

## Pseudo Clearing Temperature in Binary Polymer-Nematic Solutions

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The temperature dependence of the orientational parameter was measured by  $^1\text{H}$  NMR techniques on solutions of polystyrene dissolved in nematic liquid crystals. This temperature dependence is different from that one of pure nematogens or of solutions of small molecules in nematic phases. These results are consistent with the concept of a pseudo clearing temperature introduced theoretically by Brochard. These are general results for solutes in nematic solvents, including those previously obtained on dissolved small molecules.

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Usually, binary systems are completely defined by their phase diagrams. However, in the case of a nematic solvent, the situation is more complex; indeed, there is an additional variable, namely the liquid-crystal order parameter  $S$ . For pure nematic liquid crystals, when increasing the temperature, the order parameter decreases to reach a nonzero minimum value  $S_0$  at the clearing temperature  $T_c^0$  where the first-order transition nematic-isotropic occurs. With use of a mean-field theory, Maier and Saupe<sup>1</sup> predicted that the variation of  $S$  is an universal function of reduced temperature  $T/T_c^0$  with the same minimum value  $S_0$  for all nematic liquid crystals. In fact, this is an approximate model from which experimental results may deviate significantly.<sup>2</sup> However, in the case of a nematic solution containing a low concentration of solute, it is reasonable to expect the same variation with the reduced temperature  $T/T_c(\Phi_0)$  as for the pure nematic phase. Here,  $T_c(\Phi_0)$  is the equivalent of the "clearing point" for a nematic solution at concentration  $\Phi_0$ . Thus a complete characterization of such systems requires a thermodynamic definition of the clearing temperature which allows to evaluate  $S$  for all temperatures. The determination of this clearing temperature is not straightforward since, for binary systems, there is no unique temperature at which the two phases coexist [cf., phase diagram Fig. 1].

Thus far, various authors<sup>3,4</sup> have observed experimentally that, in nematics containing small molecules, the nematic order parameter remains constant as one moves along the lower coexistence curve of the phase diagram [ $T_n(\Phi)$  curve in

Fig. 1]; in addition, the constant is equal to  $S_0$ , the minimum value obtained for the pure liquid crystal. These experimental results would suggest the identification of  $T_c(\Phi_0)$  with  $T_n(\Phi_0)$ , the temperature at which the first isotropic drop appears when heating. Kronberg<sup>5</sup> used this argument in his theoretical interpretation of the phase diagrams obtained for macromolecule-nematic

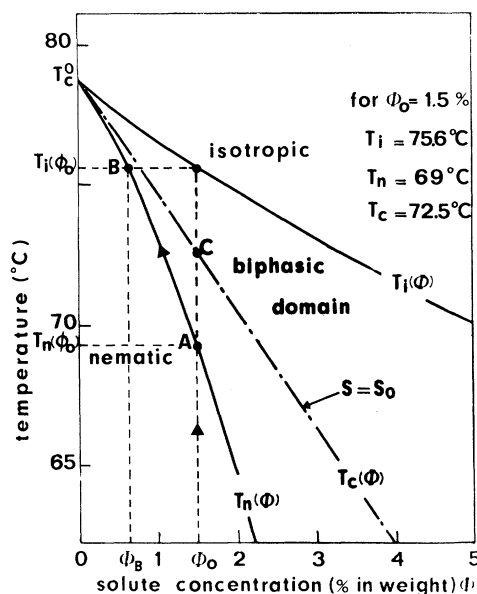


FIG. 1. Phase diagram of EBBA-polystyrene ( $M_w = 2100$ ) system. For a given polymer concentration  $\Phi$ , the nematic phase first appears on cooling at  $T_i(\Phi)$ , and the isotropic phase first appears on heating at  $T_n(\Phi)$ ;  $T_c(\Phi)$  is the "pseudo clearing temperature" as discussed in text.

solutions. However, Brochard<sup>6</sup> disputed recently this point, noting that the lower coexistence curve and the clearing temperature have different thermodynamical origins. In the framework of the analysis proposed by Brochard, we anticipate for polymer solutes a monotonous decrease of  $S(T)$  even in the two-phase regime [ $T_n(\Phi_0) < T < T_i(\Phi_0)$ , Fig. 1] and not a plateau [ $S(T) = S_0$ ] as reported for dissolved small molecules.<sup>3,4</sup> In order to choose between these two apparently different points of view, we have measured the variation of the liquid-crystal order parameter  $S(T)$  versus temperature in polymer-nematic solutions, using NMR techniques.

In this Letter, the NMR results obtained for *p*-ethoxybenzylidene-*p*-N-butylaniline (EBBA) containing polystyrene with a molecular weight  $M_w = 2100$  (PS2100) are compared to those obtained for the pure EBBA.<sup>7</sup> In Fig. 1, we report the phase diagram of the PS2100-EBBA system obtained by the slow cooling (0.1 °C/min) of different solutions previously homogenized in the isotropic phase. First, by means of the wide-line <sup>1</sup>H NMR spectra, we determine the  $\Delta H(T)$  curve of the pure nematogen.<sup>8</sup> With the PS2100-EBBA, we obtain similar spectra, which results from the low polymer concentration (cf., inset of Fig. 2): In the present experiment, the polystyrene weight fraction  $\Phi_0$  is equal to 1.5%. In Fig. 2, the variation of the dipolar splitting  $\Delta H$  for the

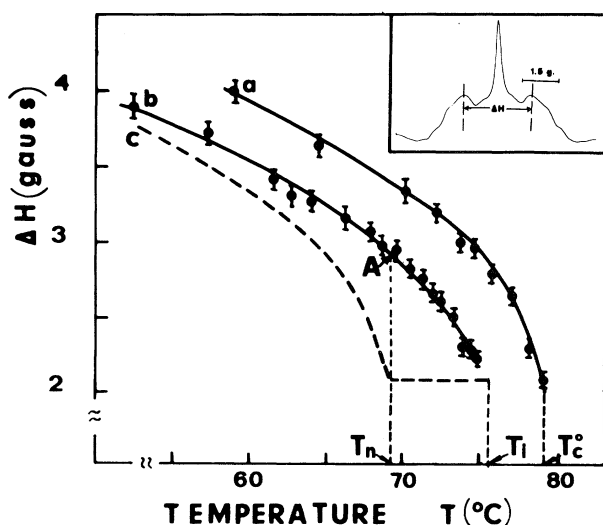


FIG. 2. NMR dipolar splitting  $\Delta H$  vs temperature: (a) pure EBBA, (b) EBBA-PS2100 (1.5% in weight), and (c)  $\Delta H$  behavior in the hypothesis where  $T_c(\Phi) = T_n(\Phi)$ . The inset shows a typical proton NMR spectrum ( $T = 68^\circ\text{C}$ ) and defines the splitting  $\Delta H$ .

pure nematogen and the solution is plotted versus the temperature.<sup>9</sup> Early investigations of nematic mesophases by proton magnetic resonance spectroscopy revealed that  $\Delta H$  values are essentially related to averaged dipolar interactions between protons of the aromatic part of the nematogen.<sup>10</sup> In EBBA, due to the rigidity of the aromatic core, the variation in  $\Delta H(T)$  is mainly related to the change in  $S(T)$ .<sup>11</sup>

Examining the curves in Fig. 2, a striking fact appears: The  $\Delta H(T)$  curve of the polymer-nematic solution *does not exhibit a plateau* like the curve obtained with small molecule-nematic systems (compare the curves *b* and *c* in Fig. 2). In addition, a more detailed examination enables us to point out that the curve *b* (polymer-nematic solution) cannot be deduced from the curve *a* (pure nematic) by a translation along the temperature axis, as observed for small molecule-nematic solutions (curve *c*) for  $T < T_n$ ; we also remark that the minimum  $\Delta H$  value measured<sup>12</sup> near  $T_i(\Phi_0)$  is higher than that which corresponds to  $S_0$  for the pure liquid crystal.

Thus, the experimental facts mentioned above, and especially the first point, show that the behavior of polymers as solutes seems to differ from that of small molecules dissolved in liquid crystals. However, we will attempt to demonstrate that these facts are consistent with the model suggested by Brochard.

Adding to the free energy of the nematic phase a supplementary term due to the liquid-crystal-solute interaction, Brochard obtains a "pseudo clearing temperature"  $T_c(\Phi)$  higher than  $T_n(\Phi)$ , i.e., within the forbidden temperature domain; in the low-concentration limit,  $T_c(\Phi)$  linearly depends on solute concentration  $\Phi$  and is given by the following expression:  $T_c(\Phi) = T_c^0 - K\Phi$ , where  $K$  is related to the anisotropic part of the nematic-solute interaction [cf., Eq. (9) in Ref. 6]. Therefore, the  $\Delta H$  variation observed for PS2100-EBBA solution can be explained in the framework of this model (recall that, in this low-concentration approximation, we expect the same dependence for the solution and the pure nematic if we plot it versus reduced temperature). Let us consider the behavior of the nematic phase of a polymer-nematic solution with initial concentration  $\Phi_0$  as the temperature is increased:

(i)  $T \leq T_n(\Phi_0)$ .—As long as the temperature is lower than  $T_n(\Phi_0)$ , we have just a single nematic phase. Its clearing temperature  $T_c(\Phi_0)$  (Fig. 1, point C) is constant and given by the expression mentioned above. In this temperature domain,

the reduced temperature  $T/T_c(\Phi_0)$  varies as  $T$  and we observe the usual dependence on temperature.

(ii)  $T_n(\Phi_0) < T < T_i(\Phi_0)$ .—The isotropic phase appears as soon as the temperature passes  $T_n(\Phi_0)$  (Fig. 1, point A), accompanied by a decrease in the solute concentration for  $T > T_n(\Phi_0)$  (Fig. 1, path AB). Hence,  $T_c$  is no longer constant and depends on the effective polymer concentration in the nematic phase which is determined for each temperature from the lower coexistence curve. Consequently, the reduced temperature does not vary linearly with  $T$  because  $T_c$  itself depends on  $T$  via the polymer concentration in the nematic phase. Thus, the evolution of  $\Delta H(T)$  of the solution differs from that of the pure nematic case; this explains why the segment AB of curve *b* in Fig. 2 cannot be obtained from curve *a* by a translation.

(iii)  $T = T_i(\Phi_0)$ .—The system becomes completely isotropic at temperature  $T_i(\Phi_0)$  (Fig. 1, point B) which is still lower but close to the “pseudo clearing temperature” associated with the lowest concentration  $\Phi_B$  of the polymer in the nematic solvent (Fig. 1, point B). Thus, for  $T = T_i(\Phi_0)$  we expect that the value of the orientational order parameter is slightly higher than  $S_0$ ; this is not inconsistent with our experimental results (cf., Fig. 2).

For a quantitative comparison of our experimental results with the theoretical model, we need to determine only one parameter, the constant  $K$  in the expression for  $T_c(\Phi)$ ; this allows us to take into account the variation of the “pseudo clearing temperature” in the biphasic domain. By adopting a value for  $K$  of  $4 \pm 0.6^\circ\text{C}$ , the variation  $\Delta H(T/T_c)$  for the polymer-nematic solution in Fig. 3 is found to be identical, within experimental errors, to the  $\Delta H(T/T_c^0)$  for the pure nematogen. For the concentration  $\Phi_0 = 1.5\%$ , the value of  $K$  so determined corresponds to a pseudo clearing temperature  $T_c(\Phi_0) = 72.5^\circ\text{C}$ , which is greater than  $T_n(\Phi_0) = 69^\circ\text{C}$  [and smaller than  $T_i(\Phi_0) = 75.6^\circ\text{C}$ ]. We obtain similar results with a polystyrene-*para*-azoxyanisole solution: The  $\Delta H(T)$  curve does not exhibit a plateau; for  $\Phi_0 = 1.2\%$ , we determine  $T_c(\Phi_0) = 134^\circ\text{C}$ , which is higher than  $T_n(\Phi_0) = 125^\circ\text{C}$ . All these results confirm the theoretical predictions of Brochard. In addition, it should be noted that knowledge of  $T_c$  is essential in interpreting physical measurements on such systems.<sup>13</sup>

It is important to note that these results do not contest the validity of the experimental results

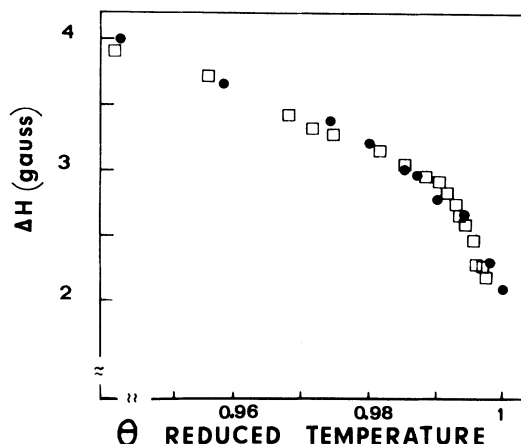


FIG. 3. NMR dipolar splitting  $\Delta H$  vs the reduced temperature  $\theta$ : solid circles, pure EBBA and  $\theta = T/T_c^0$ , with  $T_c^0 = 273 + 78.6$ . Open squares, PS2100-EBBA solution and  $\theta = T/T_c$ , where  $T_c$  depends on  $T$  for  $T_n(\Phi_0) < T \leq T_i(\Phi_0)$ .

obtained for dissolved small molecules; indeed, the proposed model requires that the difference  $T_c - T_n$  [cf., Eq. (13) in Ref. 6] diminishes with the molecular weight of the solute. It may be possible that the  $T_c(\Phi)$  curve practically coincides with the  $T_n(\Phi)$  one. Under these conditions the observed minimum value of  $S(T)$  is equal to  $S_0$  and remains constant along the lower coexistence curve  $T_n(\Phi)$ , while increasing the temperature. We conclude by stressing the singularity of this problem: It is a binary system having both a first-order transition and an order parameter in one of the two phases, which is an unusual situation. The authors do not find evidence for an analogy in other domains of physics.

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<sup>2</sup>See, for instance, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), p. 45.

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<sup>4</sup>B. Kronberg, D. F. R. Gilson, and D. Patterson, J. Chem. Soc., Faraday Trans. II **72**, 1673 (1976).

<sup>5</sup>B. Kronberg, I. Bassignana, and D. Patterson, J. Chem. Phys. **82**, 1714 (1978); B. Kronberg, Ph.D. thesis, McGill University, 1977 (unpublished).

<sup>6</sup>F. Brochard, C. R. Acad. Sci. Paris, Ser. B **289**, 229 (1979).

<sup>7</sup>The EBBA ( $\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{C}_6\text{H}_5$ ) was obtained

from the Varylight Co., and has a clearing temperature equal to 78.6°C. The PS2100 was obtained from the Pressure Chemical Co., and its molecular-weight distribution is very sharp ( $M_w/M_n$  less than 1.1).

<sup>8</sup>The  $^1\text{H}$  NMR spectra were obtained with a pulsed spectrometer; we worked at a frequency  $F=27$  MHz ( $H_0=6350$  G).

<sup>9</sup>Several spectra recorded at the same temperature permitted us to increase accuracy of the  $\Delta H$  determination; thus, we estimate that the relative uncertainty of  $\Delta H$  is about  $\pm 3\%$ . The sample temperature was controlled with use of a thermocouple immersed in the sample; the temperature was known to within  $\pm 0.1^\circ\text{C}$ .

<sup>10</sup>J. J. Visintainer, E. Bock, R. Y. Dong, and E. Tom-

chuk, Can. J. Phys. 53, 1483 (1975).

<sup>11</sup>This simple correspondence between  $\Delta H$  and  $S$  values no longer exists when the molecular conformation is strongly dependent on the temperature as discussed by J. Charvolin and B. Deloche (see, for instance, *The Molecular Physics of Liquid Crystals* (Academic, London, 1979), Chap. 15).

<sup>12</sup>With the PS2100-EBBA solution the  $\Delta H$  measurement becomes difficult for the temperatures close to  $T_i(\Phi_0)$  because the volume fraction of the nematic phase tends to zero: Our highest experimental temperature is 74.8°C (compared to  $T_i=75.6^\circ\text{C}$ ).

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