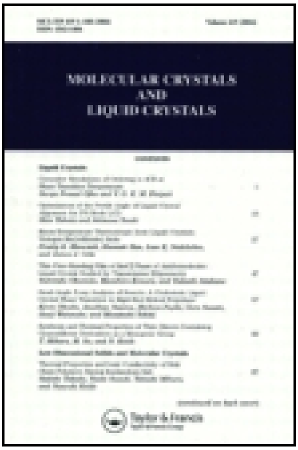

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The Twist Viscosity Coefficient of A Main-Chain Nematic Polymer: Temperature and Molecular Mass Dependences

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THE TWIST VISCOSITY COEFFICIENT OF A MAIN-CHAIN NEMATIC POLYMER : TEMPERATURE AND MOLECULAR MASS DEPENDENCES

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Abstract Measurements of the twist viscosity coefficient of the main-chain nematic polymer poly (4,4' dioxy 2,2' dimethyl azoxybenzene nonanediyl) are reported. Temperature and mass dependences are studied in detail and analyzed in terms of existing theories. This viscosity scales as the square of the order parameter. The temperature dependence is found to be the same, for different molecular masses. The process is either purely activated or free volume controlled with a rather low "freezing" temperature of the director. For the mass dependence, a power law is observed. The mean value (~ 4-5) of the exponent suggests a behaviour intermediate between those of rod-like and entangled flexible polymers. Two regimes with different exponents can however not be excluded.

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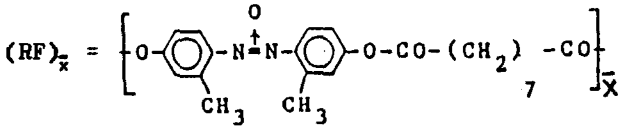
INTRODUCTION

In recent years, the viscoelastic properties of liquid crystalline polymers (PLC) have been the subject of several theoretical investigations [1-3,19]. These materials exhibit rheological and hydrodynamical behaviours which are complex combinations of properties of low molecular mass (LMM) liquid crystals and of conventional polymers. To describe the hydrodynamics of LMM nematics through the Ericksen-Leslie-Parodi (ELP) theory, five independent viscosity coefficients are required [4-6] . Among these coefficients, the twist viscosity γ_1 is of great theoretical and practical interest. In the field of LMM nematics, numerous works [7-14] have been done in order to understand the temperature dependence of this coefficient. For PLC, large values of γ_1 have been observed [15-18] and a strong dependence on chain length is predicted [2, 3, 19]. In this paper, we present systematic NMR measurements of γ_1 on poly-(4,4' dioxy 2,2' dimethyl azoxybenzene nonanediyl), a main-chain thermotropic nematic polyester usually labelled AZA9 [20], over a wide range of temperatures and molecular masses. The results are discussed in terms of the existing theories.

MATERIALS AND METHODS

Polymers AZA9 whose chemical formula is :



are based on regularly alternating rigid mesogens (R) and flexible spacers (F) [20]. They are characterized by a relatively low clearing temperature (<150°C) and a broad nematic range ($\sim$ 50°C). Seven samples of different molecular masses have been studied. The polymers are slightly polydisperse ($M_w/M_n \simeq 1.2$-1.3) and exhibit a nematic plus isotropic (N+I) biphasic domain whose width is $\sim$ 7-8°C. Sample 1 is a LMM model compound of these polymers of the form RFR (siamese twin) labelled 9AZA9 [33]. The molecular masses of the polymers were determined by gel permeation chromatography (GPC) and viscosimetric measurements. Both methods yield consistent results. The clearing temperature T_{NI} , the solidification temperature T_s and the glass transition temperature T_g were deduced from differential scanning calorimetry (DSC). All these data are collected in Table 1

TABLE 1 Physical data for polymers AZA9

sample	$\bar{M}n$	$\bar{x}$	T_{NI}(K)	T_S(K)	T_g(K)
1	696	1.6	358	301	260
2	3100	7.5	408	333	281
3	3700	9.0	409	343	283
4	4800	11.7	417	348	284
5	7300	17.8	425	353	285
6	9700	23.6	426	353	286
7	15100	36.8	428	359	287

The measurements of γ_1 were performed by proton NMR (Brucker CXP90 spectrometer). The samples were degased and sealed under vacuum in standard 5mm diameter NMR tubes. Uniformely aligned samples were prepared by equilibrating at $\sim$ 20°C above T_{NI} during $\sim$ 20 minutes and cooling in the nematic phase at the required temperature, in the magnetic field of the spectrometer. The corresponding PMR spectrum is relatively well resolved (cf. fig. 1).

The main splitting δ_0 is related to the usual nematic order parameter S by the relation :

$$\delta_0 / \text{KHz} = K.S \qquad (1)$$

with K = 24.08 [21].

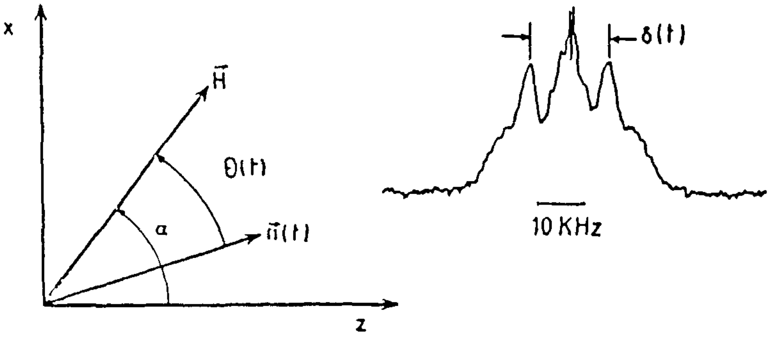


FIGURE 1. PMR spectrum of AZA9. Measurement of the splitting δ as a function of time allows to follow the reorientation of the nematic director.

Fig. 2 shows the temperature dependence of δ_0 and of the corresponding value of S deduced from Eq.(1), in the pure nematic phase of sample 2.

At t = 0, the sample is suddenly rotated at an angle α to the magnetic field. For t > 0, the nematic director relaxes back to equilibrium. This relaxation is followed by recording the PMR spectra as a function of time. This method is limited at short times by the data acquisition process of our instrument. In practice, the minimum time between two successive recorded spectra being ~ 0.5 s, the smallest values of relaxation times which can be measured correspond to a few seconds.

In ref. [17], we showed that this relaxation is qualitatively different for initial angles α smaller or larger than $\pi/4$.

(i) for $\alpha < \pi/4$, the initially homogeneous configuration of the director field is not disturbed.

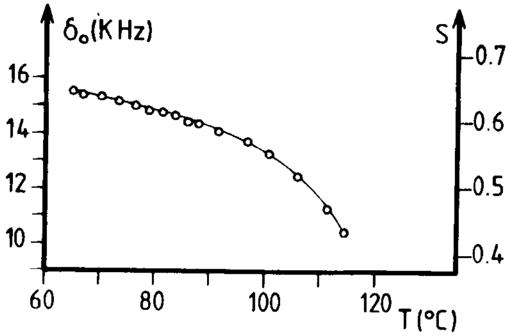


FIGURE 2. Main splitting δ_o and order parameter S of sample 2 in the pure nematic phase.

Neglecting the inertial term, the balance between viscous and magnetic torques leads to the following equation :

$$\gamma_1 \frac{d\theta}{dt} + \frac{1}{2} \chi_a H^2 \sin(2\theta) = 0 \qquad (2)$$

whose solution is

$$\tan \theta(t) = \tan (\alpha)\, e^{-t/\tau_o} \qquad (3)$$

$$\text{with } \tau_o = \gamma_1/\chi_a H^2 \qquad (4)$$

In these equations, $\theta(t)$ specifies the instantaneous director orientation relative to the magnetic field (fig. 1) and χ_a is the anisotropy of diamagnetic susceptibility per unit volume of the polymer.

(ii) when $\alpha \sim \frac{\pi}{2}$, an homogeneous reorientation does not occur. A periodic transient distorsion of the director field with accompanying backflow is induced and the relaxation process involves four out of the five viscosities through a θ-dependent effective viscosity which is (much) smaller than γ_1 [17,22].

The experiments were performed with $\alpha \simeq 30°$ in order to avoid this phenomenon. The results concerning the other coefficients deduced from the π/2 experiments will be discussed elsewhere [23]. For $\alpha<\pi/4$, the angles $\theta(t)$ are obtained from the observed main splitting $\delta(t)$ of the PMR spectrum via the simple relation :

$$\delta(t) = P_2 \; (\cos \theta(t)) \; \delta_o \qquad (5)$$

where P_2 is the second Legendre polynomial. The relaxation times τ_o is deduced by fitting Eq.(3) to these data. Fig. 3 shows two typical experimental relaxation curves and the corresponding best fits of Eq. (3) taking τ_o as single adjustable parameter. The accuracy on the value of τ_o is estimated to be better than 10 %.

The anisotropy of diamagnetic susceptibility χ_a of the polymers have been evaluated by comparison with the anisotropy of diamagnetic susceptibility of the model compound 9AZA9 (sample 1) which was measured using a SQUID magnetometer working at 4T [32]. Assuming that χ_a is proportional to the order parameter S, the final result can be written :

$$\chi_a(\text{cgs}) = (5.9 \mp 0.2) \times 10^{-9} \rho(\text{g/cm}^3)\delta_o(\text{KHz}) \; f_N \qquad (6)$$

where ρ is the volumic mass of the polymer and f_N is the nematic fraction in the N + I biphase ($f_N = 1$ in the N phase). For the present study, δ_o and f_N where deduced from the NMR spectra and ρ was assumed to be equal to 1 g/cm^3 . Density measurements have indeed not been performed on this system, but its value is expected to be near one and weakly temperature dependent in the nematic phase.

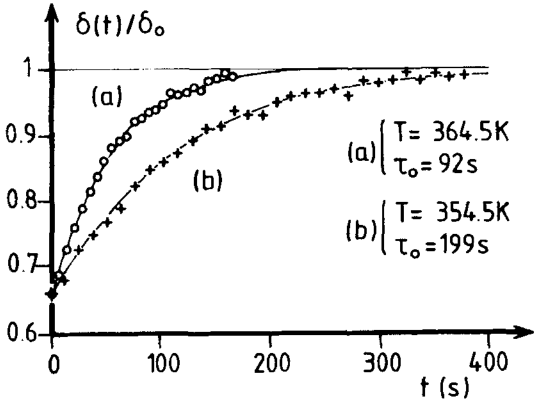


FIGURE 3. Typical relaxation curves and corresponding best fits of Eq.(3) (Sample 2).

RESULTS AND ANALYSIS

Fig. 4 collects all the results concerning the characteristic times τ_0 measured for the seven AZA9 samples. It is observed that these times are larger by several order of magnitudes than those of analogous LMM nematics ($\tau_0 \approx 10^{-3}$ s at T = 393 K for PAA [24]) and they drastically increase by reducing the temperature and/or increasing the molecular mass.

Temperature dependence

This dependence can be analyzed in terms of several models. It has been proposed [7-14] that γ_1 can be described by an equation of the form :

$$\gamma_1 = f(S).g(T) \qquad (7)$$

where f(S) scales like S^α and where g(T) is either constant [10, 12] or an exponential function of temperature with no [7, 8] or only a weak function of S [9]. Two specific forms have been proposed for this function. The first one is based on the activation energy concept, the other one on the free volume model. In the first case, an Arrhenian dependence of the viscosity coefficient is expected :

$$\gamma_1 = A\, S^{\alpha} \exp(W_{\alpha}/T) \tag{8}$$

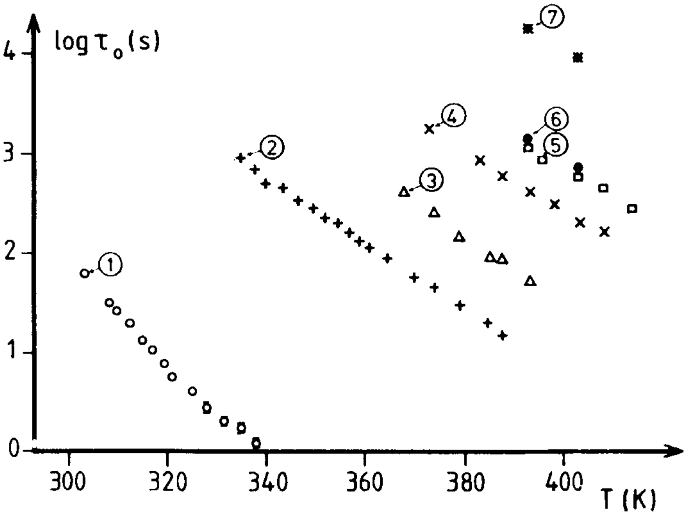


FIGURE 4. Relaxation times τ_0 versus temperature for the seven AZA9 samples described in Table 1.

Such a model has been currently employed for LMM nematics [7]. In case of the free volume model, the reorientation process, which can be described as jumps in free holes of the medium, appears as a cooperative process. These ideas have been developped for usual polymeric systems [25] and conventional nematic liquid crystals [8,14]. The expression of the viscosity can then be written through the Vogel equation :

$$\gamma_1 = B\ S^{\alpha}\ \exp(E_{\alpha}/T-T_o) \qquad (9)$$

where T_o may be understood as the temperature of motional freezing of the nematic director. It has also been proposed that the temperature dependence of γ_1 could be a combination of the Arrhenian and free volume processes [9,26].

Concerning the value of the exponent α, Prost et al [7] proposed $\alpha = 1$ for LMM nematics. The more recent work of Kneppe et al [8] shows that, in some cases, $\alpha = 1$ does not hold near the clearing point and proposed $\alpha = 2$. From theoretical considerations, Martins et Diogo showed that α is necessarily 2 and that the activation energy W_2 in Eq(8) is proportional to S [9]. Later, the same authors modified their model in adding a free volume term where E_{α} is proportional to S^2 [26]. When the experimental temperature range is relatively narrow and/or T_o is sufficiently small, a local approximation of Eq(9) can then be written :

$$\gamma_1 \approx B\ S^{\alpha}\ \exp(\varepsilon_{\alpha}/T) \qquad (10)$$

where ε_{α} is an effective activation energy. This equation is formally identical to Eq(8), but ε_{α} is either constant [7,8] or proportional to S^2 [26].

We have compared our experimental results with these models. The values of γ_1 where deduced from the values of τ_o combining Eqs(4) and (6) with H=21.14 KG, the working magnetic field of the spectrometer. The value of S was deduced from Eq(1). We have focused our attention on sample 2 for which detailed measurements have been performed over the entire nematic range.

Fig. 5 shows Ln (γ_1/S^{α}) (resp. $\alpha = 1$ and $\alpha = 2$) versus $10^3/T$. A first analysis of these data can be in terms of Eq.(8) with $\alpha = 1$ and $\alpha = 2$; good fits are obtained in both cases within experimental accuracy with values of activation energies $W_1 = 19.9 \pm 1.4$ and $W_2 = 18.0 \pm 1.4$ Kcal./mole. This situation is not satisfactory however, since such result implies that we

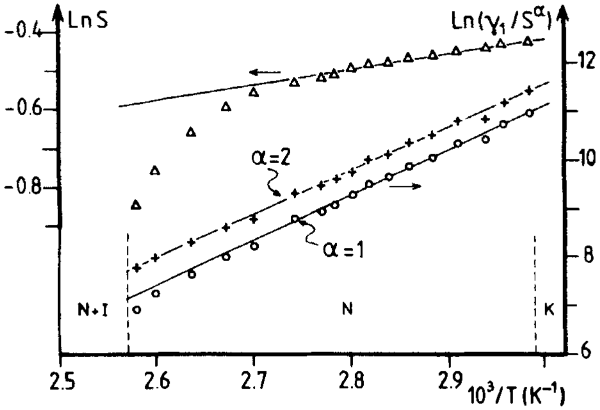


FIGURE 5 : Right hand scale : Ln (γ_1/S^α) $(\alpha = 1, 2)$ versus $10^3/T$ for sample 2. The solid lines are the best fits of Eq.(8) to the low temperature data points, with $W_1 = 18.4$ and $W_2 = 17.8$ Kcal/mole ; left hand scale : Ln S versus $10^3/T$. The solid line is the best fit of Eq.(3) to the data points in the same low temperature range (γ_1 in Poise).

have simultaneously :

$$\text{Ln}\ (\gamma_1/S) = A_1 + W_1/T \tag{11}$$

and

$$\text{Ln}\ (\gamma_1/S^2) = A_2 + W_2/T \tag{12}$$

Combining these two equations, we obtain :

$$\text{Ln}\ S = (A_1 - A_2) + (W_1 - W_2)/T \tag{13}$$

which implies that Ln S is also a linear function of

$10^3/T$. Fig.5 shows that such result holds only in the low temperature domain, i.e far enough from the region associated with the N-I transition. Consequently the above analysis is not self-consistent if all experimental points are considered for the fits. We have repeated the analysis in terms of Eq(8) by limiting the fits to the experimental points corresponding to the low temperature range where Ln S behaves linearly with $10^3/T$. The values of activation energies which give the best fits are now $W_1 = 18.4 \pm 1.4$ and $W_2 = 17.8 \pm 1.4$ Kcal/mole. The quantity $W_1 - W_2$ is consistent with the value deduced from the temperature dependence of S. (~ 0.8 Kcal/mole : fig.5). Extrapolation at high temperature shows that only the case $\alpha = 2$ predicts the correct experimental values whereas the case $\alpha = 1$ exhibits a weak but significant deviation. From this analysis, we can thus conclude that the twist viscosity of our polymeric system more probably scales like S^2 , as for the low molecular mass nematics studied by Kneppe et al [8] and in agreement with the predictions of Helfrich [10] and Martins and Diogo [9].

Analysis of the same data in terms of Eq(9) which introduces the freezing temperature T_o can be made. The case $T_o = 0$ coincides with Eq(8). For $T_o \neq 0$,fits of comparable qualities are obtained for T_o ranging between 0 and ~ 160 K, for values of E_2 ranging between 17.8 and 5.6 Kcal/mole respectively.

Finally we have considered the model described by Eq(9) in which the activation energy E_2 is proportional to S^2 [9] :

$$E_2 = E_2^0 \, S^2 \tag{14}$$

Fig.6 shows Ln (γ_1/S^2) versus $10^3 S^2/T$ and, at variance with what found in the preceding cases, a significant curvature is observed. The best fit of Eq(9) taking into account Eq(14) is obtained for E_2^0 = 1.7 ± 0.2 Kcal/mole and T_0 = 266 ± 7 K.

To summarize the results concerning sample 2, (i) the order parameter dependence of γ_1 is better described by the case α = 2. (ii) the temperature dependence is either Arrhenian (T_0 = 0) or of the free volume type with T_0 rather small ($\leqslant$ 160 K) if the activation energy is assumed to be independant of S, or only of the free volume type with a larger value of T_0 ($\approx$ 266 K) if the activation energy is assumed to be proportional to S^2.

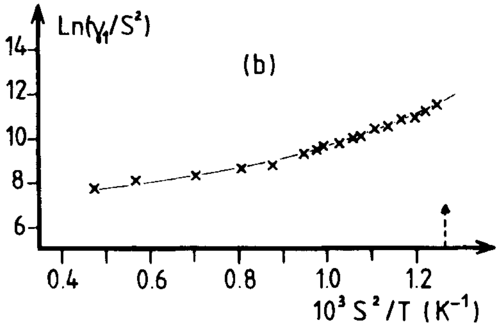


FIGURE 6 : Ln (γ_1/S^2) versus $10^3S^2/T$ for sample 2. The solid line is the best fit of Eq.(9) with $E_2 = E_2^0 S^2$, obtained with E_2^0 = 1.7 Kcal/mole and T_0 = 266 K (γ_1 in Poise)

It is thus not possible to discriminate between these models on the basis of the quality of the fits only. It should be noted however, that the third model extended by Diogo and Martins [26] to the other viscosity coefficients predicts that the ordinary viscosity α_4 is independent of temperature in the isotropic phase where S = 0 . In this system, such result does not hold [27] suggesting that this last model should be rejected.

The above analysis has been repeated for all samples studied. Very similar results are obtained for the polymeric samples 2-7. In an Arrhenian analysis, it is found that the same value of W_2 = 17.8 Kcal/mole can be chosen to describe all the data within experimental accuracy (Fig.7). Thus W_2 does not depend on the chain length. Similar results were obtained for the ordinary viscosity coefficient of conventional polymers [29] and recently for side-chain nematic polymers [30].

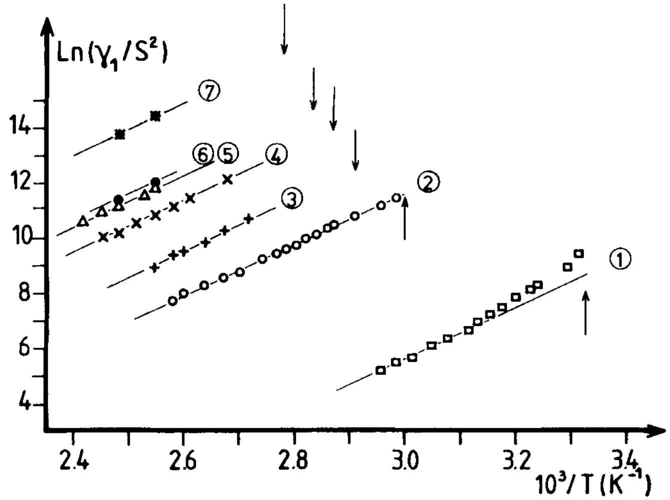


FIGURE 7. Ln (γ_1/S^2) versus temperature for samples 1-7. The solid lines are calculated from Eq.(8) with W_2= 17.8 Kcal/mole. The arrows indicate the nematic to solid transition temperatures. (γ_1 in Poise).

For the model compound (sample 1), analysis in terms of Eq(8) shows a significant deviation from linearity at low temperature implying that T_o is necessarily non-zero. The best fit of Eq(9) to these data taking E_2 and T_o as adjustable parameters, gives E_2 = 3.1 ± 0.5 Kcal/mole and T_o = 200 ± 10 K. This value of T_o is comparable to that obtained by Kneppe et al [8] for conventional nematics. Moreover, according to the W.L.F. model [25] applied to the conventional flexible polymers for ordinary viscosity or extended to the LMM nematics for γ_1 [14], the dominant parameter which controls viscosity above the glass transition is the glass temperature T_g via $T_o \sim T_g - 50$ K [14,25]. Such analysis holds for the model compound since, in this system, T_g is ≈ 260 K. giving $T_g - T_o \approx 60 \pm 10$ K.

For the polymers (samples 2-7) , the situation is different because T_g is higher (∼ 280 K) whereas the maximum possible value of T_o is lower (∼ 160 K). The difference $T_g - T_o$ is ⩾ 120 K, that is significantly larger than the 50 K of the LMM nematics. A similar situation has been found for side-chain polymers [28].

Molecular mass dependence

The molecular mass dependence of viscosity coefficients, particularly γ_1 has been the subject of several theoretical predictions [2, 3, 31]. A general expression of the form :

$$\gamma_1 = k\,M^{\beta} \tag{15}$$

is expected, where β differs according to the nature of the polymer (flexible, semi-rigid, rodlike) and to the topological constraints (with or without entanglements, with or without hairpins) which controls the viscous dynamics of the system.

For flexible polymers, using a reptation argument, de Gennes [3] predicts $\beta = 3$ when entanglements dominate. For semi-rigid polymers, Meyer [2] and de Gennes [3] predict $\beta = 2$ when the chains are fully extended in the melt. When hairpins are present, the anisotropies are less spectacular and de Gennes predicts $\beta = 1$. Finally for rigid rods, using a model of hindered rotation, Kuzuu and Doi [31] predict $\beta = 6$.

For the present system, the above results concerning the temperature dependence suggest that the mass dependence of γ_1/S^2 should be studied at constant absolute temperature.

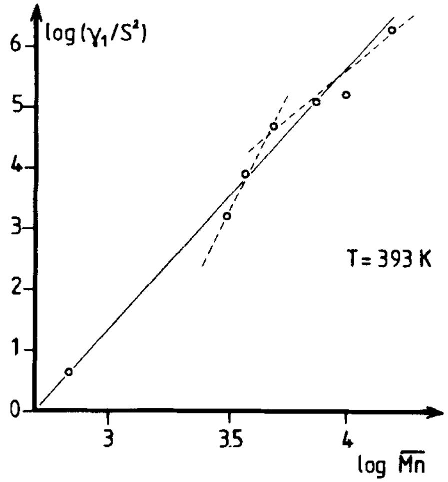


FIGURE 8. γ_1/S^2 versus molecular mass M_n in a log-log plot at constant absolute temperature T = 393 K. The solid line is the best fit of Eq.(15) with β = 4.7 . The dashed lines illustrate the possible existence of two regimes with $\beta > 7$ for $M_n < 5000$ and $\beta < 4$ for $M_n > 5000$. (γ_1 in Poise)

It is observed in Fig.8 that, in a first approximation, the plot can be considered as linear despite the fact that the experimental points are relatively scattered, due essentially to the uncertainty on the values of the molecular masses of the various samples. The exponent β is found to be 4.7 ± 0.3, a value which is predicted by none of the above mentionned theories, but which is intermediate between the rodlike and the entangled flexible polymer regimes.

However, if we except the point corresponding to the sample 1 whose polymeric character can be contested , the existence of two regimes can not be excluded for the following reason. DSC and NMR measurements show that a change in behaviour is observed for a critical molecular mass M_n^c around ~ 5000. Below this mass, both the enthalpy of transition and the order parameters at constant reduced temperature increase with the mass ; above M_n^c, they are essentially constant, which means that the true polymeric regime is reached. If this critical mass is also relevant to the viscosity problem, then it is seen that for $M_n < M_n^c$, the exponent β is larger than ~ 5, indicating a tendency for short polymers (oligomers) to behave rather as rigid rods. For $M_n > M_n^c$ on the contrary, β is smaller than ~ 4, suggesting a behaviour similar to that of entangled flexible polymers. This second interpretation in terms of two regimes is by this time only speculative and can be particularly affected by the polydispersity of the samples. More data are required for a larger number of polymer samples with well characterized molecular masses before a more definite conclusion can be drawn. Such study is underway in our laboratories.

CONCLUDING REMARKS.

The main result which emerges from this study is that in this series of main-chain nematic polymers, the physical processes which govern the twist viscosity are probably the same as in low molecular mass nematics. The relaxation mechanism appears to involve mainly the repeating unit. This result is suggested by the fact that the temperature dependence is the same for all samples, the polymeric character affecting only absolute values. This property is probably related to the rigid-flexible nature of the polymer. Because the spacer is flexible, each mesogenic unit interacts primarily with its lateral neighbours, as in usual nematics. The connectivity between mesogens only favors nematic ordering by reducing the orientational fluctuations and increases relaxation times.

The study of the model compound has allowed to deduce values of the activation energy E_2 and of the freezing temperature of the director T_o which are comparable to those of usual nematics. The situation for the polymers is different : E_2 appears to be higher and T_o is lower. The value of the exponent found for the molecular mass dependence suggests that these polymers, or at least the longest ones are entangled in the nematic phase.

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REFERENCES

1. G. Marruci, Pure & Appl. Chem., 57, 1545, (1985)
2. R.B. Meyer, In Polymer Liquid Crystals ed. by A. Cifferi, W.R. Krigbaum and R.B. Meyer ,Academic N.Y. (1982) Chap.6
3. P.G. de Gennes, Ibid Chap. 5
4. F.M. Leslie, Arch. Rat. Mech. Anal., 28, 265, (1968)
5. J.L. Ericksen, Physics Fluids, 9, 1205, (1966)
6. O. Parodi, J. Physique, 31, 581, (1970)
7. J. Prost, G. Sigaud and B. Regaya, J. Physique (Lettres), 37, L341, (1976)
8. H. Kneppe, F. Schneider and N.K. Sharma, J. Chem. Phys., 77, 3204, (1982)
9. A.F. Martins and A.C. Diogo, Port. Phys., 9, 129, (1975)
10. W. Helfrich, J. Chem. Phys., 56, 3187, (1972)
11. S. Hess, Z. Naturforschg., 30-a, 1224, (1975)
12. H. Imura and K. Okano, Jap. Appl. Phys., 11, 1440, (1972)
13. F.J. Bock, H. Kneppe and F. Schneider, Liquid

Crystals,1, 239, (1986)

14. Hp. Schad and H.R. Zeller, Phys. Rev.A, 26, 2940, (1982)
15. J.S. Moore and S.I. Stupp, Macromolecules, 20, 282, (1987)
16. S. Zheng-Min and M. Kleman, Mol. Cryst. Liq. Cryst. 111, 321, (1984)
17. A.F. Martins, P. Esnault and F. Volino, Phys. Rev. Lett., 57,1745, (1986)
18. J.M. Gilli, P. Sixou and A. Blumstein, J. Polym. Science; Polym. Lett. Ed. 23, 379, (1985)
19. M. Doi, J. Polym. Science; Polym. Phys. Ed., 19, 229, (1981)
20. A. Blumstein and S. Vilasagar, Mol. Cryst. Liq. Cryst. 72, 1, (1981)
21. F. Volino and R.B. Blumstein, Mol. Cryst. Liq. Cryst. 113, 147, (1984)
22. To be published
23. To be published
24. Orsay Liquid Crystal Group , Mol. Cryst. Liq. Cryst., 13, 187 (1971)
25. J.D. Ferry, Viscoelastic Properties of Polymers, Wiley N.Y.;(1980)
26. A.C. Diogo and A.F. Martins, J. Physique, 43, 779, (1982); Mol. Cryst. Liq. Cryst., 66, 133,(1981)
27. A. Blumstein, O. Thomas and S. Kumar, J. Polym. Science; Polym. Phys. Ed., 24, 27, (1986)
28. P. Fabre, Thesis Orsay, (1986)
29. G.V. Vinogradov and A.Y. Markin, Rheology of Polymers, Springer Verlag, (1980)
30. P. Fabre, C. Casagrande, M. Veyssié and H. Finkelman, Phys. Rev. Lett., 53, 993,(1984)
31. N.Kuzuu and M.Doi, J. Phys. Soc. Japan, 53, 1031, (1984) ; M. Doi, J. Physique, 36, 607,(1975)
32. P. Esnault, D. Galland, F. Volino and R.B.Blumstein, Proceedings of the 6th International Symposium on Liquid Crystals and Ordered Fluids, ACS National Meeting (New Orleans, 1987), Mol. Cryst. Liq. Cryst.,

(to be published)

33. R.B. Blumstein, M.D. Poliks, E.N. Stickles, A. Blumstein and F. Volino, Mol. Cryst. Liq. Cryst., 129, 375 (1985)