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## Liquid Crystals

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### Flexible polymers in solution in the isotropic phase of a nematogenic liquid crystal. Viscosity and Kerr effect

Y. Dormoy<sup>a</sup>; V. Reys<sup>a</sup>; P. Martinoty<sup>a</sup>

<sup>a</sup> Laboratoire de Spectrométrie et d'Imagerie Ultrasonores, Unité associée au CNRS, Université Louis Pasteur, Strasbourg Cedex, France

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## Flexible polymers in solution in the isotropic phase of a nematogenic liquid crystal

### Viscosity and Kerr effect

by Y. DORMOY, V. REYS and P. MARTINOTY

Laboratoire de Spectrométrie et d'Imagerie Ultrasonores,  
Unité associée au CNRS, Université Louis Pasteur, 4, rue Blaise Pascal,  
67070 Strasbourg Cedex, France

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The behaviour of flexible polymers in solution in the isotropic phase of a nematogenic solvent was studied using viscosity and electric birefringence measurements. The results obtained show the existence of an interaction between the polymer and the local orientational order for polymers of low molecular weight, which disappears for those of high molecular weight. This change in behaviour can be explained by comparing the parameters characterizing the local orientational order to those characterizing the polymeric coil.

### 1. Introduction

Several groups have studied the behaviour of flexible polymeric chains in dilute solution in a nematogenic solvent, using different methods: neutron scattering [1], N.M.R. [1, 2] and the modification of both the elastic constants [3] and the friction coefficients [3, 4] of the nematic, resulting from the presence of the chains. These studies, carried out principally on polystyrene, have revealed the existence of an interaction between the chains and the nematic orientational order, leading to anisotropy of the polymeric coil. Only polymers of low molecular weight have been studied, because of the existence of demixing phenomena [5].

We have recently carried out a study of the isotropic phase of these solutions, using Kerr effect and capillary viscosity techniques [6]. This study has shown that the conformation of the chains of polystyrene of molecular weight 2000 (PS 2000) is anisotropic, as in the nematic phase. This is due to the presence of a local orientational order, which is characteristic of the isotropic phase of nematogenic liquids. In this paper, we present a similar study carried out as a function of the molecular weight of the polystyrene. This was possible, since in the isotropic phase, the PS was found to be more soluble than in the nematic phase of the solvent used, 4-*n*-pentyl-4'-cyanobiphenyl (5CB).

### 2. Theoretical background

#### 2.1. Electric birefringence

In the isotropic phase of conventional liquid crystals, the birefringence,  $\Delta n$ , induced by an electric field  $E$  diverges as the nematic phase is approached, reflecting the presence of an important local orientational order which prefigures the nematic state. The Kerr constant  $K = \Delta n/nE^2$ , calculated according to the Landau-

de Gennes model [7] is predicted to be [6]

$$K = \frac{\epsilon_0(\Delta\epsilon)_0(\Delta n)_0}{3na(T - T^*)}, \quad (1)$$

where  $\epsilon_0$  is the vacuum permittivity,  $(\Delta\epsilon)_0$  and  $(\Delta n)_0$  the dielectric anisotropy and the birefringence of the perfectly-aligned liquid crystal respectively, and  $n$  is the mean value of the refractive index.  $a$  is a temperature independent constant and  $T^*$  a virtual second order transition temperature which is lower than the real transition temperature  $T_{NI}$ . Equation (1) shows that  $K$  diverges as  $(T - T^*)^{-1}$  in the vicinity of the nematic-isotropic transition.

## 2.2. Viscosity

Adding a polymer of gyration radius  $R$  and molecular weight  $M$  to a conventional isotropic solvent of viscosity  $\eta_0$  increases the viscosity of the latter by the increment  $\delta\eta$  [8]

$$\delta\eta = \frac{c}{N} \frac{\lambda}{6} R^2, \quad (2)$$

where  $N$  is the polymerization index, proportional to  $M$ ,  $c/N$  is the number of monomers per unit volume, and  $\lambda$  is the friction coefficient of the chain. Within the Rouse limits, valid for short or stretched chains,  $\lambda = N\mu \sim N\eta_0 l$  where  $\mu$  is the friction coefficient of a monomer of size  $l$ . Within the Zimm limits, the coil behaves like an unpenetrable sphere and  $\lambda \sim \eta_0 R$ . Using the fact that  $R \sim M^\alpha$ , equation (2) shows that

$$\frac{\delta\eta}{\eta_0} \sim M^\beta \sim N^\beta, \quad (3)$$

where  $\beta = 2\alpha$  within the Rouse limits and  $\beta = 3\alpha - 1$  within the Zimm limits. The value of  $\alpha$  is a function of the solvent quality:  $\alpha = 1/3$  for a poor solvent,  $\alpha = 1/2$  for a  $\theta$  solvent, and  $\alpha = 3/5$  for a good solvent.

## 3. Results

### 3.1. Electric birefringence

Steady state electric birefringence measurements were made using the equipment described in [6]. The polystyrene samples studied had molecular weights of 2000, 17 500 and 50 000. The mixtures, each with a polymer concentration of 1.75 per cent by weight, were prepared in test tubes at a temperature of about 60°C, and stirred slowly at this temperature, under an inert atmosphere, for one or two days, in order to obtain good dissolution of the polymer. They were then transferred into the measuring cell, which had been pre-heated to the same temperature as the mixtures. This transfer was carried out at high temperature in order to avoid any possibility of demixing of the polymer. The measurements were taken as the temperature decreased. Figure 1 shows the variation of the Kerr constants ( $K$ ) of the pure 5CB and of the mixtures as a function of  $T - T^*$ . The values of  $T^*$  were determined by plotting  $K^{-1}$  as a function of  $T$ , and extrapolating the straight lines obtained to  $K^{-1} = 0$  [9]. The Kerr constants of the mixtures were corrected to take into account the volume concentration ( $C_v$ ) of the polymer [ $K = K_{\text{measured}}/(1 - C_v)$ ]. The refractive index,  $n$ , of the mixtures was found to be identical to that of the 5CB ( $n = 1.59$ ) [10].

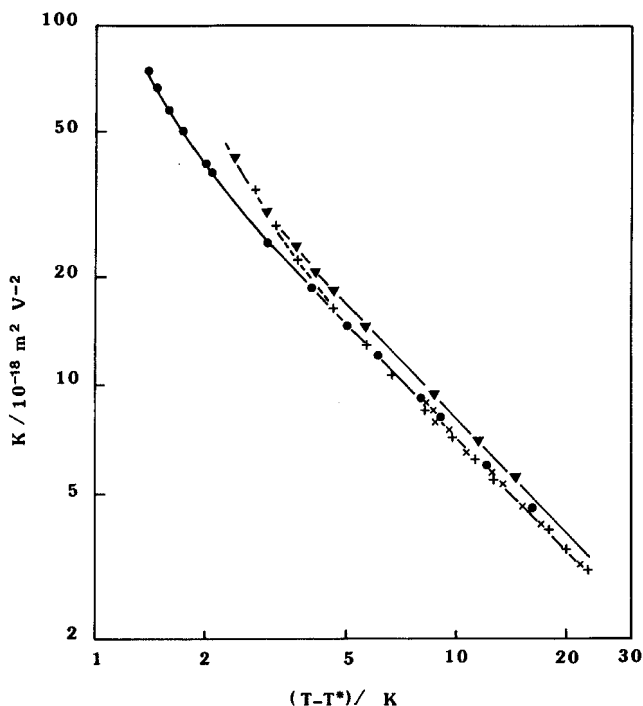


Figure 1. Log-log plot of the Kerr constant  $K = \Delta n/nE^2$  as a function of  $T - T^*$ . ●, pure 5CB; ▼, 5CB-PS 2000, +, 5CB-PS 17 500; ×, 5CB-PS 50 000. The value of the refractive index  $n$  is 1.59.

We consider first the results obtained at high temperatures ( $T - T^* > 5^\circ\text{C}$ ). The figure shows that the Kerr constant of each mixture, like that of pure 5CB, obeys a  $(T - T^*)^{-1}$  law, as predicted by equation (1). However, the value of the Kerr constants of the high molecular weight polymers (17 500 or 50 000) is different from that of the low molecular weight polymer (2000). The Kerr constant of the 5CB-PS 2000 mixture can thus be seen to be higher than that of pure 5CB. This result, already reported in [6], indicates the existence of a coupling between the polymer and the local orientational order, and can be explained [6] by a lattice model of the Flory-Huggins type. However, the Kerr constants of the 5CB-PS 17 500 and 5CB-PS 50 000 mixtures are very close to that of pure 5CB, since the discrepancies, of only a few per cent between the experimental results, are of the order of magnitude of the experimental error. These similar values of the Kerr constants indicate that high molecular weight polymers are not coupled to the local orientational order of the isotropic phase of the nematic. These polymers behave like simple impurities which have the effect of modifying the transition temperature  $T_{\text{NI}}$ .

We consider now the results obtained in the vicinity of the transition ( $T - T^* < 5^\circ\text{C}$ ). These show a divergence from the  $(T - T^*)^{-1}$  law, which appears for 5CB as well as for the mixtures. This divergence has been observed for most of the N-I transitions, and has never been satisfactorily explained [11]. On the other hand, the particular behaviour of the 5CB-PS 17 500 mixture should be noted, in which the Kerr constant becomes comparable, in the vicinity of the transition, to that of the 5CB-PS 2000 mixture, whereas it was comparable, far from the transition, to that of the 5CB-PS 50 000 mixture. This change in behaviour suggests the existence of a crossover

between a regime without coupling at high temperatures and a regime with coupling at low temperatures.

### 3.2. Capillary viscosity

The polystyrenes used for our mixtures had molecular weights of 2000, 9000, 17 500, 50 000, 90 100, and 410 000. For each mixture, the polymer concentration was 1.75 per cent by weight. Precautions similar to those used for the Kerr effect measurements were taken in the preparation of the mixtures, and also when filling the capillary; this had a diameter of 0.6 mm. All of the viscosities measured showed a newtonian behaviour for the shear gradients given by our experimental set-up. For each mixture, the thermal variation of the viscosity was determined by reducing the temperature. The results obtained are plotted in figure 2, and shows that the viscosity  $\eta_0$  of the 5CB is notably increased by the presence of the polymer, and that the viscosity  $\eta$  of the mixtures increases as the polymer weight rises. All of the viscosities exhibit an arrhenian behaviour, plotted in solid lines. For the highest weights it can be seen that this arrhenian behaviour disappears below a certain temperature  $T_d$ , which depends on the polymer weight. The more the polymer weight increases, the higher  $T_d$  becomes. We interpret this departure from the arrhenian law as the result of a demixing of the polymer in the isotropic phase. Appearance of a deposit on the

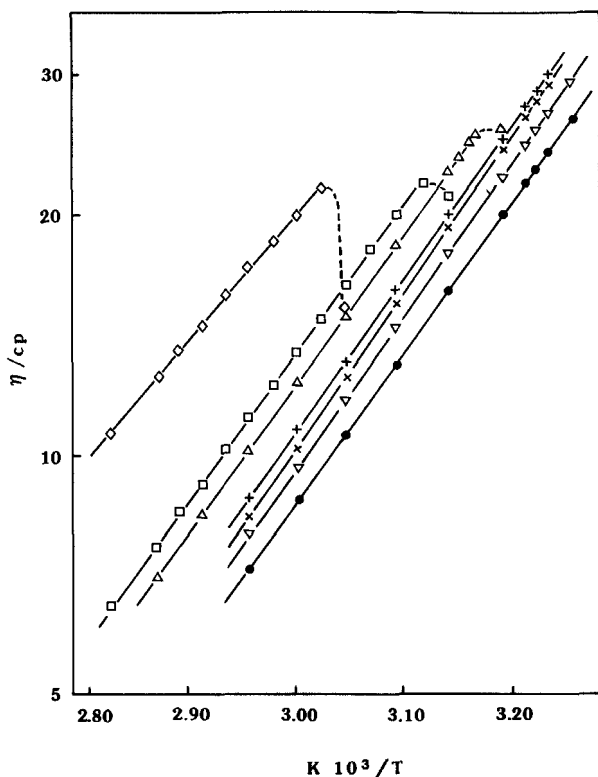


Figure 2. Logarithmic representation of the viscosity, as an inverse function of the temperature. ●, pure 5CB; ▽, 5CB-PS 2000; ×, 5CB-PS 9000; +, 5CB-PS 17 500; △, 5CB-PS 50 000; □, 5CB-PS 90 100; ◇, 5CB-PS 410 000. The solid curves are the fits to an arrhenian law.

capillary walls after a sufficient length of time at a temperature  $T < T_d$  reinforces this hypothesis. In the following discussion, only those measurements which correspond to the arrhenian regime will be taken into account.

For each of the mixtures, the results given in figure 2 enable us to determine the difference  $\delta\eta$  between the viscosity of the mixture and that of 5CB, and consequently the ratio  $\delta\eta/\eta_0$ , which, according to equation (3), is the quantity which concerns us most. Since the various viscosities do not show any critical behaviour, the variable to be used to determine this ratio is the temperature  $T$ , and not the temperature difference  $T - T^*$ . The results thus obtained are plotted in figure 3 for different temperatures as a function of the polymer molecular weight. The behaviour of  $\delta\eta/\eta_0$  can immediately be seen to be extremely different according to the molecular weight being considered. For the lowest weights ( $\leq 17\,500$ ), the variation of  $\delta\eta/\eta_0$  is linear, with a slope  $\beta$  in the vicinity of 0.33. As the molecular weight increases, the measurements diverge from this straight line, and form another straight line with a steeper slope, which tends towards  $\beta = 0.66$ . This latter value leads either to an  $\alpha \sim 0.33$  exponent in the case of the Rouse Model (poor-solvent behaviour), or to an  $\alpha \sim 0.55$  exponent in the case of the Zimm model ( $\theta$ -solvent behaviour). For the lower molecular weights, only the Rouse model applies, and the  $\sim 0.33$  value of the  $\beta$  exponent gives  $\alpha \sim 0.165$ . This value is not predicted for any conventional type of solvent, and therefore suggests the existence of a coupling between the low molecular weight polymers and the local orientational order of the isotropic phase of 5CB. The analysis of the results for polystyrenes of molecular weights 2000 and 9000 has been presented in [6], using the anisotropic dumbbell model elaborated by Brochard for the

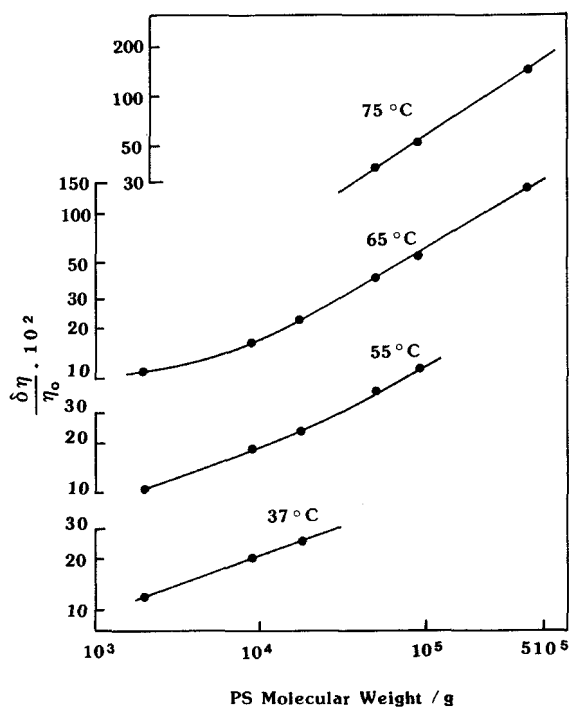


Figure 3. Log-log plot of the  $\delta\eta/\eta_0$  ratio as a function of the molecular weight of the polymer at different temperatures. The vertical scales are staggered in relation to each other for ease of interpretation of the data.

Variation of the radius  $R$  for polystyrene as a function of the molecular weight  $M$ .

| Mw/g  | $\beta$ | Rouse                      |                | Zimm                           |                |
|-------|---------|----------------------------|----------------|--------------------------------|----------------|
|       |         | $\alpha = \frac{\beta}{2}$ | $R/\text{\AA}$ | $\alpha = \frac{1 + \beta}{3}$ | $R/\text{\AA}$ |
| 2000  |         |                            | 20             | —                              |                |
| 9000  | 0.33    | 0.165                      | 26             | —                              |                |
| 17500 |         |                            | 29             | —                              |                |
| 17500 |         |                            | 29             |                                | 29             |
| 50000 |         |                            | 40             |                                | 51             |
| 90000 | 0.66    | 0.33                       | 49             | 0.55                           | 70             |
| 41000 |         |                            | 81             |                                | 162            |

The values of  $R$  were calculated from that measured for polystyrene of molecular weight 2000 using the relationship  $R \sim M^\alpha$ . The exponent  $\beta$  is associated with the variation of  $\delta\eta/\eta_0$  with  $M$ , and is deduced from figure 3. The relationship between  $\alpha$  and  $\beta$  depends on the model considered (Rouse or Zimm).

nematic phase [12]. Although this model cannot be applied rigorously to the isotropic phase, since it does not take account of the fraction of the polymer with an isotropic environment, it allows nevertheless a qualitative analysis of the results. This analysis suggests that the polymer is stretched along the director, which is the conclusion deduced from NMR and neutron measurements taken in the nematic phase [1].

#### 4. General discussion and conclusion

We are now going to see that the existence of the two types of behaviour observed by both the electric birefringence and the capillary viscosity can be explained by comparing the correlation length  $\xi$  of the local orientational order to the radius  $R$  of the polymer. For the correlation length  $\xi$  [13], having no measurements for 5CB, we have used the relationship  $\xi = 6.8 [(T/T^*) - 1]^{-0.5} \text{\AA}$ , obtained for 4-methoxybenzylidene-4'-*n*-butylaniline [14]. In addition, only the radius  $R$  of the polystyrene of weight 2000 has been measured in 5CB [1]. In order to determine the radii for other weights we used both this measurement ( $R = 20 \text{\AA}$ ) and the relationship  $R \sim M^\alpha$ , where  $\alpha$  can have different values, according to whether the molecular weight is low or high. These  $\alpha$  values were determined previously for the Rouse and Zimm models. The values of  $R$  thus obtained are given in the table together with those of the  $\alpha$  and  $\beta$  exponents.

The relative behaviour of  $R$  and  $\xi$  are shown in figure 4, assuming that  $R$  does not vary critically with temperature. We consider first the results shown in figure 4 for the lowest molecular weight. These reveal that  $\xi > R$  for all temperatures below  $65^\circ\text{C}$ . A fraction of the polymer is therefore in a nematic-like environment for all of these temperatures, and the conformation of these polymers may be modified by the local orientational order. On the other hand, the  $\xi > R$  imbalance is never experimentally demonstrated for polymers of the highest molecular weights (50 000, 90 100 and 410 000) whichever model is used (Rouse or Zimm), which indicates that these polymers are insensitive to the local orientational order. These two observations point therefore to the existence of two different regimes, characterized by the presence or absence of a coupling between the polymers and the local orientational order. These two regimes depend on polymer weight and temperature. Figure 4 also shows that the

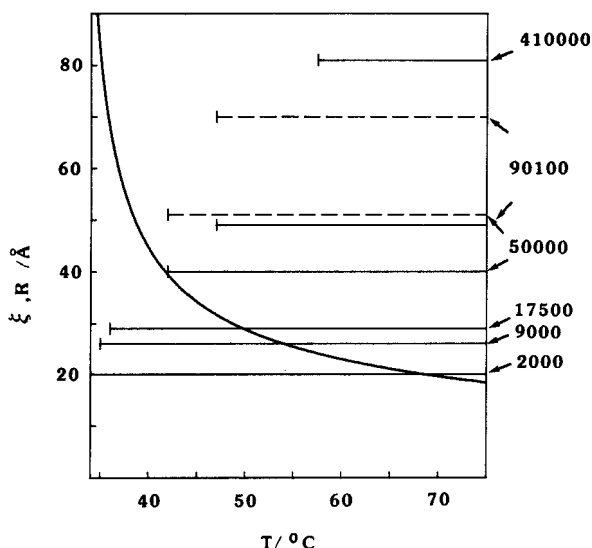


Figure 4. Estimation of the thermal behaviour of the correlation length  $\xi$  of the solvent, shown by the heavy black line, and of the radii  $R$  of the polystyrenes studied. Values of  $R$  were calculated using the Rouse (solid line) and Zimm (broken line) models. The domain in which interaction between the polystyrene and the solvent can occur is governed by the condition  $\xi > R$ . The behaviour of  $R$  is only plotted for temperatures at which the polymer is soluble.

5CB-PS 17 500 mixture corresponds to a cross-over between the two regimes, as is suggested by both the Kerr-effect measurements and the capillary viscosity data.

In order for the coupling regime to exist, it is also necessary for the characteristic time  $\tau_{5CB}$  of the local orientational order of the 5CB to be greater than the lowest correlation time  $\tau_{PS}$  of the polystyrene coil.  $\tau_{5CB}$  was measured, and found to obey the  $\tau_{5CB}^{-1} = 6 \times 10^8 [(T/T^*) - 1] s^{-1}$  law [15];  $\tau_{PS}$ , which is linked to the rotation of the coil (first Rouse mode), can be estimated by extrapolating the results obtained by Ferry and Holmes [16] for polystyrenes with molecular weights of 82 000, 267 000 and 860 000. The characteristic time so obtained shows that  $\tau_{5CB} > \tau_{PS}$  for weight 2000 and  $\tau_{5CB} < \tau_{PS}$  for weights 50 000, 90 100 and 410 000. This confirms the existence of the two regimes, i.e. with and without coupling. However,  $\tau_{PS}$  cannot be determined with sufficient accuracy for any statement to be made on the nature of the regime associated with weights 9000 and 17 500.

In conclusion, both the Kerr-effect and the capillary viscosity measurements indicate that the behaviour of a flexible polymer (polystyrene) in solution in the isotropic phase of a nematogenic liquid crystal (5CB) is highly dependent on the molecular weight of the polymer, and the temperature. To be more precise, our results show that interaction between the polymer and the local orientational order exists for low molecular weight polymers (typically 2000), but disappears for high molecular weight polymers. This change in behaviour has been explained by comparing the characteristic parameters ( $\xi$  and  $\tau_{5CB}$ ) of the local orientational order with those ( $R$  and  $\tau_{PS}$ ) of the polymeric coil. Finally, it should be noted that the coupling between the local orientational order and the low molecular weight polymers has considerable influence on the exponent  $\alpha$ , which is linked to the weight-related variation of  $R$ .



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- [9]  $T^* = 33.6^\circ\text{C}$  for pure 5CB,  $31.1^\circ\text{C}$  for the 5CB-PS 2000 mixture,  $32.3^\circ\text{C}$  for the 5CB-PS 17 500 mixture, and  $32.7^\circ\text{C}$  for the 5CB-PS 50 000 mixture.
- [10] The measurements taken with an Abbé refractometer show dispersion to be less than 0.1 per cent.
- [11] See for example ANISIMOV, 1988, *Molec. Crystals liq. Crystals, Special Topics XXXI*.
- [12] BROCHARD, F., 1979, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 1367.
- [13] Although 5CB presents antiparallel correlations, the order of magnitude and the thermal variation of the correlation length  $\xi$  should not be very different from those of 4-methoxybenzylidene-4'-*n*-butylaniline (MBBA). Indeed, the electric birefringence, the intensity of the light scattered, and the characteristic frequency of 5CB all have a mean field behaviour identical to that of MBBA. It is therefore reasonable to suppose that the same applies to  $\xi$ . It is however possible that the premultiplying scalar factor  $\xi_0$  is different from that of MBBA, but this difference must be slight; in any case it would not affect the order of magnitude of  $\xi$ .
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