kept constant while the sample temperature was lowered step-by-step down to 20°C. The extent of polymeric order X_c was measured as a function of temperature. Then, the concentration of polymer ϕ_p^f left in solution was derived from X_c, considering that the solvent was fully expelled from ordered domains. The concentration of disordered polymer ϕ_p^a was expressed as:

$$\phi_p^a = [1 - X_c(t)]\phi_p^i / [1 - X_c(T)\phi_p^i] \qquad (1)$$

Experimental points that represent the ϕ_p^a concentration for a given temperature are reported in *Figure 6a* (open symbols); for the sake of clarity, ordering temperatures lower than 105°C are not reported in *Figure 6a*. Experimental points were found to be reasonably located on the ordering curve already drawn empirically based on the first approach.

These two experimental approaches reinforce the interpretation of the ordering curve as a liquidus and the existence of two domains. However, this liquidus is lowered with respect to the melting curve; the finite size of the ordered domains yields a lowering of the ordering curve of PAN chains, as in all polymeric systems. This effect is discussed in the next section.

Finally, all ordering temperatures measured from n.m.r. in the second approach are reported in *Figure 6b*. In addition to the two domains revealed in the thermodynamic diagram, a specific behaviour of the ordering temperature is clearly observed below about 105°C when the monomeric molar fraction of disordered segments ϕ_p^a is decreased. More precisely, the specific behaviour of the ordering temperature was analysed by drawing empirical straight lines through experimental points. The inverse of the slope s of each straight line is reported as a function of the initial monomeric molar fraction ϕ_p^i in *Figure 7a*; a straight line can be reasonably drawn through the calculated points. The linear variation of s^{-1} is written as

$$s^{-1} = \kappa\phi_p^i \qquad (2)$$

with $\kappa^{-1} \simeq 4.3 \times 10^{-3}$ K. Then, the concentration ϕ_p^c corresponding to the intersection of each straight line drawn in domain II with the ordering curve was reported as a function of the initial monomeric molar fraction in *Figure 7b*; a linear variation was found. This is represented by:

$$\phi_p^c = \chi\phi_p^i \qquad (3)$$

with $\chi = 0.5$. This short analysis shows that the crossover concentration that separates the two different behaviours of polymer solutions is about equal to $0.5\phi_p^i$. Furthermore, the equation of each straight line drawn in *Figure 6b* is determined by combining empirical equations (2) and (3):

$$T - T_c = \frac{\chi}{\kappa\phi_p^c}(\phi_p^a - \phi_p^c) \qquad (4)$$

or

$$T - T_c = (\chi/\kappa)(\phi_p^a/\phi_p^c - 1) \qquad (5)$$

with $T_c = 105$°C.

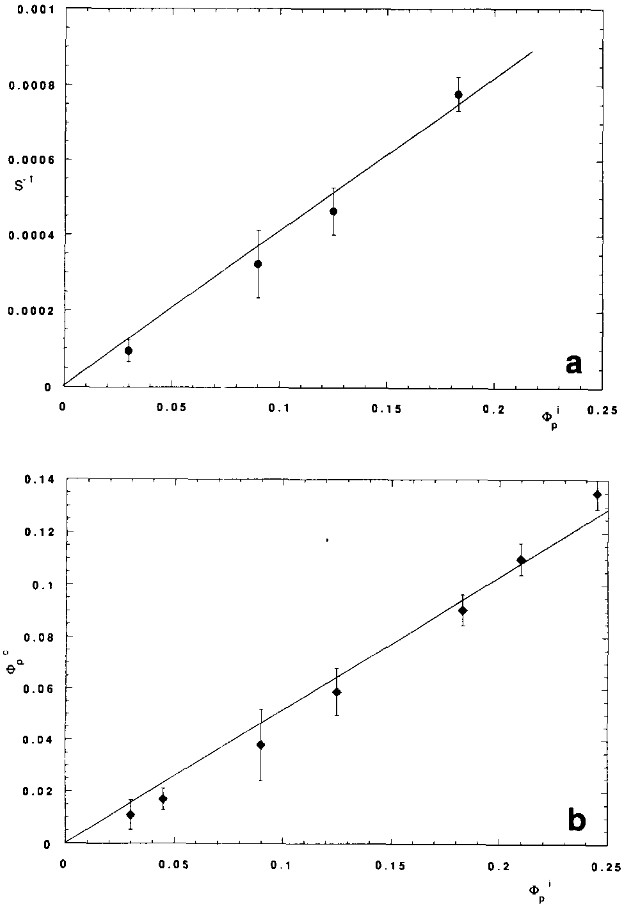

Figure 7 (a) The inverse s^{-1} (K^{-1}) of the slope of each straight line drawn in *Figure 6b* is reported as a function of the initial monomeric molar fraction ϕ_p^i; (b) The concentration ϕ_p^c of intersection of each straight line drawn in *Figure 6b* is reported as a function of the initial monomeric molar fraction ϕ_p^i

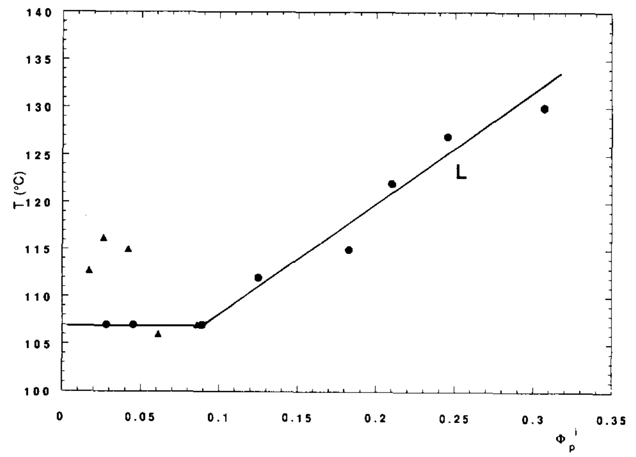

Figure 8 Temperatures of demixing (cloud points, ▲) are compared with the liquidus (L)

Consequently, a single empirical representation can be used to describe the dependence of the ordering temperature on the monomeric molar fraction whenever the concentration of segments, still in a disordered state, becomes smaller than half the initial polymer concentration; this representation relies upon the existence of a reduced variable ϕ_p^a/ϕ_p^c. Starting from domain I, an unusual behaviour of the liquidus is observed when the polymer molar fraction is decreased or when the temperature of the solution is lowered. Then, the onset of a different behaviour occurs when the reduced variable ϕ_p^a/ϕ_p^i is smaller than 0.5.

The existence of two behaviours of polymer solutions is also perceived in *Figure 4;* the crossover point is also given by $X_c = 0.5$.

It is presumed that the ordering process of PAN chains occurs in the following two ways. As long as the monomeric molar fraction of disordered segments is higher than $0.5\phi_p^i$, both segmental order and lateral order of segments are formed. However, interactions between chain segments become negligible when the molar fraction of polymer left disordered is smaller than $0.5\phi_p^i$. Then, it is supposed that there is only a segmental ordering, which takes place without the formation of any lateral order.

DEMIXING PROCESS

The demixing curve was identified by observing cloud points. Experimental results are reported in *Figure 8.* It is seen that the demixing curve is determined within the range of polymer molar fractions that define domain II. It is suggested that domain II can be identified with the demixing process of PAN chains.

MELTING-POINT DEPRESSION

The melting point was identified in n.m.r. measurements as the temperature corresponding to the onset of the

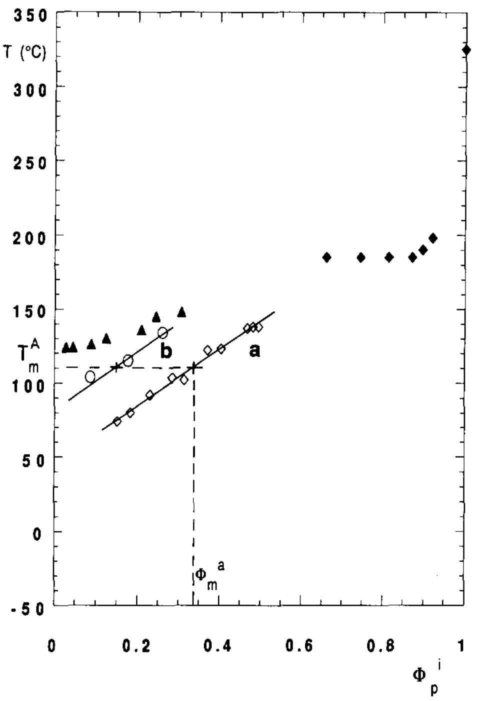

Figure 9 Melting-point depression observed as a function of poluymer mole fraction, ϕ^i_p, in pure DMF (◇) in accordance with ref. 3. Melting-point depression observed in binary solvents: equal molar fractions of water and DMF (▲); DMF molar fraction twice that of water (○). Melting-point depression induced by the presence of water in accordance with ref. 5 (◆)

regime of one-component relaxation curves of protons over a heating cycle. Melting-point depression was observed within a small range of polymer concentration because of the difficulty in preparing homogeneous concentrated solutions of PAN.

Samples were first rapidly cooled down to 20°C, after which the temperature was raised step-by-step ($\Delta T \simeq 10$°C). Experimental results are reported in *Figure 9*. Polymer melting was observed in pure DMF and also in binary solvents with two different molar fractions of water with respect to DMF.

Binary solution

The melting-point depression observed in pure DMF is illustrated in *Figure 9* (curve a). The melting temperature is lowered from 140°C to 75°C when the polymer concentration varies from 0.5 to 0.15. To analyse the melting-point depression curve, a reference temperature was arbitrarily chosen $T^A_m = 110$°C; it corresponds to $\phi^A_p = 0.34$. The melting-point depression curve is represented by a straight line within the temperature range of observation. Let $\mu^{sol}_p(T_m, p_o, \phi_p)$ and $\mu^l_p(T_m, p_o)$ denote the chemical potentials per monomeric unit in solution and in the pure polymer in the liquid state, respectively. Also, the free enthalpy of melting is expressed as:

$$\Delta g_m(T) = \Delta h_m(T^A_m)(1 - T/T^A_R) \tag{6}$$

$\Delta h_m(T^A_m)$ is the enthalpy of melting of the pure polymer defined at $T^A_m = 383$ K; it may differ from the enthalpy of melting measured at $T_m = 598$ K, the melting temperature of the pure polymer. The temperature T^A_R is defined as the ratio of $\Delta h_m(T^A_m)$ over the entropy variation $\Delta S_m(T^A_m)$. Then, at equilibrium, the following condition must be fulfilled:

$$\Delta g_m(T_m) = \mu^l_p(T_m, p_o) - \mu^{sol}_p(T_m, p_o, \phi_p) \tag{7}$$

The variation of $\mu^{sol}_p(T_m, p_o, \phi_p)$ as a function of the temperature and the polymer molar fraction ϕ_p was assigned to a pure entropic effect within the range $0.15 \leqslant \phi_p \leqslant 0.5$. The variation of entropy of mixing of the polymer and DMF was expressed as:

$$\Delta S_m = -k(n_1 \log x_1 + n_p \log \phi_p) \tag{8}$$

Here n_1 and n_p are the numbers of solvent molecules and polymer chains, respectively, while x_1 and ϕ_p are the molar fractions of solvent and monomeric units, respectively. The variation of the chemical potential per monomeric unit upon mixing is given by:

$$\mu^{sol}_p - \mu^l_p \simeq -kT(1 - \phi_p) \tag{9}$$

Therefore, the melting-point depression is described by:

$$\frac{1}{T_m} - \frac{1}{T^A_m} = -\frac{k(\phi_p - \phi^A_p)}{\Delta h_m(T^A_m)} \tag{10}$$

or

$$T_m \simeq T^A_m + \frac{k(T^A_m)^2}{\Delta h_m(T^A_m)}(\phi_p - \phi^A_p) \tag{11}$$

The numerical analysis of curve a in *Figure 9* yields $\Delta h_m(T^A_m) = 6.0 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$; enthalpic effects were neglected.

Binary solvent

The melting-point depression was also observed using a binary solvent; a straight line (b) was drawn through the three experimental points reported in *Figure 9* and corresponding to a molar fraction x_1 of DMF equal to twice the molar fraction x_2 of water. Two features are perceived from *Figure 9*:

(i) The presence of water raises the melting point of the solution for a given polymer molar fraction.

(ii) It is assumed that straight lines a and b are nearly parallel to each other within experimental uncertainty. To describe the melting-point depression, the chemical potential $\mu^{sol}_p(T_m, p_o, \phi_p)$ is replaced with $\mu^{sol\prime}_p(T_m, p_o, x_1, 1 - \phi_p - x_1)$ in equation (7). For curve b, the reference temperature is still arbitrarily chosen equal to T^A_m; it corresponds to $\phi^B_p = 0.15$. This value is determined from:

$$\Delta g_m(T^A_m) = \mu^l_p(T_m, p_o) - \mu^{sol\prime}_p(T^A_m, p_o, x_1, 1 - x_1 - \phi^B_p) \tag{12}$$

The entropy of mixing of the three components is expressed in a simple way:

$$\Delta S' = -k(n_1 \log x_1 + n_2 \log x_2 + n_p \log \phi_p) \tag{13}$$

and the entropic contribution to the variation of chemical potential per monomeric unit upon mixing is again given by equation (9). Then, the melting-point depression is described by:

$$T'_m \simeq T^A_m + \frac{k(T^A_m)^2}{\Delta h_m(T^A_m)}(\phi_p - \phi^B_p) \tag{14}$$

again neglecting enthalpic contributions.

The difference between the melting temperature T'_m observed in the presence of water and the melting temperature T_m observed in the absence of water is given by:

$$T'_m \simeq T_m + \frac{k(T^A_m)^2}{\Delta h_m(T^A_m)}(\phi^A_p - \phi^B_p) \tag{15}$$

The numerical value of Δh_m estimated from *Figure 9* is again equal to $6\,\mathrm{kJ\,mol^{-1}}$. The enthalpic contribution to

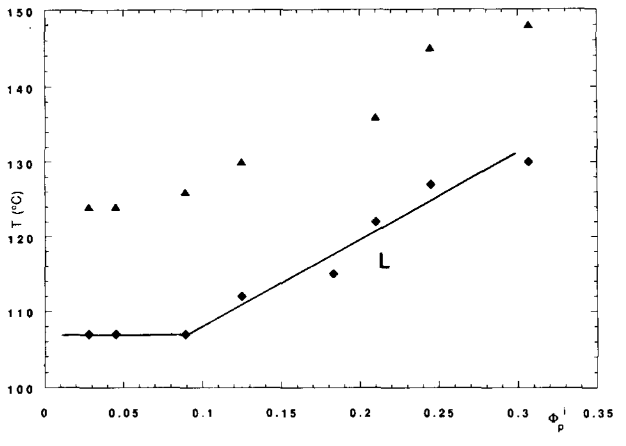

Figure 10 The liquidus (L) and the melting curve (▲) are compared with each other for PAN in solution in a binary solvent (equal molar fractions of DMF and water)

the free enthalpy of mixing is neglected in the description of linear variations of T'_m but it is involved in the concentration shift from ϕ_p^A to ϕ_p^B induced by addition of water.

In the case where the molar fraction x_1 of DMF is equal to the molar fraction x_2 of water ($x_1 = x_2 = (1-\phi_p)/2$), a new reference temperature $T_m^{A'}$ must be chosen and enthalpic effects can no longer be neglected.

Melting and ordering temperatures corresponding to equal fractions of water and DMP are reported in *Figure 10*.

DISCUSSION

One of the main problems encountered in studying the temperature–concentration phase diagram of polyacrylonitrile solutions concerns the difficult observation of ordered domains, which are induced by lowering the temperature or by increasing the polymer concentration. Conventional X-ray observations did not detect any order in solutions. However, n.m.r. proved to be a convenient tool, which disclosed the presence of solid-state domains even though their size could not be estimated. It must be noted that it is not easy to discriminate an ordered polymeric state from a disordered solid state using n.m.r. (in the absence of the preferential onset of molecular motion in one or other state). Nevertheless, the accurate n.m.r. observation of the onset of a polymeric solid state yields a phase separation curve, known as the liquidus. Two domains are clearly evident in the phase diagram, along the liquidus; the monomeric unit fraction of the crossover from one domain to the other one is about 0.1. In the range of polymer concentrations smaller than 0.1, the liquidus resembles a plateau; this domain is assigned to a demixing process because it also corresponds to the observation of a cloud-point curve. Taking d.s.c. measurements into consideration, it is assumed that the liquidus corresponds to polymer ordering when the polymer concentration is higher than 0.1; correspondingly, the solidus was shown to be defined by the pure polymer.

Although the concentration range of investigations was small because of difficulty in preparing concentrated solutions, ternary solutions of polyacrylonitrile were found to exhibit a specific behaviour induced by lowering the temperature once the liquidus is reached. More precisely, representative points of the polymer system in the phase diagram depart from the liquidus whenever the concentration of segments still in solution becomes smaller than half the initial concentration of polymer; then, the temperature–concentration curve can be described as a straight line within a reasonable approximation. This behaviour was observed below both the demixing plateau and the ordering domain of the liquidus.

According to this striking result, the change of behaviour of polymer solutions does not occur for a fixed polymer concentration; this change occurs whenever half the polymer chains are in a solid state. In the absence of any direct observation of polyacrylonitrile chains, except from n.m.r., the proposed qualitative interpretation relies upon the assumption that properties of solutions, observed on or below the liquidus, are based primarily on the formation of segmental order. The partial ordering of segments can be pictured as a coil–helix transition. The lengths of ordered segments probably obey a broad distribution function. Two cases are considered:

(i) For polymer concentrations higher than 0.1, there is a two-step process that occurs on or below the liquidus. An ordered packing of ordered segments is formed by lowering the temperature when the liquidus is reached. This segmental order is probably the source of the observed broad melting endotherm. Then, remaining disordered segments undergo an ordering process, reflected by straight lines, whenever the concentration of polymer still in solution is smaller than half the initial concentrations; there is a disordered packing of segments.

(ii) For polymer concentrations smaller than 0.1, demixing yields only a disordered solid state formed by ordered segments; the segmental ordering is also linear.

Ordered segments, whether they form ordered packings or not, probably govern the structure of the porous medium formed by polyacrylonitrile solutions cooled down to room temperature.

ACKNOWLEDGEMENT

J. P. Marchand is grateful to Hospal Research International for partial support.

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