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[b] (EBBA) → p-ethoxybenzylidene-p-n-butylaniline (PAA) → p-azoxyanisole

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FLEXIBLE POLYMERS IN NEMATIC SOLVENTS : PHASE DIAGRAMS IN DILUTE REGIME

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Abstract : We present the main types of phase diagrams obtained with flexible polymers in nematic solvents. Data deduced from experimental phase diagrams are compared with two theoretical descriptions.

INTRODUCTION

In the framework of a study of physical properties of flexible polymers in nematic solvents (1) (viscosity (2), order parameter (3)), we have been lead to investigate the phase diagrams of these new binary systems. A study of different polymer-nematic combinations has allowed us to extract the main features of these peculiar systems. Thermodynamic data deduced from our phase diagrams as well as the results obtained independently by B. Kronberg et al (4) suggest that the nematic order is destroyed near each polymeric coil.

EXPERIMENTAL SECTION

. Materials - The solutes were two polymers, polystyrene (PS) and polyethylene oxide (PEO), for which we can easily obtain samples of different molecular weight (Mw) with a low polydispersity (Mw/Mn $\leqslant$ 1.1). The PS samples (Mw = 2100, 4000 and 9000) were obtained from Pressure Chemical Company while the PEO sample (Mw = 2100) was anionically synthesized by F. Candau (C.R.M. Strasbourg).

. The solvents were two liquid crystal (EBBA and PAA)+.

+ (EBBA) → p-ethoxybenzylidene-p-n-butylaniline
(PAA) → p-azoxyanisole

The Schiff base EBBA was obtained from Varylight and exhibited a nematic phase from 36°C to 78,6°C. As for the azoxy compound (PAA), it was a zone refined sample that we obtained from Princeton Organics ; its nematic domain spread from 118°C to 136°C.

. Procedure - For a given polymer-liquid crystal combination, we prepared several mixtures with different polymer volume concentrations Φ. Each mixture contained ≈ 0,5g of liquid crystal and was kept in glass tubes which were sealed under primary vacuum. First, each sample was homogenized by smooth shaking for three hours at a temperature where the mixture was isotropic (just above the clearing temperature T_c° of the nematic solvent). Then, the samples were dipped in a heated bath which permitted a visual observation of the sealed tubes, the bath temperature was regulated with an accuracy of ± 0,1°C.

. Experimental results - A typical phase diagram is given in figure 1. Starting from an isotropic homogeneous solution of concentration Φ_o , the temperature is slowly decreased. The first nematic droplet appears at the temperature T_i (Φ_o) which defines the upper coexistence curve.

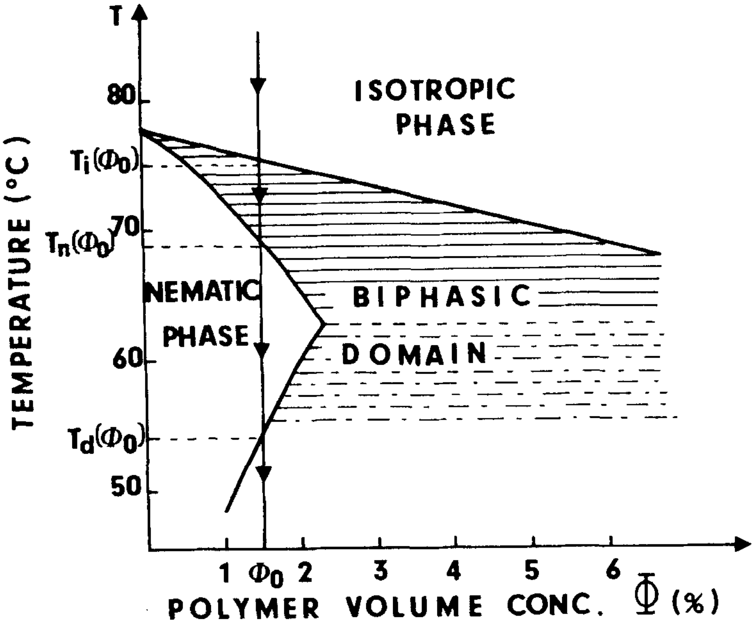

Figure 1

As the cooling proceeds, the isotropic and nematic phases coexist until the temperature reaches T_n (Φ_o) ; then, the sample becomes totally nematic. Notice that, because of the turbidity of the nematic phase, T_i is determined with greater accuracy (± 0,1°C) than T_n (± 1°C). Just below T_n we have an homogeneous nematic phase ; but at lower temperature, an another phase separation process may occur : at T_d (Φ_o) (see fig. 1), there appears an isotropic fraction rich in polymer in equilibrium with a nematic solution. This demixtion process is caracterized by large relaxation times as it is typical in polymeric solutions ; phase separation sometimes requires several days. This explains that B. Kronberg et al do not mention such a phase separation on similar mixtures.

. Thus, the typical diagram in figure 1 appears to be the superposition of two classical ones which correspond to :

. a phase transition in a binary mixture, with a biphasic domain much broader than in the case of small molecule solutes.

. a liquid-liquid phase separation (demixtion) with a coexistence curve which, at low concentration, sharply increases as usually observed in polymeric solutions.

. We have observed several variants of the above behavior for differents polymer-liquid crystal systems. For instance, in the case of "PS2100-PAA" system (see fig. 2a),

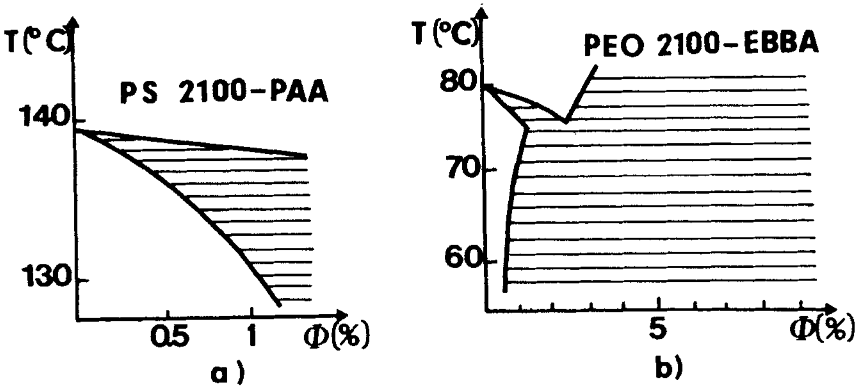

Figure 2

the low-temperature phase separation T_d is not observed before the nematic solution crystallizes. On the other hand, in the "PEO2100-EBBA" case the demixtion process occurs even in the isotropic phase (see fig. 2b). But, in all cases, the biphasic domain becomes larger as the molecular weight of the solute increases ; a homogeneous nematic phase becomes inobservable for $M_w \geqslant 10^4$.

DISCUSSION

. Two physical parameters can be obtained from our data :

. ΔH_o , the molar enthalpy of transition for the pure nematic.

. ΔF_{ch} , the free energy which is necessary to transfer a polymeric chain from the isotropic phase to the nematic phase.

. For low concentrations, i.e, near T_c° ($T_c^\circ - T \ll T_c^\circ$), a first order approximation leads to the following relations :

$$\phi^i - \phi^n = \frac{M_2}{M_1} \frac{\Delta H_o}{\mathcal{N} kT} \frac{(T_c^\circ - T)}{T_c^\circ} \qquad (1)$$

$$\phi^n / \phi^i = \exp\left[- \frac{\Delta F_{ch}}{kT} \right] \qquad (2)$$

where Φ^i and ϕ^n are respectively the polymer concentration in the isotropic and nematic fractions at the temperature T while M_1 (M_2) is the molecular weight of the solute (solvent) ; k is the Bolztmann constant and $\mathcal{N}$ the Avogadro number.

. The values obtained with the different systems that we have studied are listed in table 1. As for the ΔH_o data, we find a reasonable agreement between the value deduced from the phase diagram and the direct measurement by differential scanning calorimetry.

Table 1

Nematic Compound	Polymer	N (Subunits)	ΔF_{ch} (°K)	$\frac{\Delta F_{ch}(°K)}{N}$	ΔH_o (J/mole)	ΔH_o by DSC
EBBA	POE2100	48	312	6,5	470	500
	PS2100	21	399	19	475	
	PS4000	40	720	18	500	
	PS9000	90	1300	14,5	370	
PAA	PS2100	21	189	9	940	800

We obtain a poorer agreement in the case of higher molecular weight (PS9000) ; this discrepancy is due to a large uncertainty in the determination of the lower coexistence curve which becomes very steep as the molecular weight increases.

. The interpretation of ΔF_{ch} is more delicate than that of ΔH_o. For instance, B. Kronberg et al have proposed a description based on an extended Flory-Huggins lattice model. This model introduces two different Flory parameters χ^i and χ^n which caracterize the interactions of a chain subunit with solvent respectively in the isotropic (i) and nematic (n) phase :

$$\Delta F_{ch} = N\Delta F_{sub} \quad \text{with} \quad \Delta F_{sub} \alpha \; kT \; (\chi^n - \chi^i)$$

. So, we expect that $\Delta F_{ch}/N$ is constant for a polymer nematic combination as the molecular weight varies. In fact, Table 1 shows that $\Delta F_{ch}/N$ decreases as M_w increases ; indeed, B. Kronberg et al found similar results on PS-EBBA systems. This lead F. Brochard (5) to imagine another description in which the nematic order is destroyed near the polymeric coil ("Strong coupling model"). In this model, ΔF_{ch} is mainly related to the creation of an isotropic droplet and varies as $N^{1/2}$; consequently, $\Delta F_{ch}/N$ decreases as $N^{-1/2}$. Therefore this "Strong coupling model" seems to be qualitatively supported by the experimental results. One more argument can be deduced from the comparison between two different polymeric compounds (POE2100 and PS2100) in the same solvent EBBA :

. Table 1 shows that F_{ch} has roughly the same value for both systems and thus depends more on the polymeric solute size than on its chemical nature. This last experimental fact, straightforward in the "Strong coupling model" would be difficult to interpret in the framework of the Kronberg model. However, we emphasize that our experimental values $\Delta F_{ch}/N$ do not quantitatively verify the (−1/2) scaling exponent. This discrepancy is perhaps due to the very restricted range of M_w variation which is experimentally accessible.

CONCLUSION

. The phase diagrams obtained for different flexible polymer-nematic compound systems clearly show that a homogeneous nematic phase becomes inobservable when the molecular weight M_w of the polymeric solute becomes higher than 10^4. In spite of this restriction, this study demonstrates the polymeric features of this new type of binary phase diagram : an enlarged biphasic domain and important demixtion process. Moreover, the evolution of the two phases domain as M_w increases, seems to indicate that the nematic order is destroyed near each polymeric coil. For the future, we plan to repeat this study with polymeric solutes which reinforce the nematic order.

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