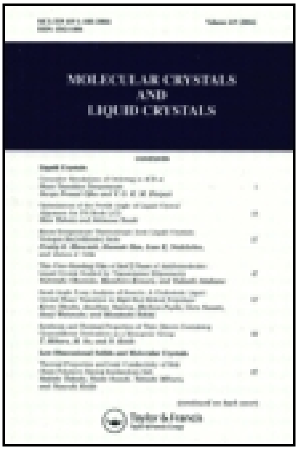

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Nematic Solutions of Side Chain Nematic Polymers; A Viscoelastic Study

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Nematic Solutions of Side Chain Nematic Polymers; A Viscoelastic Study†

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We have studied, by analogy with ordinary solutions, the viscoelastic properties of nematic solutions of side chain mesomorphic polymers, for a large domain of concentrations ($0 \leq c \leq 20\%$ (w/w)). While the splay elastic coefficient K_1 stays constant as c increases to 20%, the twist viscosity coefficient which involves dynamic properties strongly increases and shows a complex behavior. These results are compared to previous results on comparable systems. They are also correlated with an independent and complementary determination of chains sizes and geometry by a SAXS.

Keywords: side chain polymers, nematic solutions, viscoelastic properties

I. INTRODUCTION

Recently there has been intensive study into the physics and chemistry of thermotropic side chain nematic polymers.[1] One possible approach for probing these systems is to study their solutions in conventional

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low molecular liquid crystal solvent, by analogy with the well-understood physics of the solutions of ordinary flexible polymers. In particular, it is well-known that the dissolution of a small quantity of polymeric chains in a solvent has a great effect on the dynamic properties of these systems, because of large volume fraction occupied by chains; and that the shear viscosity coefficient exhibits different behavior when varying the concentration, depending on the case when the chains are isolated or overlapping.[2] So one expects similar effects in the nematic solutions of nematic polymers.

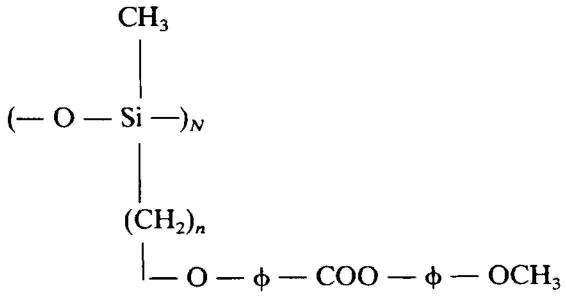
Therefore, we have measured the typically nematic twist viscosity coefficient for a larger range of polymer concentration in a conventional low molecular weight liquid crystal ($0 \leqslant c \leqslant 20\%$). The experimental set-up provides at the same time the splay elastic constant for the studied systems.

The present results are discussed by comparison with an hydrodynamical model[3] which is valid for very dilute systems; with the information we obtained on the conformation of the chains from small angle X-ray scattering study (SAXS), and with other previous results on comparable systems.

II. EXPERIMENTAL SECTION

1. Materials

The polymers we used are largely described in Refs. 4,5. They have been synthetized by H. Finkelmann. We only recall that they are derivatives of polydimethylsiloxane with the formulae:



$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad\ \ | \\ (-O-Si-)_N \\ \qquad\quad\ \ | \\ \qquad\quad (CH_2)_n \\ \qquad\quad\ \ \lfloor -O-\phi-COO-\phi-OCH_3 \end{array}$$

and are symbolized by P_N^n; n is the spacer length and N is the polymerization index. In the present study we used odd spacer lengths $n = 3$ and 5 while keeping the total chain length constant $N = 95$.

The solvent (symbolized by M) is a phenylbenzoate very similar to the mesomorphic moieties in the polymer chain, with the formulae:

$$H_{13}C_6 — O — \phi — COO — \phi — O — C_2H_5$$

We checked that M and P^n_N ($n = 3$ and 5; $N = 95$) are totally miscible in the nematic phase. We also notice that the clearing point $T_{N \to I}$ varies slightly with the concentration c in the range used for viscoelastic measurements and that the biphasic domain corresponding to the nematic to isotropic transition is narrow ($\Delta T < 2°C$). This insures a precise determination of the clearing temperature $T_{N \to I}(c)$ for the different mixtures. Moreover, we have checked that these mixtures are chemically stable and suffer no degradation when heated.

2. Experimental procedure

To deduce the twist viscosity coefficient γ_1 and the Frank elastic constant K_1, we use the classical method of studying the dynamic of a Frederickzs transition under magnetic field as described in details by Piéranski *et al.*[6] and in Reference 4. The samples, with thickness of the order of 100 μm, were oriented in the planar geometry by uniaxially rubbing the limiting surfaces. This allows us to determine, with a good accuracy K_1/χ_a and γ_1/χ_a, where K_1 and γ_1 are the coefficients introduced above. χ_a is the anisotropy of the diamagnetic susceptibility.§ We have measured γ_1/χ_a and K_1/χ_a for P^3_{95} and P^5_{95} solutions, as function of the concentration c and of the reduced temperature T_R ($T_R = T/T_{N \to I}$).

3. Experimental results

In Figure 1, we plotted the values of K_1/χ_a as a function of the reduced temperature T_R for different concentrations c. We observe that there is no systematic departure from the pure solvent values when c increases from 0 to 20%. The dispersion of the different values is within the uncertainty of the thickness measurements for different samples, which are used in the calculation of K_1/χ_a from the threshold field.

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§χ_a has been measured for several low molecular weight phenylbenzoate liquid crystals and several P^n_N polymers.[7] The conclusion of this study was that the order of magnitude and the dependency with the order parameter was very similar for all compounds. Thus we may neglect the effect of soluted polymer (at relatively low concentration values) on the χ_a behavior.

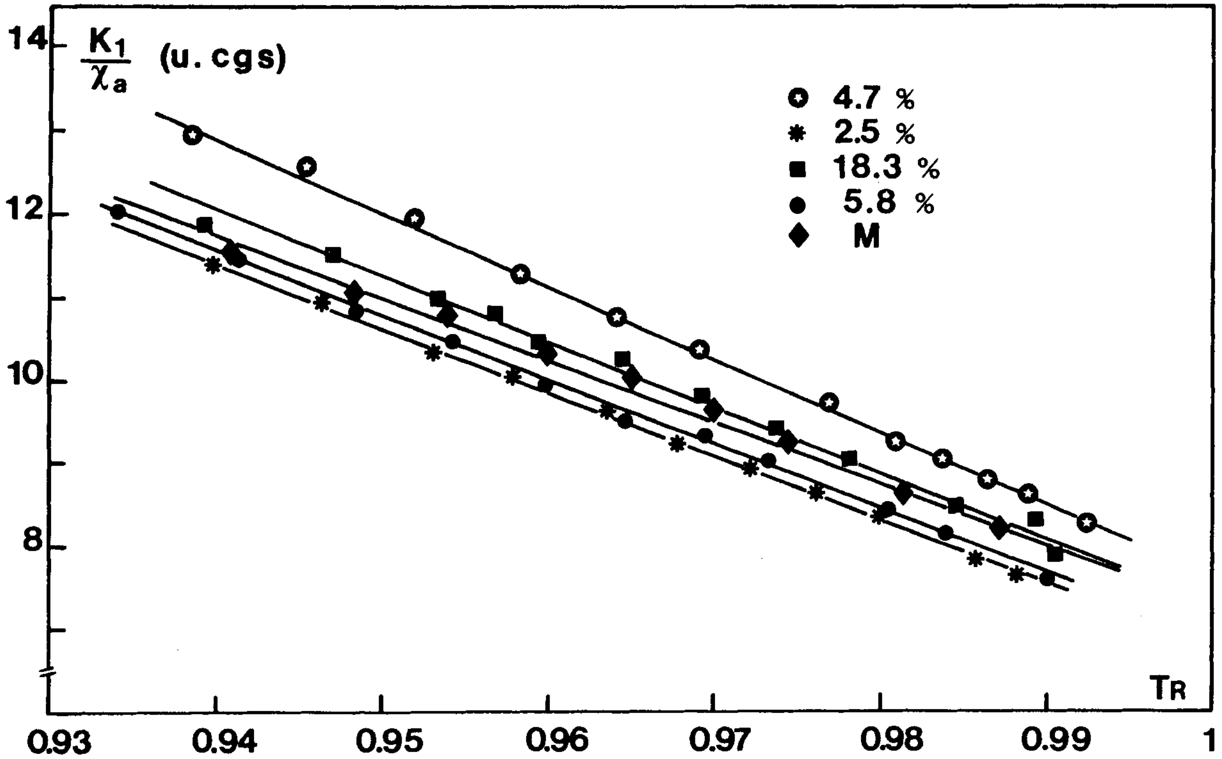

FIGURE 1 Values of the splay elastic constant K_1 versus T_R ($T_R = T/T_{N \to I}$) for different values of the concentrations c: $P_5^{95} + M$ mixtures.

In Figure 2(a,b) we represented the relative variation $\Delta\gamma_1(\phi)/\gamma_1(0)$ of the twist viscosity coefficient as a function of ϕ, number of polymeric chains per unit volume (ϕ is proportional to c). $\Delta\gamma_1(\phi)$ is defined by the difference $\gamma_1(\phi) - \gamma_1(0)$,[||] and χ_a is supposed to be independent of the concentration as discussed above. The curves for P^5_{95} and P^3_{95} solutions, as function of the concentration c and of the reduced temperature T_R are very similar.

We first notice that the viscosity coefficient strongly increases even at low concentrations. For example, $\Delta\gamma_1/\gamma_1$ reaches 90% for (P^3_{95} + M) at $T_R = 0{,}96$ and $c = 7\%$ (w/w) (this corresponds to $\phi = 12.5 \cdot 10^{17}$ ch/cm^3). Secondly, for each curve one can distinguish three regions (Figure 2a,b):

a) The first one, noted I at lower concentration values, where $\Delta\gamma_1/\gamma_1$ is proportional to ϕ (linear behavior).

b) The second one, noted II, corresponds to an inflexion in the curve. It must be emphasized that this zone is very narrow in concentration ($8\% < c < 11\%$; $13 \cdot 10^{17} < \phi < 19 \cdot 10^{17}$ ch/cm^3).

c) The last one, noted III, where the increment of the viscosity starts increasing again. In this domain, the $\Delta\gamma_1(c)/\gamma_1(0)$ data are reasonably fitted by an exponential law as it appears for a logarithmic plot on Figure 3(a,b)

$$100 \times \frac{\Delta\gamma_1(c)}{\gamma_1(0)} \simeq A\exp(\kappa c)$$

For instance, the A and κ constants are listed in the following table, for $T_R = 0.94$.

Compounds	A	κ
P^5_{95} + M	37	0, 102
P^3_{95} + M	49	0, 103

Note that the change from regime I to regime II can be clearly seen when the data are plotted as in Figure 2. This change of regime is

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[||] To be more accurate, one would consider $\Delta\gamma_1$ the difference $\gamma_1(\phi) - \bar{\gamma}_1(0)$, where $\bar{\gamma}_1(0)$ is the renormalized solvent viscosity coefficient taking into account its dependence with absolute temperature as done in Ref. 4. This correction allows comparison of γ_1 between solvent and solutions at the same value both for T and T_R. Nevertheless, in the present case, this correction is not important due to the weak variation of $T_{N\to I}$ with c. Therefore, we take directly $\Delta\gamma_1 \sim \gamma_1(c) - \gamma_1(0)$. $\gamma_1(0)$ has an Arrhenian form: $\gamma_1/\chi_a \simeq Ke^{\frac{w}{T}}$ with $w \simeq 4600$ K.

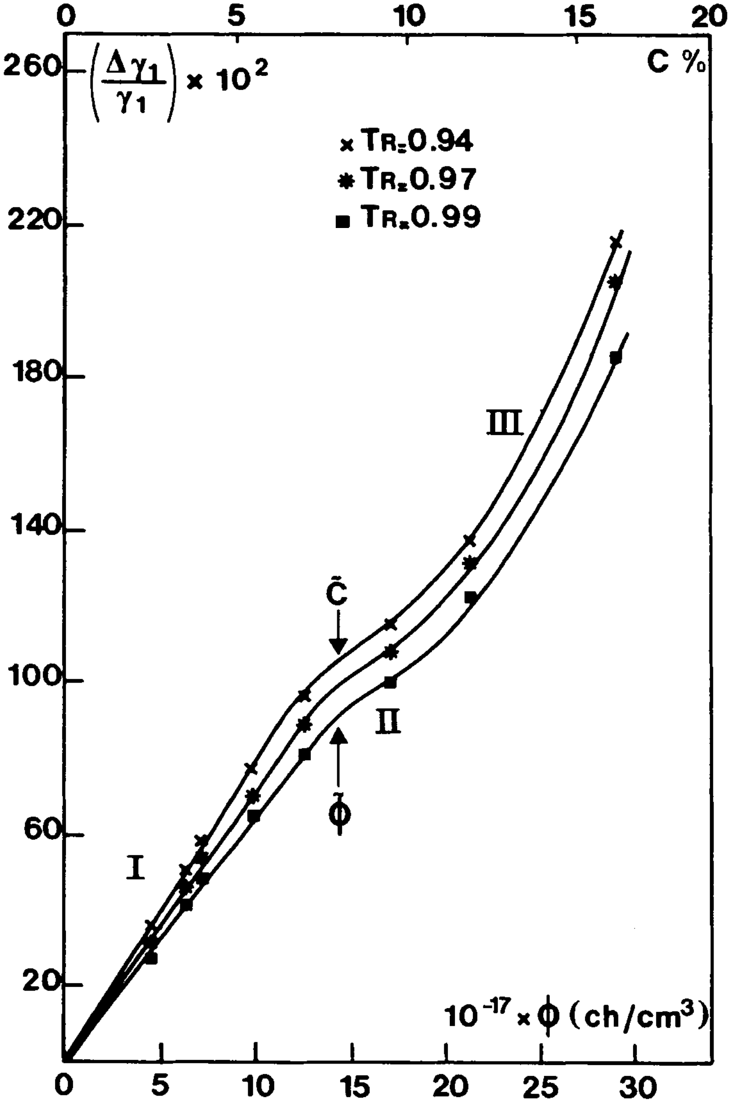

FIGURE 2 Relative viscosity increments $\Delta\gamma_1/\gamma_1$ versus concentrations; c is the concentration in weight, ϕ is the number of chains per cm^3
a) P_3^{95} + M mixtures; b) P_5^{95} + M mixtures.

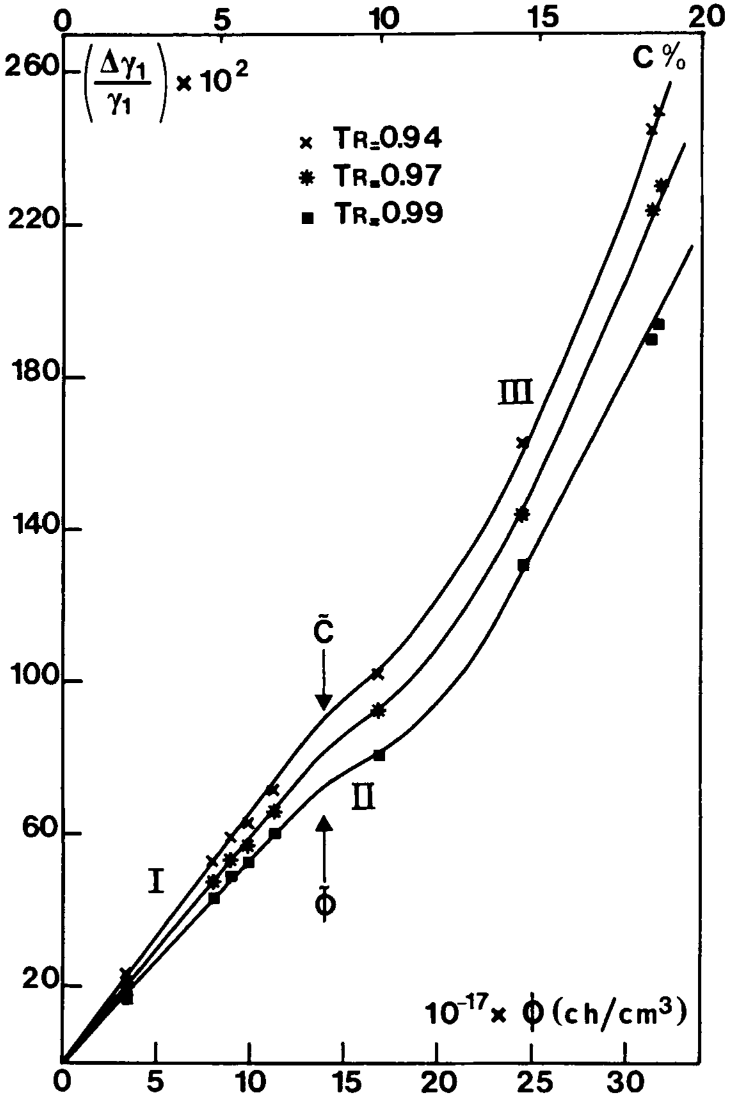

Figure 2 (*Continued*)

not obvious if one simply plots Log γ_1 vs. c, as was done by the authors of Ref. 8; this probably explains that, for similar products in the same range of concentrations, these authors had not detected this phenomenon.

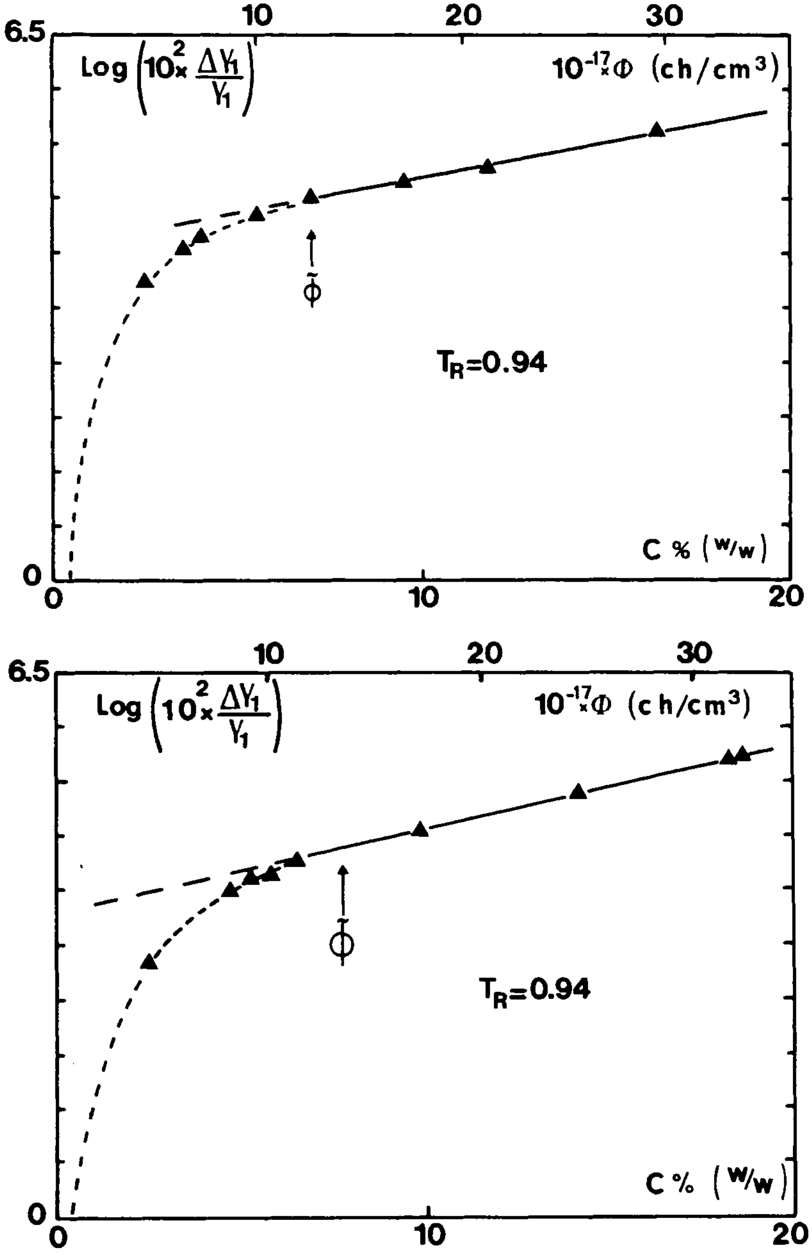

FIGURE 3 Semi-logarithmic plot of $\Delta\gamma_1/\gamma_1$ versus c. a) P_3^{95} + M mixtures; b) P_5^{95} + M mixtures.

III. DISCUSSION

1. Frank elastic constant K_1

The constancy of the splay elastic coefficient K_1 over a range of polymer concentration up to 20% is consistent with previously reported results for analogous nematic solutions[4] (polymer with even spacer $n = 4, 6$). More significantly, it is consistent with measurements for pure melts of these side chain polymers.[10] In this work it appears that the elastic constants that have been measured (K_1 and K_3) are of the same order of magnitude as in the conventional low molecular liquid crystals. It is clear that if $K_1/\chi_a(0) \simeq K_1/\chi_a$ (100%), we do not expect special effect for solutions, except eventually for pathological points in the phase diagrams. However, the present study offers supplementary information compared to the previous one. We used here *odd* values for the spacer length ($n = 3$ and 5), while the pure polymer measurements are reported only for *even* ones ($n = 4$ and 6); we thus may conclude that there is no significant effect of the spacer parity on the Frank elasticity in solutions.[¶]

2. Twist viscosity coefficient

As γ_1 is an hydrodynamical constant, we may expect that it is very sensitive to the polymer concentration, differing from the static properties. An analogy could be drawn with the classical results for polymer solutions, where small amounts of polymer are known to greatly increase the ordinar shear viscosity values: at low concentration, the swelling of the chains, which thus occupy a large volume fraction of the total volume, affects the viscosity; at higher concentration the overlapping process dominates the hydrodynamical properties.

But the equivalent situation is not obvious in the present case, where γ_1 is a typically nematic friction coefficient, just referring in principle to the rotation of the director. F. Brochard has pointed out that this director rotation may be coupled with cooperative motion of the chains if the backbone conformation was nonspherical.[3] The chain conformation has indeed to adjust itself to the director orientation, resulting in supplementary dissipative effect. It is in this frame-

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[¶] It would be interesting to determine if the elastic constant for odd spacer lengths (3 and 5) are also of the same order of magnitude as in low molecular weight liquid crystals, but till now, we do not succeed in preparing well-oriented sample for pure P_3 and P_5.

work that we discuss the three regions experimentally observed in the variation of $\Delta\gamma_1/\gamma_1$ as a function of ϕ (ϕ is proportional to c).

a) *Very dilute regime* ($0 < \phi < 13 \cdot 10^{17}$ ch/cm^3; $0 < c < 7\%$) At low concentrations where we use the simplifying hypothesis that there are no chain interactions, the Brochard model leads to an explicit expression for $\Delta\gamma_1$:[3]

$$\Delta\gamma_1 \simeq kT\phi\, \tau_R \frac{(R_\parallel^2 - R_\perp^2)^2}{R_\parallel^2 R_\perp^2} \tag{1}$$

where T is the absolute temperature, $R_\parallel$ and $R_\perp$ are the characteristic sizes of the backbone respectively parallel and perpendicular to the director ($\vec{n}$), and τ_R is the relaxational time of the chain. In the present study, we observe that there is indeed a domain where $\Delta\gamma_1$ linearly increases with ϕ (Figure 2, region I), as previously observed by C. Weill *et al.*[4] for $n = 4$ and $n = 6$. This is insufficient for a quantitative check of Eq. (1) in which both τ_R and the anisotropy function $(R_\parallel^2 - R_\perp^2)^2/R_\parallel^2 R_\perp^2$ are *a priori* unknown.

We have independently measured $R_\parallel$ and $R_\perp$ in the P_{95}^3 and P_{95}^5 polymer solutions by using the small angle X-ray scattering technique.[5] We found that there was, in fact, a significant difference in chain sizes in direction parallel and perpendicular to $\vec{n}$ (about 20%), with $R_\parallel > R_\perp$. From these measurements one can deduce the anisotropy function and using the $\Delta\gamma_1$ values reported here, we may calculate the values of characteristic time τ_R and its evolution with the reduced temperature T_R (Figure 4). Notice that the values of τ_R for this kind of polymer that we deduced here ($\tau_R \simeq 10^{-5}$ sec.) are consistent with an independent estimation obtained from a quasi-elastic light scattering experiment in a conventional isotropic solvent.[9] Notice also that τ_R obeys an Arrhenian law

$$\tau_R \simeq \tau_{R_0} \exp\left(\frac{E}{T}\right) \tag{2}$$

where the activation energy $E = 4600\ K$ is close to that relative to the pure solvent γ_1 viscosity (seen above). This is satisfying as we expect the relaxation time to vary as the viscosity of the solvent medium when $\phi \rightarrow 0$ ($C \rightarrow 0$).

We thus conclude that, in the very dilute regime the theoretical model of F. Brochard, the measured anisotropy of the backbone conformation, and the hydrodynamical properties of the solutions, are in good agreement.

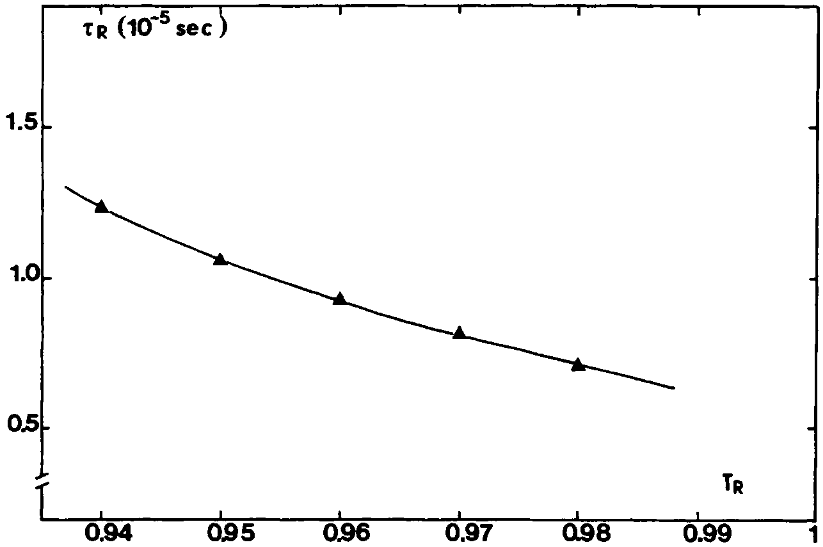

FIGURE 4 Relaxation time τ_R versus T_R in the very diluted regime (zone I in Figure 2); P_5^{95} + M mixture.

b) *Intermediary region* ($\phi \simeq 15 \cdot 10^{17}$ ch/cm; $c \simeq 8.5\%$) We previously noticed that on Figure 2, there is an "inflexion point" in the $\Delta\gamma_1/\gamma_1$ versus ϕ plot for concentration ϕ of order of $15 \cdot 10^{17}$ ch/cm^3. This intermediary regime is also evidenced on Figure 3(a,b) where it corresponds to the cross-over from the initial linear law ($\Delta\gamma_1/\gamma_1 \simeq \alpha\phi$ or $\Delta\gamma_1/\gamma_1 \simeq \alpha' c$) to the exponential one ($100 \times \Delta\gamma_1/\gamma_1 \simeq A \exp(\kappa c)$).

The $\bar{\phi}$ value may be compared to that of ϕ^*, which is used in classical theory of polymer solutions[2] to characterize the cross-over from dilute regime to semi-dilute one, when the chains start overlapping. In the present case, ϕ^* is estimated from measurements of the radius of gyration R_G by SAXS technique[5] ($\phi^* \simeq 1/(4/3)\ \pi R_G^3$). We obtain:

$$\phi^* = (24 \pm 6) \cdot 10^{17}\ \text{ch/cm}^3;\ c = (13 \pm 3)\ \%\ (w/w)\ \text{for}\ P_3^{95}$$

$$\phi^* = (13 \pm 3) \cdot 10^{17}\ \text{ch/cm}^3;\ c = (7.9 \pm 1.7)\ \%\ (w/w)\ \text{for}\ P_5^{35}$$

which in both cases is of order of magnitude of $\bar{\phi}$ in the inflexion region.

We then conclude that the anomaly in the $\Delta\gamma_1/\gamma_1(\phi)$ curve is correlated to the overlapping of the polymers backbone. A quantitative interpretation of the effect, i.e. the appearance of a narrow plateau in the $\Delta\gamma_1/\gamma_1$ evolution, would require a detailed hydrodynamical model taking into account the coupling between chains and director motion. A simple qualitative argument may be that, when the concentration increases tending to $\bar{\phi}$ the interchain interactions become important and the anisotropy of the conformation may significantly change from the one case observed for isolated objects. So this may result in a transient reduction of the γ_1 increase.

c) Region III (relatively high concentrations: $\phi \geqslant 19 \cdot 10^{17}$ ch/cm^3; $c \geqslant 11\%$) This region corresponds to relatively high values of ϕ and we observe a much more rapid increase of the twist viscosity coefficient. This is very similar to the experimentally observed variation of the shear viscosity coefficient (η) in the conventional polymer solutions. However from the theoretical point of view, it would be illusory to hope getting a model for the γ_1 coefficient evolution in this concentrations range while in the present state, there is no general description of the effect of concentrations on the ordinary viscosity in the simplest systems. Several semi-empirical laws have been proposed to interpret the numerous experimental data on η; the most largely used are the Martin equation[11]

$$\Delta\eta \simeq c \exp(\kappa\, c) \tag{4}$$

or the Cornett scaling law[12]

$$\Delta\eta \simeq \eta_s F\left(\frac{c}{[\eta]}\right) \tag{5}$$

with: $[\eta]$ is the intrinsic viscosity

We have tried, by analogy, to fit our experimental results with similar expressions; but none of them appeared appropriate. The best fit was obtained by the simple exponential law as indicated in II.3 and represented on Figure 3(a,b). It would be interesting to extend the range of concentration c, in order to determine how the twist viscosity coefficient of the concentrated solutions extrapolate to the pure melt nematic polymer.

IV. CONCLUSION

We have presented here a viscoelastic study of side chain mesomorphic polymer solutions with odd spacer length $n = 3$ and 5 in a relatively wide concentrations domain. The results obtained on the Frank elasticity are in good agreement with other previous results in solution or in melt for even spacer length ($n = 4; 6$). The viscosity behavior in the very dilute region also confirms the results obtained on even spacer compounds. Moreover, the present study has put into evidence the effect of increasing concentrations on the twist viscosity coefficient γ_1. The most striking result is the cross-over from dilute to semi-dilute regime, which is clearly shown on the $\Delta\gamma_1/\gamma_1$ (ϕ) plot. The corresponding concentration is in good agreement with an independent estimation deduced from a measurement of the radius of the chains by a small angle X-ray scattering study. We also distinguished a complex behavior for viscosity constant at the relatively high concentrations region. This may correspond to the transition from dilute to semi-dilute regime. These results were compared to other study on chain comformation independently done on these systems: SAXS.

We are currently achieving this study by performing coupled SAXS and viscoelasticity experiments on even spacer molecules. In the future, it would be interesting to carry out similar experiments on nematic solutions of main chain polymers, and compare to the present results; in particular, due to the rigidity of main chain systems, we may expect more pronounced effects on the splay elastic constant.

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References

1. *Advance in Polymer Science*, **60**, **61** (Springer-Verlag, 1984).
2. P.G. De Gennes, "*Scaling Concepts in Polymer*," (Cornell University Press, 1979), Chap. 6.
3. F. Brochard, *J. Poly. Sci.*; *Poly. Phys. Ed.*, **17**, 1367 (1979).
4. C. Weill, C. Casagrande, M. Veyssié and H. Finkelmann, *J. Physique* (Paris) **47**, 887 (1986).
5. H. Mattoussi, R. Ober, M. Veyssié and H. Finkelmann, *Europhys. Lett.*, **2**, 233 (1986).
6. P. Piéranski, F. Brochard and E. Guyon, *J. Physique* (Paris), **33**, 681 (1972). P. Piéranski, F. Brochard and E. Guyon, *J. Physique* (Paris), **34**, 35 (1973).
7. M. F. Achard, G. Sigaud, F. Hardouin, C. Weill and H. Finkelmann, *Mol. Cryst. Liq. Cryst.*, **92**, 111 (1983).
8. H. J. Coles and M. S. Sefton, *Mol. Cryst. Liq. Cryst. Lett.*, **5**, 159 (1985).
9. C. Weill, thèse troisième cycle, Paris VI (1984).

10. P. Fabre, C. Casagrande, M. Veyssié and H. Finkelmann, *Phys. Rev. Lett.*, **53**, 993 (1984).
11. W. W. Graessley, "in" *The Entanglement Concepts in Polymer Rheology*, in *Advance in Polymer Science*, **16**, Springer and Verlag edition, 1974.
12. Cornet, C. F., "*The Determination of Unperturbed Dimensions of Polymer Molecules by Viscometry of Moderately Concentrated Soltutions.*" Polymer, (London), 373–384 (1965).