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Correction of the reduced viscosity of a polymer near the critical point of a partially miscible binary liquid mixture

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Near the critical point of two nonmiscible liquids the reduced viscosity of a polymer diverges to infinity. These very high values of the reduced viscosity must be characterized as "apparent" values because they are not due to an increase of the dimensions of the macromolecular coils but to an increase of the correlation length of the two liquids by the presence of the polymer.

Over the last years a great interest has been expressed in the study of critical phenomena related to partially miscible binary liquid mixtures.[1,2] It is known[3,4] that the critical solution temperature, T_c, of two partially miscible liquids is increased or decreased by the presence of a third substance, and it was found recently that T_c is always increased by the presence of a polymer.[5-9]

Shear viscosity measurements of binary liquid mixtures near the critical point have shown that the viscosity of liquid mixtures presents an anomalous increase when one approaches the critical point, either by changing the composition or the temperature of the system.[10] In a relatively recent article,[11] de Gennes has predicted that the presence of macromolecular chains in the vicinity of the critical point of two partially miscible liquids must provoke "dramatic" effects expressed through viscosity measurements. Indeed, some viscometric studies of polymer dilute solutions have shown that either the reduced viscosity, $\eta_{\rm red}$, of a polymer or its intrinsic viscosity, $[\eta]$, become abnormally high near the critical point of the two liquids.[5,6,12]

In this paper we will try to explain this dramatic increase of $\eta_{\rm red}$ of the polymer and try to see if this increase is due to an increase in the dimensions of the macromolecular coil or to a change in the structure of the binary liquid mixture by the presence of the polymer. Our answer is that the second hypothesis seems to be true, and that the measured reduced viscosity could be characterized as "apparent" reduced viscosity.

In the following, we give our viscometric results for two polymer samples, polystyrene (PS) and polyethyleneglycol (PEG), in the binary solvent mixture cyclohexane (CH)-methanol (MeOH), at its critical composition, 70 vol% CH. The viscosity measurements have been conducted with a modified hermetically closed Ubbelohde-type viscometer. The solvents used, CH and MeOH, were reagent grade, and the polymer samples, PS and PEG, were of very narrow molecular weight distribution.

The $\eta_{\rm red}$ of the polymers has been calculated by the relation

$$\eta_{\rm red} = \frac{t - t_0}{t_0 c} , \tag{1}$$

where t is the flow time of the polymer solution, t_0 is the flow time of the solvent, and c is the polymer concentration.

In Fig. 1 we present the reduced viscosity $\eta_{\rm red}$ of the PS sample at the critical composition of the binary solvent mixture CH-MeOH, as a function of the temperature T. The molecular weight, M_w, of the PS sample was 7.700 and its concentration, c, was equal to 5.00×10^{-3} g/cm^3. Figure 1 shows that the $\eta_{\rm red}$ diverges to infinity as one approaches T_c', the critical solution temperature of the ternary system PS-CH-MeOH.

The same viscosity measurements have been conducted with a PEG sample ($M_w = 6.000$, $c = 2.00 \times 10^{-3}$ g/cm^3) and the results are given in Fig. 2. We observe that the $\eta_{\rm red}$ of the PEG presents, as a function of T, the same behavior as the $\eta_{\rm red}$ of PS.

The study of the critical phenomena is tightly related with characteristic critical exponents[13] obtained when one presents the variation of a physical property of the system as a function of the reduced temperature, $\epsilon = (T - T_c)/T_c$, where T_c is the critical temperature. Here we will try to obtain a critical exponent using our viscometric results. In Fig. 3 we present the variation of the $\log_{10}\eta_{\rm red}$ as a function of the $\log_{10}\epsilon'$ [ϵ' is the reduced temperature for the ternary system, equal to $(T - T_c')/T_c'$] for the above two systems. The points fit well in two straight lines presenting practically

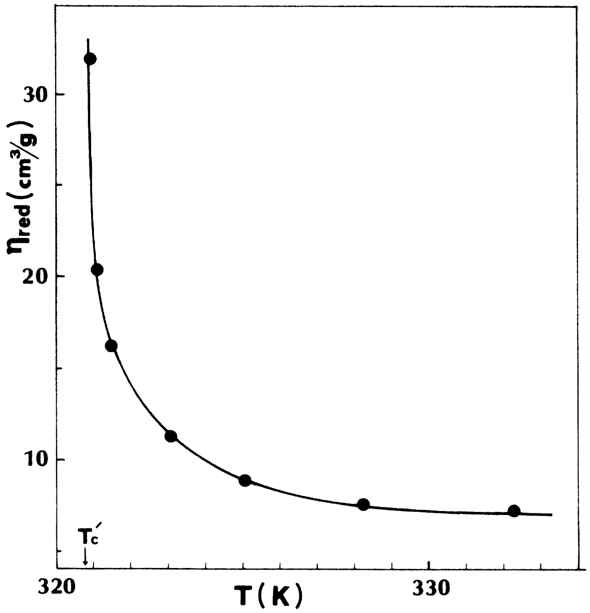

FIG. 1. Variation of the reduced viscosity, $\eta_{\rm red}$, of PS in the solvent mixture 70 vol% CH-30 vol% MeOH, as a function of the temperature T. T_c' is the critical solution temperature of the ternary system PS-CH-MeOH equal to 320.72 K.

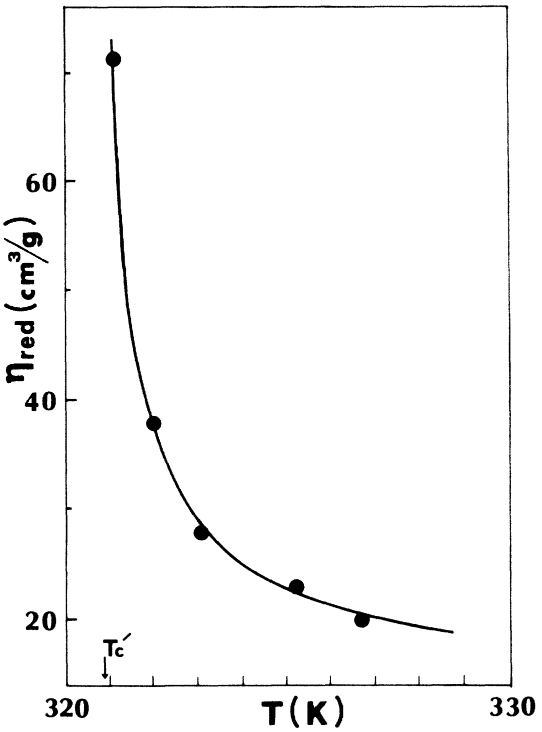

FIG. 2. Variation of the reduced viscosity, η_{red}, of PEG in the solvent mixture 70 vol% CH-30 vol% MeOH, as a function of the temperature T. $T_c' = 320.80$ K.

the same slope and giving the same critical exponent ν' equal to -0.33. These results indeed show that the variation of the η_{red} of the polymers dissolved in a binary liquid mixture at its critical composition obeys a scaling law.

In order to explain this peculiar behavior of the η_{red}, we will try to see if this is due to an increase in the correlation length of the binary liquid system provoked by the presence of the polymer. As is known,[14,15] the shear viscosity η of a binary liquid mixture at its critical composition obeys the following analytical form

$$\eta = K \exp\left(\frac{A}{T}\right)\epsilon^{-\gamma} \ . \tag{2}$$

The theoretically predicted value[16] of the exponent γ is 0.04. Treating, according to this formula, our shear viscosity measurements of the critical binary solvent mixture CH-MeOH, we obtain the following expression for the flow time t_0, as a function of the temperature:

$$t_0 = 1.682 \exp\left(\frac{1250}{T}\right)\left(\frac{T-T_c}{T_c}\right)^{-0.036} , \tag{3}$$

where $T_c = 318.92$ K is the critical solution temperature of the binary system and has been determined by turbidimetry. In the following, we calculate another solvent flow time t_0' by putting in Eq. (3) the higher critical solution temperature of the ternary system PS-CH-MeOH, $T_c' = 320.72$ K, instead of T_c. It is evident that the calculated flow time t_0' is always higher than the measured flow time t_0, especially near the critical point. We suppose that this calculated value t_0' corresponds to a solvent structure more ordered by the presence of the polymer in the binary system CH-MeOH. Returning to Eq. (1) which gives the η_{red} of the polymer sample and now using the calculated value t_0' for the solvent instead of the measured one t_0, we obtain curve (a) of Fig. 4 for the system PS-CH-MeOH. The same calculation for the ν' system PEG-CH-MeOH gives curve (b) of Fig. 4. These two curves represent the corrected reduced viscosity, $\eta_{red.\,cor.}$, of the two polymer samples and they have to be compared with the experimental curves of Figs. 1 and 2, respectively.

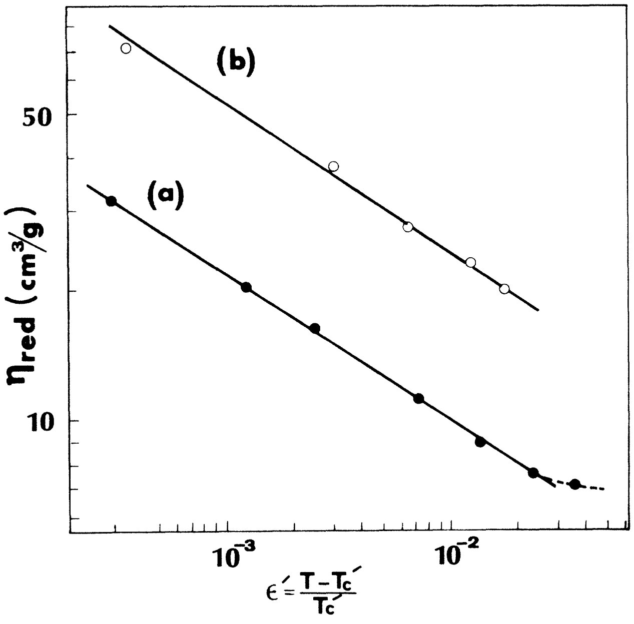

FIG. 3. Variation of the reduced viscosity, η_{red}, of the polymer, as a function of the reduced temperature, $\epsilon' = (T-T_c')/T_c'$, in double logarithmic scale. Curve (a), PS in CH-MeOH. Curve (b), PEG in CH-MeOH.

The above results show that the hydrodynamic dimensions of the macromolecular coils near the critical point of the binary liquid mixture do not increase (Fig. 4). The increase of the η_{red} (Figs. 1 and 2) of the polymer near the critical point seems to be due to an increase of the correlation length of the binary liquid mixture, provoked by the presence of the polymer and, consequently, of its shear viscosity.

It has been shown[17,18] that when a polymer is dissolved in a mixture of solvents it is preferentially solvated by one of

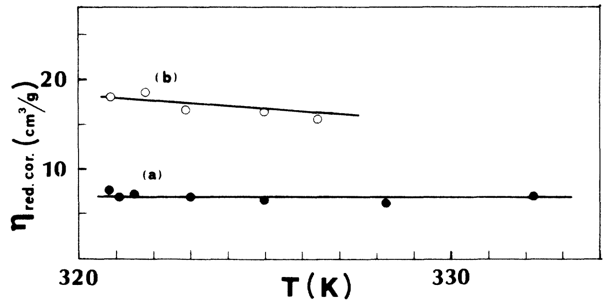

FIG. 4. Variation of the corrected reduced viscosity, $\eta_{red.\,cor.}$, as a function of the temperature T. Curve (a), PS in CH-MeOH. Curve (b), PEG in CH-MeOH.

the two liquids. Near the critical point, this preferential solvation must give a coalescence of the droplets which are richer in the good solvent of the polymer and this assembly leads to an increase of the correlation length ξ of the two liquids,[19] expressed as an increase of their shear viscosity (t_0 becomes t_0'). We have to point out here that in our systems the preferential solvation of the polymer is very much favored by the fact that one of the solvents is a precipitant of the polymer (MeOH for PS and CH for PEG). This is also in agreement with the observed increase of the critical solution temperature of binary liquid mixtures provoked by the presence of a small quantity ($\sim 0.2\%$) of a polymer.[5–9] We might conclude that a polymer added in a critical liquid mixture presents a cooperative action for the observed correlations at the critical point, and it operates as an "internal" ordering field.

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