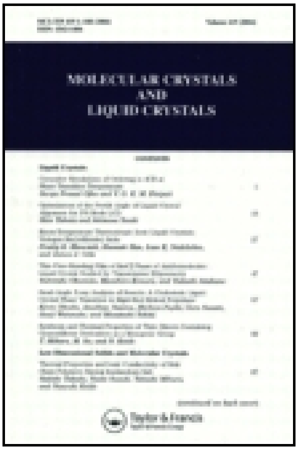

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Behavior of a Flexible Polymer in Solution in the Isotropic Phase of a Nematic Liquid Crystal

Y. Dormoy [a], J. L. Gallani [a] & P. Martinoty [a]

[a] Laboratoire de Spectrométrie et d'Imagerie Ultrasonores, Unité Associée au C.N.R.S., Université Louis Pasteur, 4, rue Blaise Pascal, 67070, Strasbourg Cedex, France

Version of record first published: 04 Oct 2006.

To cite this article: Y. Dormoy, J. L. Gallani & P. Martinoty (1989): Behavior of a Flexible Polymer in Solution in the Isotropic Phase of a Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 170:1, 135-149

To link to this article: http://dx.doi.org/10.1080/00268948908047754

Mol. Cryst. Liq. Cryst., 1989, Vol. 170, pp. 135–149
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Behavior of a Flexible Polymer in Solution in the Isotropic Phase of a Nematic Liquid Crystal

Y. DORMOY, J. L. GALLANI and P. MARTINOTY
Laboratoire de Spectrométrie et d'Imagerie Ultrasonores, Unité Associée au C.N.R.S., Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France

(*Received October 20, 1988; in final form November 4, 1988*)

Viscosity and Kerr effect were used to study the behavior of a low molecular-weight flexible polymer (polystyrene) in solution in the isotropic phase of a nematic solvent. The comparison between the results obtained for the pure solvent and the mixture shows the existence of a coupling between the local orientational order and the polymer, which changes the conformation of the chains.

I. INTRODUCTION

One of the problems facing polymer physics at the present time is the statistical conformation of the chains in a complex environment, i.e. anisotropic (liquid crystal) or non-homogeneous (gel). Recent studies[1–5] have attempted to discover whether the chain conformation is modified by the orientational order of a nematic solvent. The results show that these chains have an anisotropic conformation and that solubility problems exist, imposing the use of polymers with low-molecular weight at low concentration. In this article we present the first observations which demonstrate that chain configuration is also modified in the isotropic phase of a nematic liquid crystal. These observations were obtained by studying the influence of dissolved chains on two properties of the solvent:

—the birefringence induced by an electric field (Kerr effect), which measures the local orientational order typical of the isotropic phase of nematics;

—the viscosity, a parameter which is sensitive to the presence of polymer chains, even in small concentrations.

Before presenting and discussing our measurements, we shall first review the theoretical results required later.

II. THEORETICAL BACKGROUND

A. Influence of the local orientational order on the Kerr constant of the isotropic phase of liquid crystals

In the isotropic phase of liquid crystals, some physical properties, such as, for example, the birefringence induced by an electric field, diverge as the nematic phase is approached. These divergences reflect the presence of an important local orientational order which prefigures the nematic state, and have been discussed by de Gennes on the basis of a Landau-type model.[6] In the Landau-de Gennes model the free energy is assumed to be an analytical function of the temperature and of an order parameter Q. In the presence of an electric field E, the free energy can be written per unit volume and at the lowest order, as[7]

$$F = F_0 + \frac{1}{2} a\,(T - T^*)\,Q^2 - \frac{1}{6}\,\varepsilon_0\,(2(\Delta\varepsilon)_0 Q + 3\bar{\varepsilon} - 3)\,E^2 \qquad (1)$$

where F_0 is independent of Q and a is a constant independent of temperature. T^* is a second order virtual transition temperature, which is smaller than the real transition temperature T_c. Q is defined by the relation

$$Q = \frac{\Delta\varepsilon}{(\Delta\varepsilon)_0} \qquad (2)$$

where $\Delta\varepsilon$ is the dielectric anisotropy of the fluid (assumed to be uniaxial) and $(\Delta\varepsilon)_0$ is the dielectric anisotropy when all molecules are perfectly aligned in one direction $(Q = 1)$. $\bar{\varepsilon}$ is the mean permittivity of the fluid and ε_0 the vacuum permittivity.

The order produced (i.e. Q) by the electric field may be calculated from minimization of F in respect of Q, and its value is given by

$$Q = \frac{\varepsilon_0\,(\Delta\varepsilon)_0\,E^2}{3\,a(T - T^*)} \qquad (3)$$

This induced order gives rise to a birefringence (Kerr effect) given by:

$$\Delta n = (\Delta n)_0\,Q \qquad (4)$$

where $(\Delta n)_0$ is the birefringence of the perfectly aligned liquid crystal.

The Kerr constant is defined as $K = \Delta n/\bar{n}E^2$, and is written, using Equations 3 and 4, as:

$$K = \frac{\varepsilon_0\,(\Delta\varepsilon)_0\,(\Delta n)_0}{3\,\bar{n}\,a(T - T^*)} \qquad (5)$$

where $\bar{n}$ is the mean value of the refractive index. Equation 5 shows that the Kerr constant diverges as $(T - T^*)^{-1}$. This behavior, which is now well known, is confirmed by our own measurements carried out on EBBA (para-ethoxybenzylidene-*p*-*n*-butylaniline) and on PCB (pentylcyanobiphenyl), the two solvents used in the present study. It should be noted that the temperature range in which $K \sim (T - T^*)^{-1}$ is much wider for compounds with a positive Kerr constant like PCB, than for compounds with a negative Kerr constant, like EBBA.[8] This difference in behavior is the result of competition between the contributions of the induced dipolar moment and the permanent dipolar moment.[9]

B. Influence of the polymer chains on the viscosity

In this paragraph, we shall sum up the Dumbbell models which have been elaborated to describe the viscous behavior of flexible polymers in solution in both classic and nematic solvents. It should be noted that there is no model which describes the viscous effects associated with the isotropic phase of a nematic solvent.

a. The Dumbbell model. Adding a polymer to a classic solvent considerably increases the viscosity of the latter, even at low concentration. In the Dumbbell model,[10] the increase in viscosity $\delta\eta$ is given by $\delta\eta \sim C\,\lambda\,R^2/N$, in which C, N, λ, and R are respectively the number of monomers per unit volume, the degree of polymerization, the friction coefficient, and the radius of gyration of the chain. Since λ is proportional to the viscosity η of the solvent within the limits given by Rouse (short chains), the relation given above shows that:

$$\delta\eta \sim \eta\,R^2 \tag{6}$$

As a result, if $\delta\eta/\eta$ is represented as a function of temperature, the conventional Arrhenius dependence of the viscosity is eliminated, and the influence of temperature on the size of the chains can be seen.

b. The anisotropic Dumbbell model. F. Brochard has adapted the Dumbbell model to the particular case of a nematic solvent, and has calculated the influence of dissolved chains on the viscosities associated with certain types of flow.[11] In her calculation, the anisotropy of the solvent is supposed to lead to anisotropy of both the polymer coil and the friction forces. The anisotropy of the polymer coil is characterized by two lengths $R_\parallel$ and $R_\perp$ where the signs $\parallel$ and $\perp$ represent the directions parallel and perpendicular to the director **n**, and the anisotropy of the friction forces is characterised by two friction coefficients $\lambda_\parallel$ and $\lambda_\perp$ corresponding to a polymer movement parallel to n and perpendicular to **n** respectively. $\lambda_\parallel$ and $\lambda_\perp$ are related to the diffusion coefficients of the polymer, $D_\parallel$ and $D_\perp$, by the relations $\lambda_\parallel = kT/D_\parallel$ and $\lambda_\perp = kT/D_\perp$.

The effect of the polymer has been calculated for the viscosity coefficients γ_1 and γ_2 linked to the torque generated by the influence of movement of the liquid on the director, and for the three Miezowicz viscosities η_a, η_b and η_c. These three viscosities are associated with flows performed in the presence of a magnetic field sufficiently intense to prevent disorientation of the molecules due to the flow, and correspond to the following orientations of the director: η_a, perpendicular to the velocity gradient and to the flow; η_b, parallel to the flow; and η_c, parallel to the velocity gradient. The three Miezowicz viscosities, and the two torque viscosities can be expressed as a function of the five friction coefficients α_i introduced by Ericksen and Leslie[12] to describe the dynamic properties of nematics.

The variations of the viscosity coefficients resulting from the presence of dissolved chains are given by the following expressions:

$$
\begin{aligned}
\delta\eta_a &= \frac{C}{2N} \lambda_\perp R_\perp^2 \\
\delta\eta_b &= \frac{CkT}{N} \frac{R_\perp^2}{R_\parallel^2} \tau_R \\
\delta\eta_c &= \frac{CkT}{N} \frac{R_\parallel^2}{R_\perp^2} \tau_R \\
\delta\gamma_1 &= \frac{CkT}{N} \frac{(R_\perp^2 - R_\parallel^2)^2}{R_\parallel^2 R_\perp^2} \tau_R \\
\delta\gamma_2 &= \frac{CkT}{N} \frac{R_\perp^4 - R_\parallel^4}{R_\parallel^2 R_\perp^2} \tau_R
\end{aligned}
\tag{7}
$$

where τ_R represents a characteristic rotational time of the coil, given by:

$$\tau_R = \frac{1}{kT} \frac{\lambda_\perp \lambda_\parallel R_\perp^2 R_\parallel^2}{\lambda_\parallel R_\parallel^2 + \lambda_\perp R_\perp^2} \tag{8}$$

These expressions, which integrate the four microscopic parameters, $R_\parallel$, $R_\perp$, $\lambda_\parallel$, and $\lambda_\perp$, show that the viscosities concerned are significantly modified by the presence of the polymer.

We shall now consider the viscosity η corresponding to a capillary flow which, in the absence of any magnetic field, is given by Reference 12:

$$\eta = \alpha_1 \sin^2\theta \cos^2\theta + \eta_c \sin^2\theta + \eta_b \cos^2\theta \tag{9}$$

where η_b and η_c are two of the Miezowicz viscosities previously defined, and α_1 one of the Ericksen-Leslie friction coefficients. θ is the angle between the director and the direction of flow, defined by:

$$\cos 2\theta = -\gamma_1/\gamma_2 \tag{10}$$

where γ_1 and γ_2 are the friction coefficients associated with the viscous torque. In fact there are two regions of alignment at the angle θ separated by a transition layer of thickness *e*. When *e* is small ($e \simeq 1$ μm[13]) in comparison to the diameter of the capillary, the influence of the disoriented molecules on the flow can be considered as negligible.

In order to calculate the increase in viscosity η due to the presence of the polymer, the friction coefficients α_1, η_b, η_c, must be replaced by their respective variations. However, the variation in α_1 was not calculated by Brochard. It should nevertheless be noted that α_1 is small compared to η_c,[14] and that it is therefore reasonable to neglect the $\alpha_1 \sin^2\theta \cos^2\theta$ term in comparison with the $\eta_c \sin^2\theta$ term. Taking this approximation into account, $\delta\eta$ is written

$$\delta\eta = \frac{CkT}{N} \tau_R \tag{11}$$

This formula can be explicited by replacing τ_R by its value. If, in addition, the polymer is assumed to change in shape without changing in volume ($R_\parallel R_\perp^2 = R^3$), we obtain:

$$\delta\eta \sim \lambda_\perp \frac{q\, p^{2/3}}{q + p^2} \tag{12}$$

where $q = \lambda_\parallel/\lambda_\perp$ and $p = R_\perp/R_\parallel$.

In order to estimate $\lambda_\perp$, it should be pointed out that formula 7 shows that $\delta\eta_a$ obeys a similar law to that obtained in a classic isotropic solvent. This result is due to the fact that the η_a viscosity does not entail any coupling between the flow and the director. $\lambda_\perp$ can thus be assumed to be proportional to η_a, and we can write:

$$\frac{\delta\eta}{\eta_a} \sim \frac{q\, p^{2/3}}{q + p^2} \tag{13}$$

The behavior of $\delta\eta/\eta_a$ as a function of T therefore gives information on the microscopic parameters of the systems, $R_\perp/R_\parallel$ and $\lambda_\parallel/\lambda_\perp$.

III. KERR EFFECT

A. Experimental

The measurements of the steady-state birefringence Δn where performed at 6328 Å, using a 5 mw He-Ne laser as the light source. The beam, polarized at $3\pi/4$ radians to the vertical, propagated parallel to the surfaces of two flat stainless steel electrodes, which were set vertically, 2.5 mm apart, in a quartz spectrophotometer cell of 4 cm path length filled with the liquid under study. The cell temperature was held constant to within 0.005°C. High voltage rectangular pulses were applied to the electrodes, with adjustable amplitude up to 500 V. The light beam emerging from the Kerr cell passed through a quarter-wave plate whose slow axis at $3\pi/4$ was parallel to the polarization direction, and through an analyzer, before detection by a photodiode. The output signal was digitized by a Datalab DL 922 transient recorder (8 bits, 2 Kb memory, 20 MHz maximum sampling rate) together with the high voltage electric pulse applied to the electrodes. The digital signals were

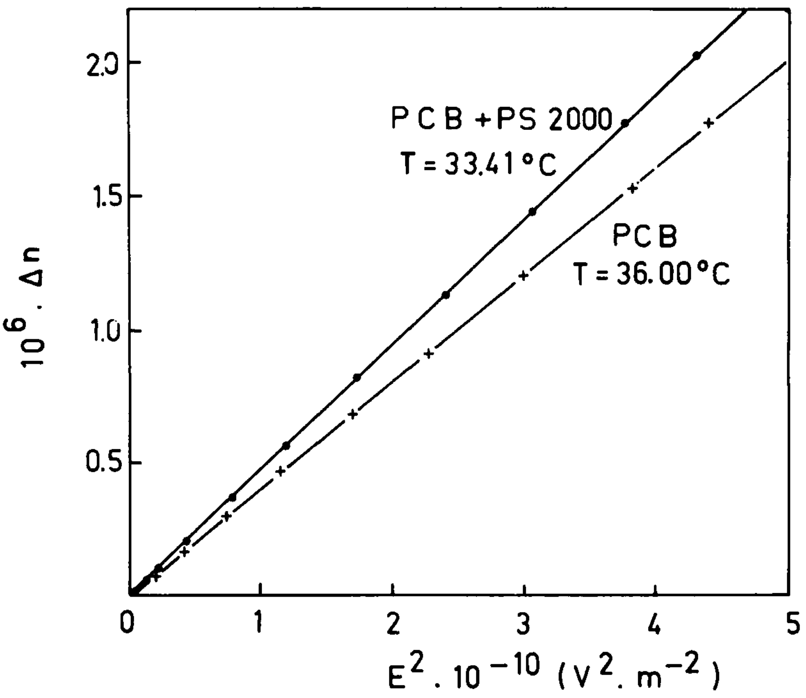

FIGURE 1 Typical results of measurements on the induced birefringence versus the square of the applied dc electric field for PCB ($T-T^* \approx 3.1$°C) and PCB + 1.75% PS 2000 ($T-T^* \approx 3.0$°C). The slope of each line yields the Kerr constants K. $K = 2.54 \cdot 10^{-17} m^2 . V^{-2}$ (PCB) and $K = 3.02 \cdot 10^{-17} m^2 . V^{-2}$ (PCB + 1.75% PS 2000). The data, taken at practically the same $T-T^*$, also show that the polymer increases the Kerr constant of the solvent.

processed by a local computer and stored for further analysis. During the measurements the cell was kept under inert atmosphere.

The measurements were carried out on solutions of polystyrene (PS) dissolved either in EBBA or in PCB. Both the weight of the polymer (M_w = 2000) and its concentration (c = 1.75% in weight) were comparable to those used in the experiments performed in the nematic phase.[1-5] As we have already seen, measurements were also taken on pure EBBA and pure PCB. The temperature T_i above which the various samples become isotropic was determined during the experiment by measuring the temperature at which the first nematic drops appear. For pure EBBA and the EBBA-PS mixture, T_i = 78.6°C and 76.2°C respectively; for pure PCB and the PCB-PS mixture, T_i = 34.3°C and 32.75°C respectively. The Kerr constant K at a given temperature was determined from the slope of the line representing the variation of the induced birefringence Δn as a function of the square of the electrical field E^2. A typical example of this is shown in Figure 1. We shall use in the following, as the Kerr constant of the mixture, the specific Kerr constant K_{sp}, given by $K_{sp} = K/(1 - C_v)$, where C_v is the volume fraction of the polymer.

B. Results

Let us first present the results obtained for pure EBBA and the EBBA-PS mixture. Figure 2, giving the variation of K as a function of T–T* in logarithmic coordinates, shows that the Kerr constants of pure EBBA and the mixture both present a linear variation in the last four or five degrees before the phase transition. The values of T* were determined by representing K^{-1} as a function of T and by extrapolating the line obtained at $K^{-1} = 0$. This extrapolation gives T* = 77.8°C for pure EBBA, and T* = 74.5°C for the mixture. Notice that the Kerr constants of pure EBBA and the mixture are negative.

Although the results obtained for pure EBBA and the mixture show similar overall behavior, there are nonetheless two points on which they differ.

Firstly the T_i–T* difference is greater for the mixture (T_i–T* ≃ 1.7°C) than for pure EBBA (T_i–T* ≃ 0.8°C). This increase indicates that the first order nature of the nematic–isotropic transition is more clearly marked in the case of the mixture than for pure EBBA.

The other difference concerns the absolute value of the Kerr constant itself, greater for the mixture than for pure EBBA. If there were no interaction between the PS and the local orientational order of EBBA, the polymer should simply

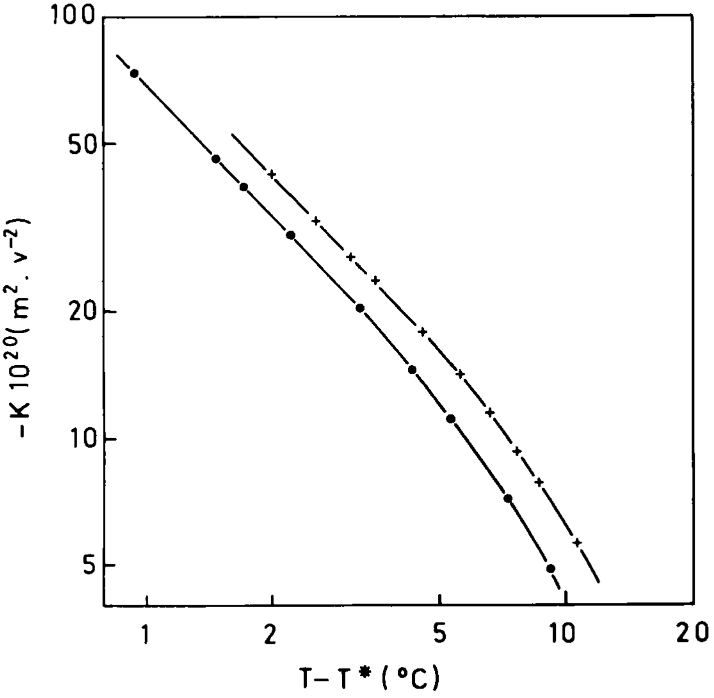

FIGURE 2 Log–Log plot of the absolute value of the Kerr constant as a function of T–T*. T^*_{EBBA} = 77.8°C, T^*_{mixt} = 74.5°C. ●: Pure EBBA; +: Mixture of EBBA + 1.75% PS 2000. For pure EBBA, $K = \Delta n/\bar{n}E^2$, and for the mixture $K = K_{sp}$ (see text); $\bar{n} = 1.59$.

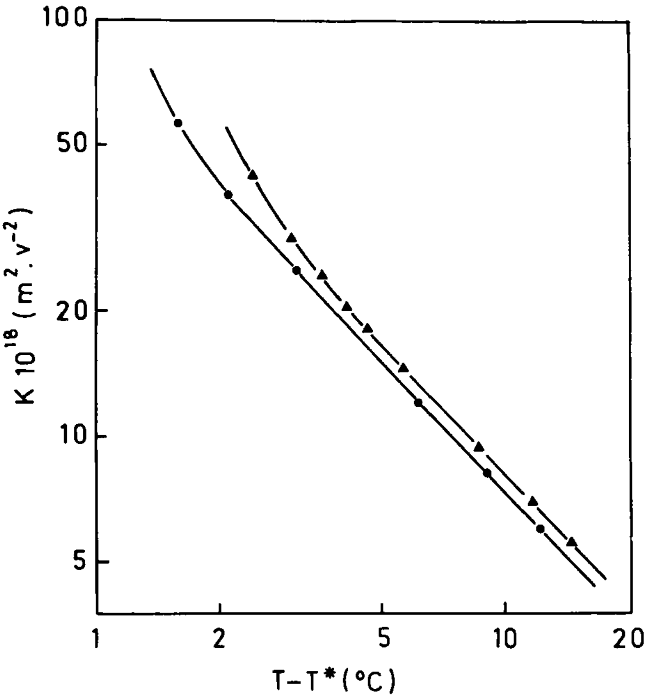

FIGURE 3 Log–Log plot of the Kerr constant as a function of T–T*. $T^*_{PCB} = 32.9°C$, $T^*_{mixt} = 30.4°C$. ●: Pure PCB; ▲: Mixture of PCB + 1.75% PS 2000. For pure PCB, $K = \Delta n/\bar{n}E^2$, and for the mixture $K = K_{sp}$ (see text); $\bar{n} = 1.59$.

reduce the T* temperature of EBBA, and the curves representing the variation of K as a function of T–T* for pure EBBA and the mixture should be superimposed. Since this is not the case, we can conclude that there does exist some interaction between the polymer and the local orientational order.

In order to check that this is a general effect, we varied the solvent used, choosing PCB which has a positive birefringence. The results obtained are given in Figure 3. They show that the T–T* law is verified over a wider range of temperatures than those involving EBBA (cf. Figure 2) for the reasons given in Chapter II, and that deviation from this law occurs in the vicinity of T_i. This deviation has already been reported for PCB, but has not been explained.[7] These results also show that Kerr constant of the mixture is greater than that of pure PCB. For the purposes of the present study, this is the important point, since it confirms the existence of an interaction between the polymer and the local orientational order.

C. Discussion

Polymer-solvent interaction was envisaged for the nematic phase, and this can lead to either an orientation of the polymer by the nematic order,[15] or a decrease of the nematic order itself.[16] The latter possibility would, in our case, lead to a decrease of the electrical birefringence, which would be in contradiction with our observations. We shall therefore discuss our results using a Flory Huggins lattice model, which assumes that the local orientational order is not too greatly disturbed by the presence of the polymer. In this model the free energy per unit volume is written[17]:

$$F = kTn(1 - \varphi)\mathrm{Log}(1 - \varphi) + kTn\frac{\varphi}{N_s}\mathrm{Log}\varphi + kT\chi\varphi(1 - \varphi) + \mu(1 - \varphi) \quad (14)$$

where φ is the volume fraction occupied by the chains; $\varphi = ca^3$, where c is the concentration (number of monomers per cm^3) and a^3 the volume of an elementary cell of the lattice. N_s is the number of sites occupied by one chain and n the number of sites per unit volume. $\chi = \bar{\chi}n$ is the Flory parameter describing the polymer-solvent interaction per unit volume and $\bar{\chi}$ the Flory parameter per site. μ is the chemical potential of the solvent. In the present case, one site is supposed to be occupied by one liquid crystal molecule.

χ and μ must depend on the order parameter Q, and can thus be developed as a power series in Q and written as follows,[15] without going beyond the second order:

$$\chi = \chi_0 + \chi_1 Q^2 \quad (15)$$

$$\mu = \mu_0 + \frac{1}{2}a(T - T^*)Q^2 \quad (16)$$

χ_0 and μ_0 represent the Flory parameter and the solvent's chemical potential in the isotropic phase, respectively. χ_1 is positive when the nematic phase is a poorer solvent than the isotropic phase. In the following, a and T^*, which refer to the pure liquid crystal, will be labeled a_{pure} and T^*_{pure}.

In order to determine the Kerr constant of the mixture, we must add to Equation 14 the electric term of Equation 1, and minimize, as with the pure liquid crystal, the free energy in relation to Q. The Kerr constant so obtained can be expressed as follows:

$$K_{mixt} = \frac{\varepsilon_0}{3}\left[\frac{(\Delta n)_0(\Delta\varepsilon)_0}{\bar{n}}\right]_{mixt}\frac{1}{a_{mixt}(T - T^*_{mixt})} \quad (17)$$

with

$$a_{mixt} = a_{pure}(1 - \varphi)\frac{T^*_{pure}}{T^*_{mixt}} \quad (18)$$

and

$$T^*_{mixt} = T^*_{pure}(1 + 2n\varphi\bar{\chi}_1 k/a_{pure})^{-1} \quad (19)$$

The form of Equation 17 is similar to that obtained for the pure solvent (Equation 5). If we assume that the ratio $(\Delta n)_0(\Delta\varepsilon)_0/\bar{n}$ is the same for the mixture and for the pure solvent, Equations 5, 17 and 18 show that $K_{mixt}/K_{pure} = (1/(1 - \varphi))$.

(T^*_{mixt}/T^*_{pure}) for the same (T−T*) difference. Since $T^*_{mixt}/T^*_{pure} \simeq 1$ and since φ is a number between 0 and 1, the ratio of the Kerr constants must be positive, and greater than 1, as is the case in our experimental observations. Figures 2 and 3 enable the Kerr constants ratio, and thus φ and a ($\varphi = ca^3$), to be determined. K_{mixt}/K_{pure} is found to be of the order of 1.25 or 1.1 depending on the solvent used, EBBA or PCB. As a result, $\varphi \simeq 0.2$ and $a \simeq 9.5$ Å for polystyrene in EBBA, and $\varphi \simeq 0.1$ and $a \simeq 7.5$ Å for polystyrene in PCB. It should be noted that these values are consistent with those which can be deduced from the relationship $n = 1/a^3$, where n is the total number of sites per unit of volume.[18]

Equation 9 allows us to give an estimation of $\overline{\chi}_1$ provided the value of a_{pure} is known. The later can be calculated from the slope of the line giving K^{-1} as a function of T. For PCB, we find $a_{pure} = 0.141\ 10^6\ J \cdot m^{-3} \cdot K^{-1}$ taking $(\Delta n)_0 = 0.30$[7] and $(\Delta\varepsilon)_0 = 21.3$.[7] This value of a_{pure} leads to $\overline{\chi}_1 \simeq 0.2$. For EBBA, we find $\overline{\chi}_1 \simeq 0.5$ ($a_{pure} = 0.65\ 10^6\ J \cdot m^{-3} \cdot K^{-1}$ if we suppose $(\Delta n)_0 = 0.30$ and $(\Delta\varepsilon)_0 = -0.80$[19]).

There is some uncertainty on the values of $\overline{\chi}_1$ arising from the fact that the values for the birefringence and dielectric anisotropy of the fully aligned nematic phase (i.e. $(\Delta n)_0$ and $(\Delta\varepsilon)_0$) are not known with accuracy. Dubault[20] found $\overline{\chi}_1 = 1.17$ for the system EBBA + PS2100 and $\overline{\chi}_1 = 0.4$ for the system PAA + PS2100. As noticed by Dubault, these values, deduced from the analysis of the phase diagrams, also present some uncertainty, related to the fact that the determination of the lower coexistence curve in the phase diagram is not very accurate. Taking into account these various uncertainties, one can therefore consider that the agreement between our values of $\overline{\chi}_1$ and those obtained by Dubault is satisfactory. It should also be noted that the Flory-Huggins model cannot be applied with complete rigor, since the polymer concentration is low and the size of the site greater than that of the monomer.

At first sight, it may seem surprising for the polymer to be surrounded by a nematic-type local order while the nematic phase is a poorer solvent than the isotropic phase. This apparent contradiction can be explained by comparing the correlation length ξ of the nematic order with the mean distance $\bar{x}$ travelled by the polymer during the lifetime τ of the nematic order. In the vicinity of the transition $\xi \simeq 100$ Å.[21] In order to estimate $\bar{x}$, the formula $\langle \bar{x}^2 \rangle = 6D\tau$ can be used, where D is a translation diffusion coefficient which, in the case of a spherical coil with radius R, is given by $D = kT/6\pi\eta R$. In the vicinity of the transition, $\tau \simeq 2\ 10^{-7}$ sec,[22] and $\eta \simeq 0.3$ P; assuming that R = 20 Å[4] the value of $\bar{x}$ is found to be ≃20 Å. This value, smaller than that of ξ, indicates that, over the time interval considered, the polymer does not have time to diffuse from a nematic domain to an isotropic domain. The isotropic phase cannot, therefore, be considered as a mixture of a nematic solvent and an isotropic solvent, in which the polymer might choose the best solvent.

IV. CAPILLARY FLOW

The coupling of the nematic orientational order with the polymer induces a change in the conformation of the polymeric coil. Since this change should be manifest in the flow properties, we have chosen to study the influence of the dissolved chains on viscosity.

A. Experimental

The viscosity was measured by means of an Ostwald viscosimeter. The capillary had a diameter of 0.6 mm and was immersed in a water-bath regulated to within 0.005°C. Measurements were taken on pure PCB and on PCB-PS mixtures. Polymer-weight of 2000 and 9000 were studied, with a polymer concentration of 1.75% in weight in each case. Both the mixtures and the solvent showed Newtonian behavior for the shear gradients available with the experimental set-up. Direct observation of the sample during the experiments ensured that the measurements were indeed taken in the isotropic phase of the 3 compounds.

B. Results

The results obtained, given in Figure 4, show that the viscosity of the pure PCB is noticeably increased by the presence of the polymer. It can be seen that all three viscosities present an Arrhenian-type behavior (the solid curves in the figure) throughout the whole temperature-range studied. This behavior, predicted by the de Gennes theory of the nematic–isotropic phase transition,[6] shows that capillary viscosity does not present a critical behavior, although the local orientational order is aligned by the flow.

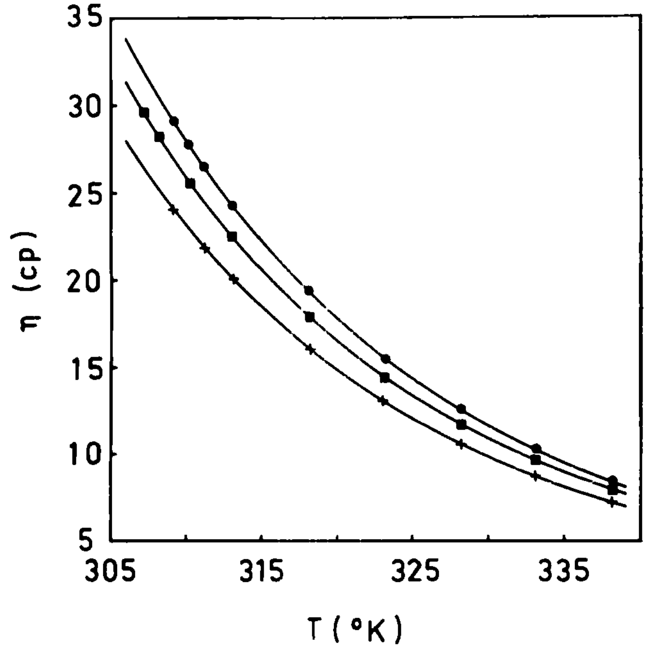

FIGURE 4 Temperature dependence of the viscosity. + : pure PCB; ■: mixture of PCB + 1.75% PS 2000; ●: mixture of PCB + 1.75% PS 9000. The solid curves are the fits with an Arrhenian law.

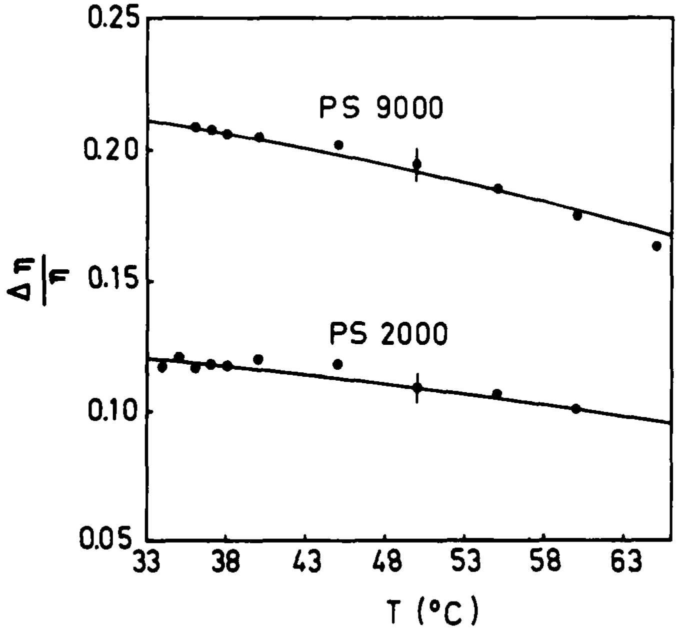

FIGURE 5 Behavior of the $\delta\eta/\eta$ ratio as a function of temperature for PS 9000 and PS 2000 using PCB as solvent. The solid curves are guides for the eye.

From the results given in Figure 4, the $\delta\eta/\eta$ ratio can be determined, in which $\delta\eta$ is the difference between the viscosity of the mixture and that of the pure solvent, η. Since the viscosity has no critical behavior, the thermal behavior of $\delta\eta/\eta$ must be represented as a function of T, and not as a function of T−T*. The results obtained are plotted on Figure 5, and show that $\delta\eta/\eta$ increases as the temperature decreases.

C. Discussion

Let us first suppose that the coil is spherical in shape, with a radius of gyration R, as in the case of a classic solvent. The Dumbbell model will then show that the thermal variation of the $\delta\eta/\eta$ ratio reflects the thermal variation of the radius of gyration R of the polymeric coil (cf. formula 6). The increase of $\delta\eta/\eta$, which is of the order of 22% for both the polymers studied, would then correspond to an increase of ≃11% of their respective gyration radii. This result would indicate a progressive rise in solvent quality when $T \rightarrow T_i$, which is not possible, since the nematic phase is a poorer solvent than the isotropic phase. Neither is it possible for the increase in R to stem from a stiffening of the polymer due to the orientational order,[23] since this effect can only occur if R is greater than the correlation length ξ, and this is contrary to the present case, where R ≃ 20 Å and ξ ≃ 200 Å.

Since the increase of $\delta\eta/\eta$ cannot be explained by the isotropic coil approach, it must be assumed that the coil is anisotropic. Such a deduction does, however, suppose a nematic-type environment for the polymer. This is indeed so, provided that R is smaller than ξ, which is the result observed, and that the characteristic time of the polymeric coil (1st Rouse mode) is comparable to the life time τ of the local nematic order, which is also the case.[24]

Since there is no theory which describes the flow of a polymer in solution in the isotropic phase of a nematic solvent, we shall discuss our results on the basis of the anisotropic dumbbell model elaborated for the nematic phase (see paragraph II,B,b). 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 should allow qualitative analysis of our measurements. In order to do this, we shall use Equation 13, in which the η_a viscosity of the nematic phase is replaced by the η viscosity of the isotropic phase. This is made possible by the fact that the activation energies of these two viscosities are identical.[25] Equation 13 is thus written as:

$$\frac{\delta\eta}{\eta} \sim \frac{qp^{2/3}}{q + p^2} \tag{20}$$

The variation of $\delta\eta/\eta$ as a function of p is given in Figure 6 for various values of q, and values of p between 0.7 and 1.2. The values of $\delta\eta/\eta$ were normalized at 1 for $p = 1$. Using as a reference the isotropic coil for which $p = 1$, $\delta\eta/\eta$ can be seen to increase notably when p decreases and $q < 1$. Deformation of the coil can therefore lead to an increase of the $\delta\eta/\eta$ ratio, which is precisely the experimental

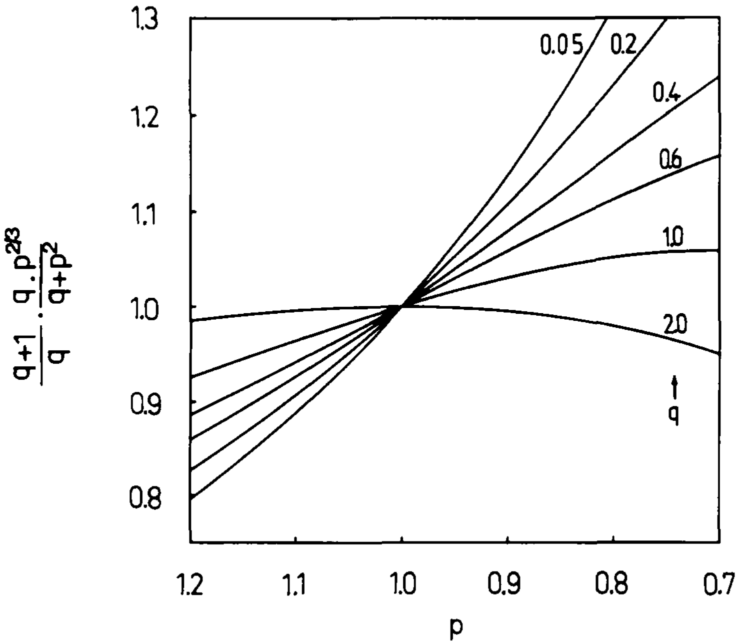

FIGURE 6 Behavior of $\delta\eta/\eta \sim q\, p^{2/3}\, (q + p^2)$ as a function of the conformational-anisotropy factor p for various values of the friction-anisotropy factor q. The curves have been normalized (with a $(q + 1)/q$ prefactor) to 1 for $p = 1$.

result observed. Although the model is not quantitatively applicable to the isotropic phase, we have attempted to determine parameters p and q, corresponding to the $\delta\eta/\eta$ increase observed experimentally. The fit of the experimental points with formula 20 shows that these parameters cannot in fact be determined because of the large number of parameters involved in the fit (p, q, the proportionality coefficient of formula 20, the temperature at which $p = 1$), and experimental error. The most important information supplied by the model is the fact that $p < 1$, i.e. that the polymer is stretched along the director ($R_\parallel > R_\perp$).

In theory, the rate of anisotropy of the polymeric coil can be directly determined by small-angle neutron scattering. A study[4] carried out in the nematic phase of a similar mixture (polystyrene of weight 2.100 in solution in para-azoxyanisole) has shown that $R_\parallel = 27$ Å ± 4 Å and $R_\perp = 22$ Å ± 4 Å. Although the ($R_\parallel - R_\perp$) difference is of the same order of magnitude as experimental error concerning $R_\parallel$ and $R_\perp$, these measurements tend to show that $R_\parallel > R_\perp$. This conclusion, which has also been deduced from NMR measurements,[4] is quite consistent with that obtained from the anisotropic dumbbell model, which thus seems to give a reasonable result, even though this model can only strictly apply in the nematic phase. A more appropriate theory will be necessary in order to supply a quantitative description of the dynamic effects associated with the isotropic phase of nematic-polymer mixtures.

V. CONCLUSIONS

In this article, we have shown that the static (Kerr effect) and dynamic (capillary viscosity) properties of the isotropic phase of a nematic solvent (PCB and EBBA) are modified by the presence of low molecular-weight polymeric chains (polystyrene). This indicates the existence of a coupling between the polymer and the local orientational order, which changes the conformation of the chains. Analysis of the viscosity measurements suggests that the polymer is stretched along the director, which would also seem to be the result produced by neutron and NMR experiments conducted in the nematic phase. The fact that the polymer is more soluble, and viscosity measurements easier to analyze in the isotropic phase than in the nematic phase, in which we must take into account not only Arrhenian dependence but also the T/T_c dependence associated with the order parameter, allows us to envisage studies which are a function of weight and concentration.

Acknowledgment

We would like to thank F. Brochard for a critical reading of the manuscript and V. Reys for discussions.

References

1. A. Dubault, C. Casagrande and M. Veyssie, *Mol. Cryst. Liq. Cryst. Lett.* **72**, 189 (1982).
2. A. Dubault, C. Casagrande and M. Veyssie, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 239 (1978).

3. A. Dubault, C. Casagrande, M. Veyssie and B. Deloche, *Phys. Rev. Lett.*, **45**, 1645 (1980).
4. A. Dubault, R. Ober, M. Veyssie and B. Cabane, *J. Physique*, **46**, 1227 (1985).
5. P. Martinoty, A. Dubault, C. Casagrande and M. Veyssie, *J. Physique Lettre*, **44**, 935 (1983).
6. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971); and "The Physics of Liquid Crystals" Oxford University Press, London (1974).
7. D. A. Dunmur, A. E. Tomes, *Mol. Cryst. Liq. Cryst.*, **76**, 231 (1981).
8. J. C. Filippini and Y. Poggi, *J. Physique Lettres*, **35**, 99 (1974); *Physics Letters* **49A**, 291 (1974).
9. T. Bischofberger, R. Yu and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **43**, 287 (1977).
10. See, for instance, R. B. Bird, O. Hassager, R. C. Armstrong and C. F. Curtiss, Dynamics of Polymeric Liquid, Vol. II, Kinetic Theory (Wiley) (1977).
11. F. Brochard, *J. Polym. Sc.*, *Polym. Phys. Ed.* **17**, 1367 (1979).
12. See, for instance, W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach Science Publishers (1980).
13. $e \simeq (Kd/\eta)^{1/3}$ where K is an elastic constant, η the viscosity and d the diameter of the capillary. (see P. G. de Gennes, "The Physics of Liquid Crystals", page 174, Oxford University Press, London (1974)).
14. For MBBA $\alpha_1 = 6.5$ cP, $\eta_c = 121$ cP at T = 25°C (see Reference 12).
15. F. Brochard, *C. R. Acad. Sci. Paris*, **289 B**, 229 (1979).
16. F. Brochard, *C. R. Acad. Sci. Paris*, **290 B**, 485 (1980).
17. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca (1979); P. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca 8th printing (1971).
18. These two values of a can, however, be seen to be slightly different, whereas estimation from the $n = 1/a^3$ relationship gives $a \simeq 7.5$ Å for both solvents. This slight difference could be explained by the fact that the ratio $(\Delta n)_0\,(\Delta\varepsilon)_0/\bar{n}$ may not be the same for the mixture and the pure solvent, which is not the assumption we made.
19. N. V. S. Rao, P. R. Kishore, T. F. S. Raj, M. N. Avadhanlu and C. R. K. Marty, *Mol. Cryst. Liq. Cryst.*, **36**, 65 (1976).
20. A. Dubault, Thesis Paris (1981).
21. T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **30**, 688 (1973).
22. H. J. Coles and B. R. Jennings, *Molec. Phys.*, **36**, 1661 (1978).
23. P. G. de Gennes, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 95 (1984).
24. The first characteristic time of the coil can be estimated by extrapolating the results reported by J. Ferry (Viscoelastic Properties of Polymers, Wiley London, 1970, p. 230) for polystyrenes with molecular weights of 82 000, 267 000 and 860 000. The characteristic time thus obtained is of the order of $10^{-7} - 10^{-8}$ sec. The life time τ of the local nematic order is of the order of 10^{-7} sec near the transition (see Ref. 22).
25. F. Kiry and P. Martinoty, *J. Physique*, **38**, 153 (1977).