



HAL
open science

Flexible polymers in a nematic medium : ultrasonic measurements

P. Martinoty, A. Dubault, C. Casagrande, M. Veyssié

► **To cite this version:**

P. Martinoty, A. Dubault, C. Casagrande, M. Veyssié. Flexible polymers in a nematic medium : ultrasonic measurements. *Journal de Physique Lettres*, 1983, 44 (23), pp.935-945. 10.1051/jphyslet:019830044023093500 . jpa-00232285

HAL Id: jpa-00232285

<https://hal.science/jpa-00232285>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
61.30 — 61.40K

Flexible polymers in a nematic medium : ultrasonic measurements

P. Martinoty

Laboratoire d'Acoustique Moléculaire (*), Université Louis Pasteur,
4, rue Blaise Pascal, 67070 Strasbourg Cedex, France

A. Dubault, C. Casagrande and M. Veysié

Laboratoire de Physique de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France

(Reçu le 13 juillet 1983, accepté le 14 octobre 1983)

Résumé. — Nous présentons une étude de deux coefficients de friction d'un mélange nématique-polymère, effectuée au moyen de la technique d'absorption des ondes ultrasonores transversales. Les résultats obtenus montrent que la présence du polymère augmente de façon considérable les deux coefficients de friction du nématique pur, bien que les chaînes soient courtes et en faible concentration. Les mesures effectuées en fonction de la température mettent en évidence deux régimes correspondant à des conformations différentes des chaînes polymériques. Ces résultats sont compatibles avec les prévisions théoriques de Brochard.

Abstract. — Using a shear wave reflectance technique, two viscosity coefficients in solutions of flexible polymers in a nematic solvent were measured. A large increase in the viscosities was observed when the chains were solubilized in the nematic solvent even at very low concentration. The variation of this effect as a function of the temperature shows the existence of two different situations for the polymer chains. The results are consistent with the theoretical expectations of Brochard.

1. Introduction.

The study of dilute solutions of flexible polymers in nematic solvents has only recently been undertaken [1, 2]. In particular, an important question related to these new systems is the effect of the nematic field on the conformation of the polymer chains.

To begin with, a study of phase diagrams has been necessary to determine the conditions of the compatibility between classical flexible chains (polystyrene, polyoxyethylene) and nematic solvents. It appeared [3] that homogeneous nematic solutions may be obtained within a restricted range of molecular weight and concentration ($\overline{M}_w < 10^4$, $c < 2 \times 10^{-2}$). Thus, physical measurements may be only achieved in the dilute regime. However, even under these conditions, one may expect significant effects on the hydrodynamic properties, as observed for classical polymer solutions. In particular, the viscosity measurements appear attractive because the nematic

(*) E.R.A. au C.N.R.S.

medium is characterized by five independent viscosity coefficients ; one may thus expect to get information on the conformation of polymer coils by studying the effect of the solubilized chains on these viscosity coefficients and on their anisotropy. In fact, measurements of the twist viscosity γ_1 reveal a large increase of that coefficient, which suggests an anisotropical shape of the coils [2].

In order to get more informations about these new systems, an ultrasonic impedometric technique was used, which has already been successful in the determination of the viscosity coefficients in pure liquid crystals [4]. In the present case, it allows two viscosity coefficients (different from γ_1) to be measured ; one of them η_a , which corresponds to an ordinary viscosity, is of particular interest, as it may be interpreted simply in terms of the size of polymeric coils.

2. Experimental procedure.

2.1 IMPEDOMETRIC DEVICE. — The impedometric technique consists in measuring the real and imaginary parts of the shear mechanical impedance $Z = R_L + iX_L$ defined as the ratio of shear stress to transverse particle velocity.

For a Newtonian fluid R_L and X_L are equal, and the steady flow viscosity η is given by [5] :

$$\eta = \frac{R_L^2}{\rho\pi f} \quad (1)$$

where ρ is the liquid density and f the shear wave frequency. In this case, the impedometer becomes a viscometer. Equation 1 may be used only if $2\pi f\tau \ll 1$ where τ is the characteristic relaxation time of the system (low frequency approximation).

The experimental method is based upon the determination of the reflection coefficient of a pulse of shear waves at the surface of a fused silica bar. The values of R_L and X_L are obtained from the changes in amplitude r and phase ϕ of the reflected wave which occur when the liquid is placed on the reflecting surface.

In this study the standard inclined incidence method illustrated in figure 1 was used. Details of the technique are described in reference 6. Briefly, a pulse of shear waves is generated by an AT-cut quartz crystal transducer fixed to one end of the fused silica bar. After reflection on the upper surface and at the other end of the bar, the pulse of shear waves re-excites the transducer, successive reflections giving a train of echoes of decreasing amplitudes. The real part is deduced from the measured value of r , by the relation :

$$R_L = Z_s \cos \theta \frac{1 - r}{1 + r} \quad (2)$$

where Z_s is the shear mechanical impedance of the fused silica and θ is the angle of incidence of the shear waves.

The imaginary part X_L , which requires the measurement of the phase change ϕ was not measured here.

The values of r are obtained by comparing the amplitude of the echo for the fused silica-air and the fused silica-sample interfaces. This was done at a frequency equal to 5 MHz as a function of temperature. The accuracy is improved as r is determined from a signal which had undergone several reflections at the interface. In this study, the 15th echo was selected for the determination of r which ensures an accuracy better than ~ 1 cp in determining the viscosities.

The transducer was bonded to the bar by cooling a film of nematic liquid crystal (p-azoxyphenetole) into its crystalline phase [6]. This simple bonding method gives good performance in transmitting shear waves (as many as 50 echos were observed), and allows measurements up to temperatures of the order of 65 °C. The sample was placed between the reflecting surface of the bar and a coverglass which were both treated in order to orient the nematic sample. The two different geometries illustrated in figure 1 were used. In both cases, the shear polarization was

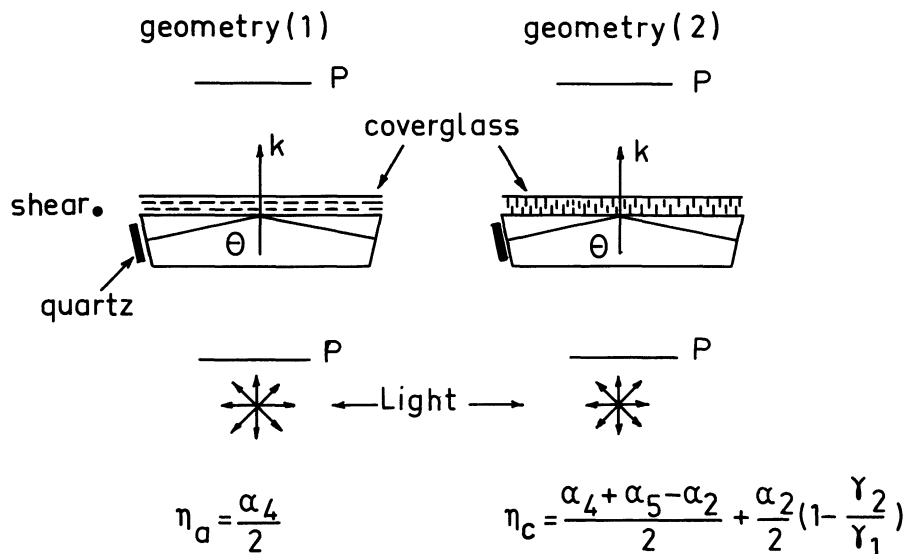


Fig. 1. — Schematic diagram of the acoustic system showing the 2 orientations in which the viscosity coefficients were measured. The shear vibration is parallel to the reflecting surface; θ is the angle of incidence and \mathbf{k} the wave vector of the shear wave in the nematic. The shear wave propagates in the nematic practically along the normal to the reflecting surface. The viscosity η_a corresponds to the viscosity of an isotropic liquid (no coupling between the director and the flow). This coupling exists for the viscosity η_c and gives rise to the term $\frac{\alpha_2}{2} \left(1 - \frac{\gamma_2}{\gamma_1}\right)$.

perpendicular to the director \mathbf{n} , but in case (1), the wave vector \mathbf{k} was perpendicular to \mathbf{n} while in case (2), \mathbf{k} was parallel to \mathbf{n} . The corresponding friction coefficients are given by [4, 7] :

$$\eta_a = \frac{\alpha_4}{1} \quad \eta_c = \frac{\alpha_4 + \alpha_5 - \alpha_2}{2} + \frac{\alpha_2}{2} \left(1 - \frac{\gamma_2}{\gamma_1}\right) \quad (3)$$

where the various α_i are the Ericksen-Leslie coefficients, $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_3 + \alpha_2$. The alignment was obtained by rubbing in case (1) and by applying a thin lecithin layer in case (2); it was controlled by optic observation between crossed polarizers. The shear cell was tested by using dibutylphthalate. Temperature was controlled to within 0.01 °C.

2.2 MATERIALS. — All measurements were performed on a solution of polystyrene ($M_w = 2\,100$) in a para-ethoxy-benzylidene p-n-butylaniline (EBBA), used as a solvent; the polymer concentration was 1.7 % in weight.

The phase diagrams for the PS-EBBA systems were determined by A. Dubault *et al.* [3]. For a polymer concentration equal to 1.7 % the mixture becomes completely nematic when the temperature is lower than 66 °C (T_N), but a demixtion process occurs at a lower temperature ($T_d = 55$ °C). However, it must be stressed that these characteristics remain constant with time, only if the samples are kept in glass tubes, sealed under primary vacuum. Under free atmosphere, the characteristic temperatures T_N and T_d may decrease significantly due to hydrolysis of the Schiff-basis liquid crystal. However, it has been verified that the sample no longer evolves when placed in the impedometric apparatus; in particular, ultrasonic data are reproducible over several days.

3. Experimental results.

The real part R_L of the impedance has been measured at the frequency $f = 5$ MHz for pure EBBA and for the mixture, as a function of the temperature, for both (1) and (2) geometries. Moreover, in order to make further comparisons, similar experiments were performed on a classical isotropic solution of polystyrene; the solvent used was dibutylphtalate, with a viscosity at room temperature close to that of EBBA.

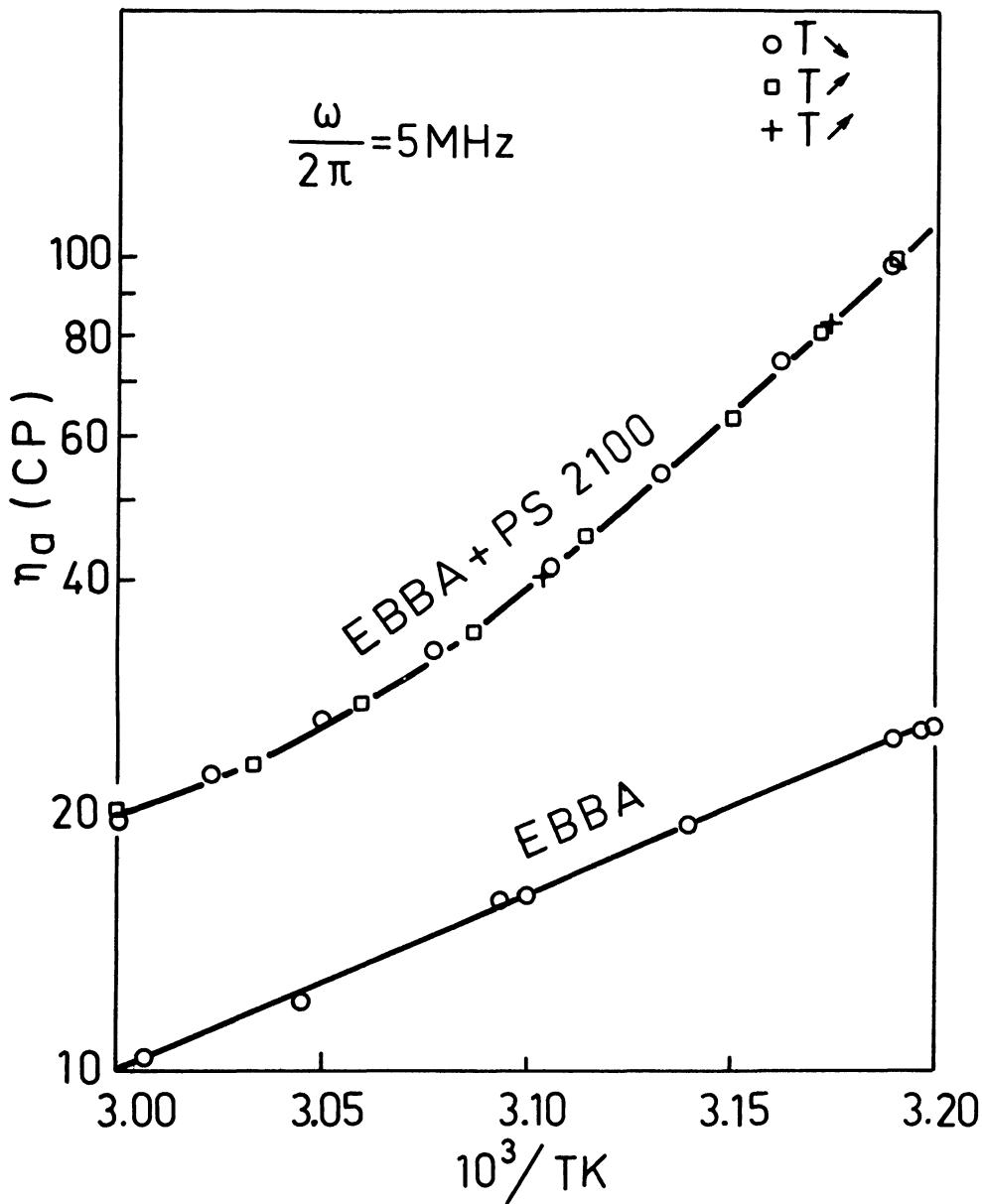


Fig. 2. — Temperature dependence of the friction coefficient η_σ for EBBA and the mixture EBBA-PS 2100. Several runs (cooling and heating) were made over a period of 2 days in order to test the reproducibility of the results. The temperature scale is in $1/T$ to allow comparison with the usual temperature-dependence of viscosities.

For pure EBBA it has been verified that the expression $R_L^2/\rho\pi f$ can be identified with the viscosity η [8].

For the mixture, this identification implies that the characteristic frequency of the polymer coils is considerably higher than 5 MHz, which is probably verified given the low molecular weight of the polymer [9].

Figures 2, 3 plot $\log \eta_{a,c} = R_L^2/\rho\pi f$ as a function of $1/T$. These figures call for the following remarks :

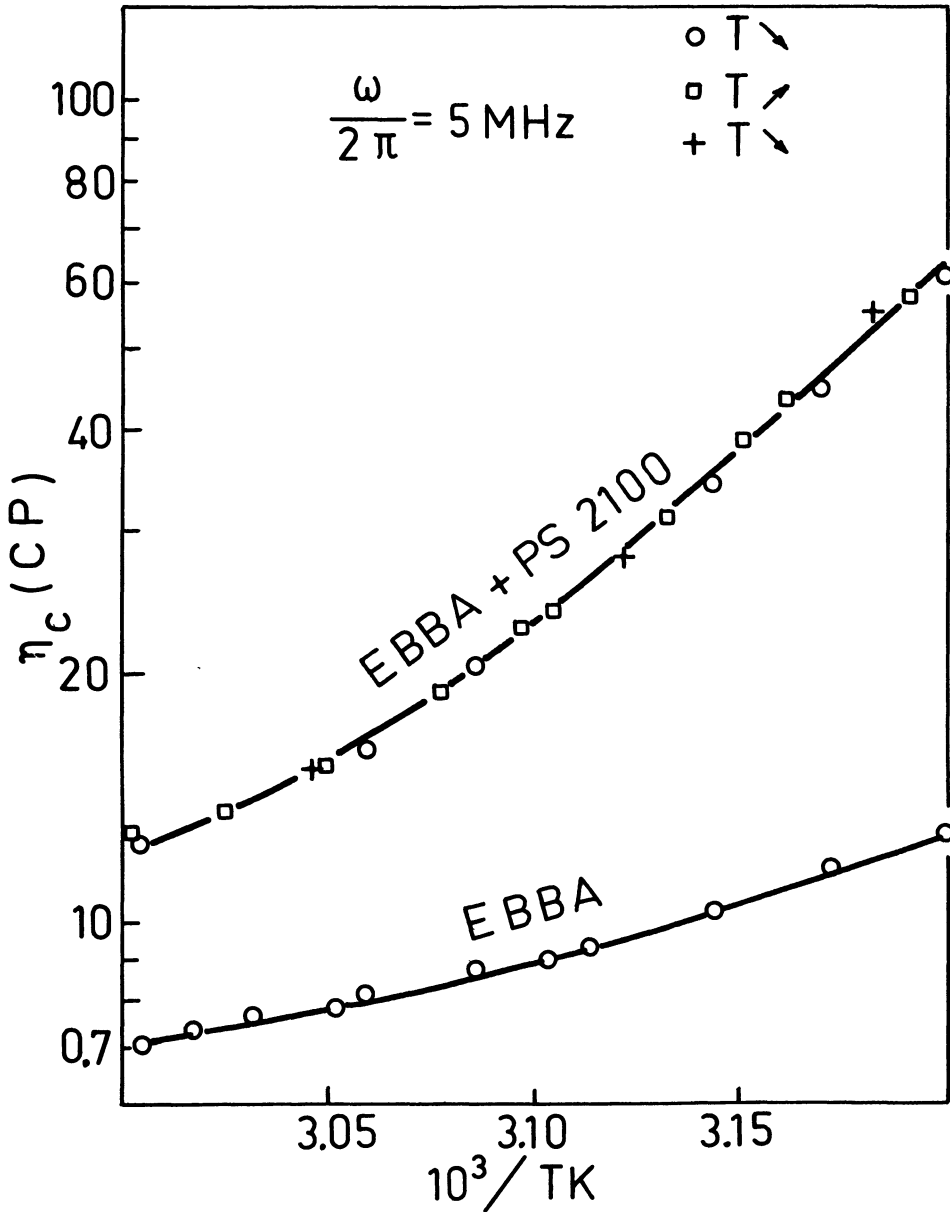


Fig. 3. — Same as for figure 2 but for η_c .

a) *Pure EBBA.*

The viscosity η_a shows an Arrhenian behaviour as expected for this coefficient which is independent of the order parameter in a first order approximation.

For η_c departure from an Arrhenian law is observed at higher temperatures. This can reasonably be supposed to be due to the γ_1 and γ_2 terms, occurring in η_c , which are dependent on the order parameter.

b) *PS-EBBA mixture.*

The first striking fact is the considerable enhancement of η_a and η_c when dissolving a small amount of PS in the liquid crystal ($\Delta\eta_a/\eta_a \approx 1$, $\Delta\eta_c/\eta_c \approx 1$).

The second point is the significant increase of this effect when the temperature is decreased, with a noticeable departure from an Arrhenian law. So, these two points appear as marked differences compared to the situation of a classical isotropic solution, such as polystyrene in dibutylphthalate (cf. Fig. 4).

Finally, the anisotropy of the viscosity coefficients is increased by the polymer chains, and varies sharply with the temperature : this fact appears on figure 5 where the values of $(\eta_a - \eta_c)$ versus T have been plotted for the pure liquid crystal and for the mixture.

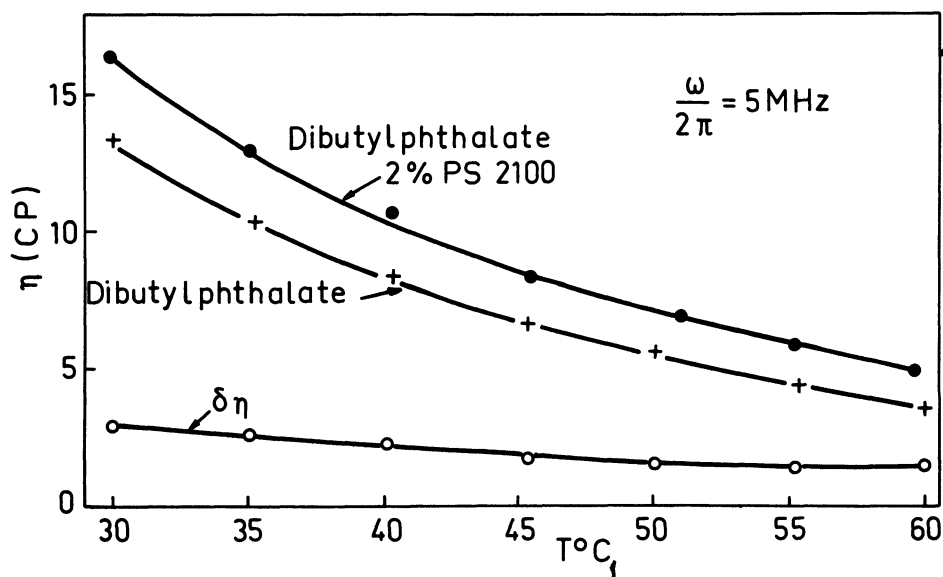


Fig. 4. — Temperature dependence of the viscosity of dibutylphthalate and of the mixture PS 2100 - dibutylphthalate.

4. Discussion.

It must be pointed out that these data are perfectly reproducible when making a thermal cycle over a period of several days, as long as the temperature is not decreased below 37 °C. This high reproductibility seems to exclude any chemical degradation during the ultrasonic measurements, as well as any phase separation process in the temperature range studied. On the contrary, the scattering of the results below 37 °C would lead to identification of this temperature with the demixtion temperature T_d .

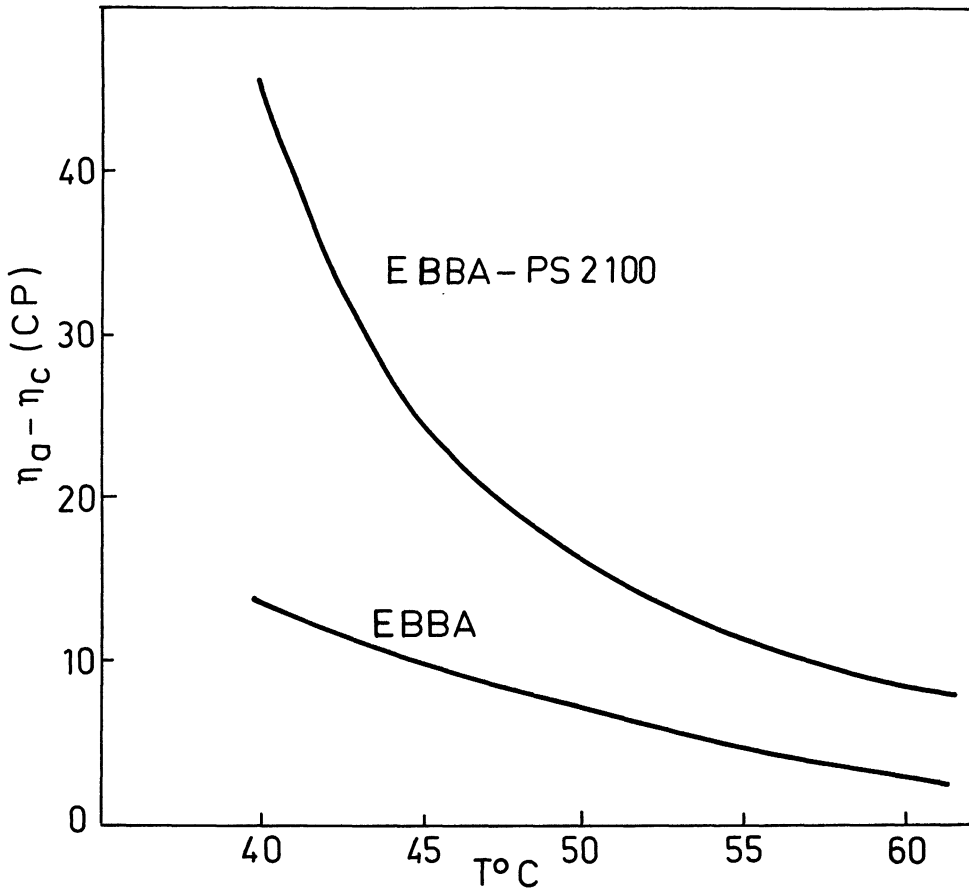


Fig. 5. — The anisotropy of the viscosity for EBBA and the mixture EBBA-PS 2100.

At present, this study will consider what information about the polymer coils can be deduced from experimental results in the homogeneous nematic phase ($T_a < T < T_d$). The simpler analysis consists in correlating the evolution of the viscosity with the typical size R of coils. In a conventional isotropic solvent, the dumbbell model [10] leads to a simple expression for the viscosity increment :

$$\delta \eta \propto \frac{c}{N} \lambda R^2 \tag{4}$$

where c is the concentration of the chains, N the degree of polymerization and λ the friction coefficient of the chains which is proportional to the viscosity in either the Rouse limit (short chains or elongated chains) or the Zimm limit (long chains).

In an anisotropic solvent, a very similar expression for the η_a coefficient was obtained by F. Brochard [11] :

$$\delta \eta_a \propto \frac{c}{N} \lambda_{\perp} R_{\perp}^2 \tag{5}$$

where R_{\perp} and λ_{\perp} are respectively the size and the friction coefficient of the chains along the direction perpendicular to the alignment axis of the solvent.

Since λ_{\perp} is proportional to the viscosity η_a [11] relation 5 reads as follows :

$$\delta \eta_a \propto \eta_a R_{\perp}^2. \quad (6)$$

Thus, by plotting the ratio $\delta \eta_a / \eta_a$ as a function of the temperature, one eliminates the conventional Arrhenian dependence of the viscosity and can expect to show up the influence of the temperature on the size of the chains.

Two different regimes can be observed on figure 6.

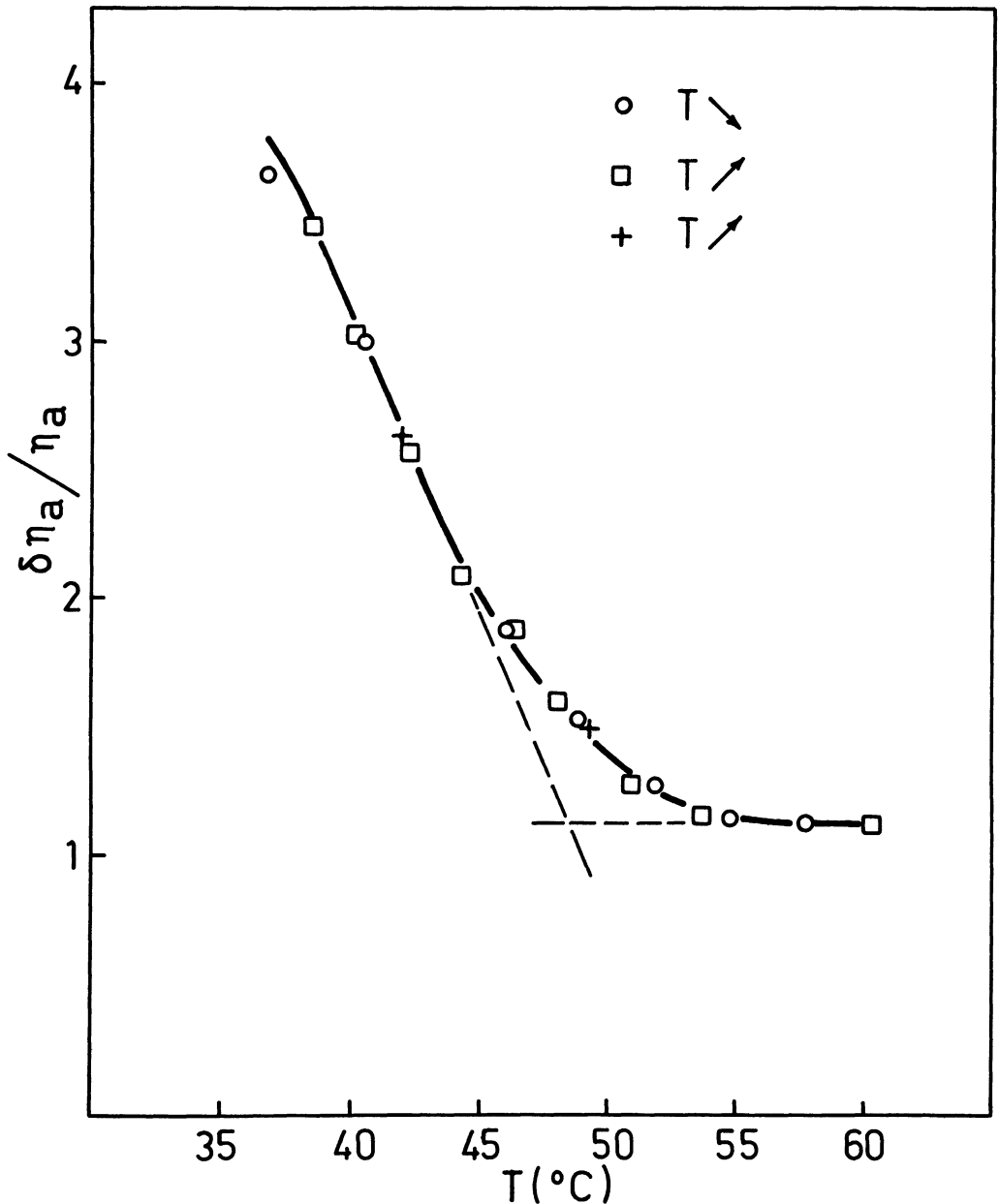


Fig. 6. — Temperature dependence of the ratio $\delta \eta_a / \eta_a \sim R_{\perp}^2$. The data show the existence of two regimes. T_N of the mixture is slightly below 65 °C.

Close to T_N , $\delta\eta_a/\eta_a$ remains constant and then sharply increases at lower temperature. These results would imply a drastic change in the behaviour of the chain sizes with temperature. Of course, in a nematic solvent one may expect a non-trivial variation of the coil sizes due to a specific effect of the nematic order. But, this may not explain the observed R_1 variation because the order parameter rapidly decreases near T_N contrary to the plateau observed for $\delta\eta_a/\eta_a$ at the higher temperatures.

A more probable hypothesis would be that the two observed regimes would correspond to a change in the coupling between the chains and the nematic medium. This problem has been theoretically discussed by F. Brochard who has predicted two different physical situations :

i) The « strong coupling » model [12] : the perturbations caused by the chains locally destroy the nematic order ; this corresponds to a situation where isotropic microglobules are dispersed among the nematic medium.

ii) The « weak coupling » model [1] : the chains are swollen within the nematic solvent ; this situation is quite similar to the classical solvent, except that the polymer coils may be distorted due to their coupling with the nematic field.

These two different physical situations are governed by the two following parameters :

– $\tau = \frac{T_c - T}{T_c}$ is the reduced temperature relative to the nematic-isotropic transition of the mixture.

– χ^n is a Flory parameter depending on the order parameter S that may be expressed by $\chi^n = \chi^1 + \chi_1 S^2$ where χ^1 is the Flory parameter in the isotropic state.

Brochard's analysis predicts that the strong coupling regime (SCR) occurs at temperatures close to T_c where τ is small, and shows that the weak coupling regime (WCR) may appear at temperatures far enough from T_c for τ to be large. The main conclusions of this analysis are summarized in table I which also includes the scaling laws for the microglobules radius R .

The experimental results presented on figure 6 may be explained within the frame work of this analysis. Indeed, it is possible to identify the plateau with the SCR because a large temperature dependence of the size R of the microglobules is not theoretically expected [13] ; the low temperatures range would then correspond to the WCR where the expression of $\delta\eta_a/\eta_a$ is given

Table I. — Main results deduced from the analysis of Brochard showing a change in the coupling between the chains and the nematic solvent as the temperature decreases. χ_1 is defined in the text, N is the index of polymerization and Φ_1 indicates the concentration in monomers inside the coil : $\Phi_1 \sim Na^3/R^3$ where a is the monomer size.

	Condition on $\tau = \frac{T_c - T}{T_c}$		Coil radius R
Strong coupling regime	$\tau < \chi_1 \Phi_1$	$\tau < N^{-1}$	$R \propto N^{1/2}$
		$\tau > N^{-1}$	$R \propto N^{1/3}$
Weak coupling regime	$\tau > \chi_1 \Phi_1$		anisotropic coils

N.B. : Brochard's analysis is based on scaling law arguments, and give essentially the trends of the phenomena.

by formula 6. In that case, the sharp increase of $\delta\eta_a/\eta_a$ as the temperature decreases would reflect an increase of R_{\perp} with the order parameter. In other words the polymer coils would go to a flat disc as the temperature decreases.

The interpretation of η_c is more complicated than that for η_a because of the coupling between the director and the shear flow, which appears for this friction coefficient (see Fig. 1). However, the change in $(\eta_a - \eta_c)$ when passing from pure EBBA to the mixture (cf. Fig. 5) reinforces the idea of anisotropic coils.

The present results can be compared with previous results obtained on analogous systems by other techniques [2], i.e., thermodynamic analysis of the phase diagrams and twist viscosity γ_1 measurements.

First of all, it must be noticed that the temperature range explored in these previous studies was more restricted than in the present study, because the demixtion process in those studies occurred at a temperature higher than for the mixture used for the present ultrasonic measurements.

In the high temperature region, the thermodynamic data [3] are consistent with the strong coupling model in agreement with the ultrasonic results, and measurements of the twist viscosity γ_1 [2] show an increase of that coefficient. However, the interpretation for $\delta\gamma_1$ is not as easy as for $\delta\eta_a$; in fact, in this situation of microglobules, the $\delta\gamma_1$ effect may be related to relaxation processes of the defects appearing in the boundary zone around the isotropic droplets.

5. Conclusion.

The ultrasonic method has revealed an important effect of polymer coils on the dissipative properties of the nematic solvent, even in the dilute regime. These new measurements confirm previous results obtained on twist viscosity measurements by means of a quite different method [2].

Measuring the two viscosity coefficients η_a and η_c , has shown that the anisotropy of the hydrodynamic properties is modified by the presence of polymer coils. Moreover, a strong effect of temperature has been observed, the viscosity coefficients varying much more rapidly than the classical Arrhenian dependence. Confronting the whole of the results with different theoretical models, it can be concluded that they are consistent in the high temperature range with the « strong coupling model » [12], reinforcing the conclusions obtained from thermodynamic data. Due to the larger explored temperature range, this ultrasonic investigation has revealed a cross-over with temperature between two different situations for the polymer chains. The analysis of the data on the basis of F. Brochard's model indicates a disc-like conformation perpendicular to the nematic director. These conclusions on the size and the shape of the polymeric coils obtained here by macroscopic measurements are conjectural and would deserve to be verified by a microscopic investigation such as small angle neutron scattering.

Acknowledgments.

We would like to thank F. Brochard for the fruitful discussions that we have had in the course of this study.

References

- [1] KRONBERG, B., BASSIGNANA, I. and PATTERSON, D., *J. Chem. Phys.* **82** (1978) 1714.
 - [2] DUBAULT, A., Thesis, Paris (1981).
 - [3] DUBAULT, A., CASAGRANDE, C. and VEYSSIE, M., *Mol. Cryst. Liq. Cryst. Lett.* **72** (1982) 189.
 - [4] MARTINOTY, P. and CANDAU, S., *Mol. Cryst. Liq. Cryst.* **14** (1971) 243.
- KIRY, F. and MARTINOTY, P., *J. Physique* **38** (1977) 153.

- [5] See, for example, HERZFELD, K. F. and LITOVITZ, A., *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, London) 1965.
- [6] THIRIET, Y. and MARTINOTY, P., *J. Physique Lett.* **43** (1982) L-137.
- [7] See, for example, DE GENNES, P. G., *The Physics of Liquid Crystals* (Clarendon, Oxford) 1974.
- [8] The ratio $R_L^2/\rho\pi f$ is frequency-independent in the range 5-85 MHz and the values of $R_L^2/\rho\pi f$ for geometry c are similar to those measured in capillary flow.
- [9] Studies as a function of frequency are currently underway to test this point.
- [10] See, for example, BIRD, R. B. HASSAGER, O. ARMSTRONG, R. C. and CURTISS, C. F., *Dynamics of Polymeric Liquid, vol. II, Kinetic Theory* (Wiley) 1977.
- [11] BROCHARD, F., *J. Polym. Sc. Phys.* **17** (1979) 1367.
- [12] BROCHARD, F., *C. R. Hebd. Séan. Acad. Sci.* **290 B** (1980) 485.
- [13] $R \sim T^{1/4}$ for $\tau < N^{-1}$; $R \sim T^{1/6} \tau^{-1/6}$ for $\tau > N^{-1}$ (see Ref. 12).
-