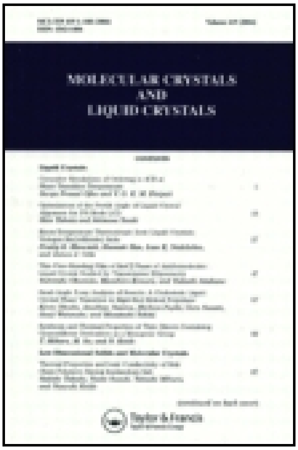

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Correlations Between Dynamic and Structural Properties of Liquid Crystal Polymers in Mesomorphic Solutions

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Correlations Between Dynamic and Structural Properties of Liquid Crystal Polymers in Mesomorphic Solutions

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Keywords: Mesomorphic Polymers, X-ray scattering, Conformational properties.

We present a combination of results from two seemingly unrelated studies undertaken on comb-like liquid crystal polymers in a low molecular weight (l.m.w.) mesomorphic solvent: rotational viscosity measurements and conformational study by X-ray scattering. The results deduced from the two experiments turn out to be intimately correlated. Moreover they provide consistent and complementary information. The explanation of viscoelastic results done in the framework of a hydrodynamic model due to F. Brochard admits the hypothesis of anisotropic macromolecules in ordered medium. The X-ray study provides us with the direction and the magnitude of the anisotropy

We indicate a regime change in the viscosity behavior at a concentration ($\bar{c}$) very close to the overlap concentration c* as deduced from size measurements in ordinary solvent. At higher concentrations the viscosity increment shows an exponential increase with c. This behavior is consistent with the viscosity behavior in pure melt systems. The close investigation of the experimental viscosity data shows that the anisotropy factor behaves like the order parameter with reduced temperature, and also suggests that the Brochard hypothesis of anisotropy of conformation is still valid at higher concentrations where the macromolecules are believed to interpenetrate.

INTRODUCTION

Studying liquid crystal polymers in nematic solutions promises to be a powerful way to learn about their physical behavior. The same operation for conventional polymers in ordinary solvents has proven to be a fruitful and strong method for understanding these systems.[1]

Thermotropic mesomorphic polymers have great application potential.[2] In fact,

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these materials have the advantage of combining two important but conflicting properties: the polymer aspect which, because of entropic considerations, will tend to give the chain a 3 dimensional extension on one hand; and on the other hand the liquid crystal aspect which will tend to induce an orientational order. Important physical and chemical studies have been devoted to these mesomorphic systems to unveil their characteristics.[2] Many structural studies by X-ray diffraction,[2] N.M.R. technique and I. R. spectroscopy,[4-5] to check the correlation between flexibility and orientational order in such materials, have been reported. In addition, small angle scattering has focused on the chain conformation in such systems.[6-9]

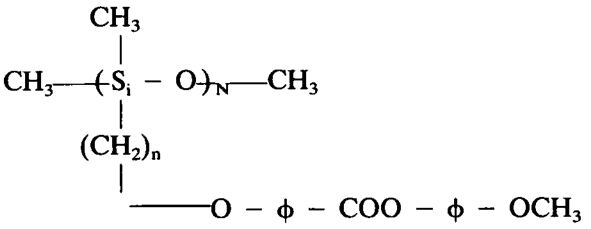
The static and dynamic aspects, even though less extensively studied, have also revealed interesting features for both systems i.e., side chain and main chain components.[10-16] This has given an insight into the understanding of the mutual influences of the polymer and nematic aspects. For instance, typical nematic rotational viscosity γ_1 has revealed a "polymer" behavior for the side chain system although the mesomorphic moieties are similar to conventional nematics.[10] However, the Frank elastic constants do not show any visible difference from those of l.m.w. liquid crystals.[10,17] Other studies, as well as some theoretical considerations, suggest that the two sets of properties (static and dynamic) are affected by the polymer aspect for the main chain case.[18-20] We have previously reported preliminary viscoelastic studies on both systems in menatic solutions.[21-23] In parallel, we have performed a structural study by small angle X-ray scattering on side chain components in nematic and ordinary solvents.[9,22]

We present in this report a combination of these two sets of data obtained from these respective measurements. We show that these two studies, a priori independent, are intimately correlated. More precisely, they provide coherent and complementary information. In fact, the viscosity data explained in the framework of a hydrodynamical model by F. Brochard admits a conformational anisotropy of the macromolecules.[28] The small angle X-ray scattering measurements provide a direct check to the degree of validity of this hypothesis. Therefore, this comparison enables us to come up with answers to the questions left by each study individually. In addition to this, the close investigation of the viscoelastic data in the high-concentration regime allows us to bridge the information deduced in the dilute regime to that for melt case. It also allows us to anticipate that the anisotropy of conformation is still valid, even if the macromolecules interpenetrate. This observation although consistent with previous and other independent works, should be checked by direct structural measurements. We start by presenting a short review of the materials and the experimental techniques. The previous and complementary results will be presented in the second section. We then discuss the correlation between them, within the framework of the Brochard model, in the third section.

II. EXPERIMENTAL SECTION

1. Materials

We used side chain polymethylsiloxane components synthesized by H. Finkelmann (W. Germany) and largely described in previous studies.[17-22] We recall here that they have the following chemical formulae:



$$CH_3-(\underset{\underset{O-\phi-COO-\phi-OCH_3}{|}}{\underset{(CH_2)_n}{\underset{|}{\overset{\overset{CH_3}{|}}{Si}}}}-O)_N-CH_3$$

They are symbolized by P_n^N where N is the degree of polymerization and n is the methylene chain length (spacer). We used N = 95 and varied n between 3 and 6. As a low molecular weight (l.m.w.) solvent we used a phenylbenzoate component similar to the pendent groups in the chains symbolized by M_2.[9,22] For the main chain case we used a copolyester component largely described in previous studies.[22,24] It has an average molecular weight $M_W \simeq 220{,}000$ and an index of polymerization $N_W \simeq 400$. It has a nematic state at high temperatures. As a solvent we used the classical component p-azoxyanisole (PAA), which has the advantage of being nematic at relatively high temperatures.

2. Experimental Techniques

For viscosity measurements, we have used the dynamics of the Fredericks transition under a magnetic field. The principles of this technique are well described in many previous studies.[17,22,25,26] We simply mention here that this technique provides us with the typical liquid crystal rotational viscosity γ_1 and the splay Frank elastic constant K_1 or the bend elastic constant K_3, depending on whether we use planar or homeotropic geometry.[25-26] A large concentration domain was scanned for side chain solutions $0 \leq c \leq 18\%$ (w/w). However for the main chain case we were limited to dilute solutions: $0 \leq c \leq 6\%$ (w/w).[23]

The small angle X-ray scattering study (S.A.X.S.) has been limited to the comb-like macromolecules, because of the absence of electronic contrast in the main chain case. The set-up characteristics are well described elsewhere.[9] This set-up allows us to scan scattering vectors in the interval $10^{-2} < q < 3.10^{-1}$ ($Å^{-1}$). We determine either $R_\parallel$ and $R_\perp$ in the nematic phase, where $R_{\parallel(\perp)}$ designates the dimension parallel or perpendicular to the nematic director ($\vec{n}_0$). For the isotropic state and for ordinary solutions, the measurements provide us with the radius of gyration in these systems. All structural studies have been done in dilute solutions.

III. RESULTS

1. Viscosity Measurements

For both systems the presence of even a small quantity of added macromolecules in solution is accompanied by a significant increase of the rotational viscosity γ_1.

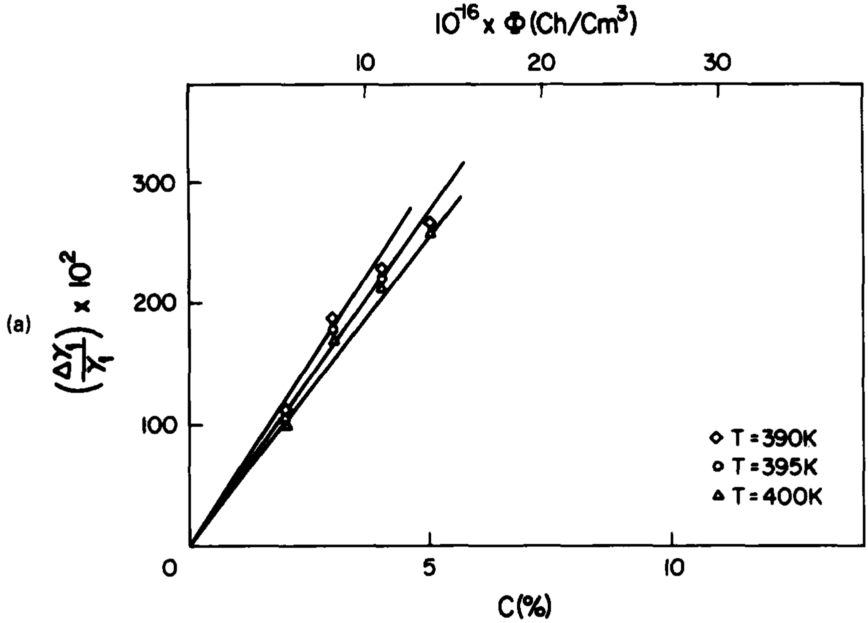


FIGURE 1 Typical relative viscosity increments $\Delta\gamma_1/\gamma_1$ versus concentrations. c is the concentration in weight (%) and Φ is the number of chains per unit volume (ch/cm^3): a) Copolyester + PAA mixture. b) $P_5 + M_2$ mixture.

To isolate a concentration (c) dependence of this increase, we plotted the experimental values of the relative viscosity increment ($\Delta\gamma_1/\gamma_1$) * versus c(Φ). This allows us to eliminate the absolute temperature (T) dependence of the viscosity increment, since γ_1 obeys an Arrhenian law in T : $\gamma_1(c) = A \exp(W/T)$,[22,23] where W is an activation energy and A is a constant.

(a) For main chain solutions (M.P.S.), the relative viscosity increment versus concentration plot shows a linear behavior. Even though limited to very dilute solutions, the viscosity increment is very important (Figure 1a).

(b) For side chain solutions (S.P.S.), a typical curve is represented in Fig. 1b.[21,22] One can distinguish three regions in this plot:

—The first region (Zone I) corresponds to a linear increase: $\Delta\gamma_1 \propto c(\Phi)$. It is limited to low concentrations $0 \leq c \leq 7\%$, $0 < \Phi < 11 \times 10^{17}$ (ch/cm^3).

—In the second region (Zone II), the viscosity increase goes through an inflection point. It is confined to a small concentration domain: $7 < c < 11\%$; $11 \times 10^{17} < \Phi < 16 \times 10^{17}$ (ch/cm^3).

—The last region (Zone III) is for high concentrations: ($c \geq 11\%$; $\Phi \geq 16 \times 10^{17}$ (ch/cm^3) where the viscosity increase is much more pronounced

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* $\frac{\Delta\gamma_1}{\gamma_1} = \frac{\gamma_1(c) - \gamma_1(0)}{\gamma_1(0)}$ and Φ is the concentration of chains per unit volume [ch/cm^3].

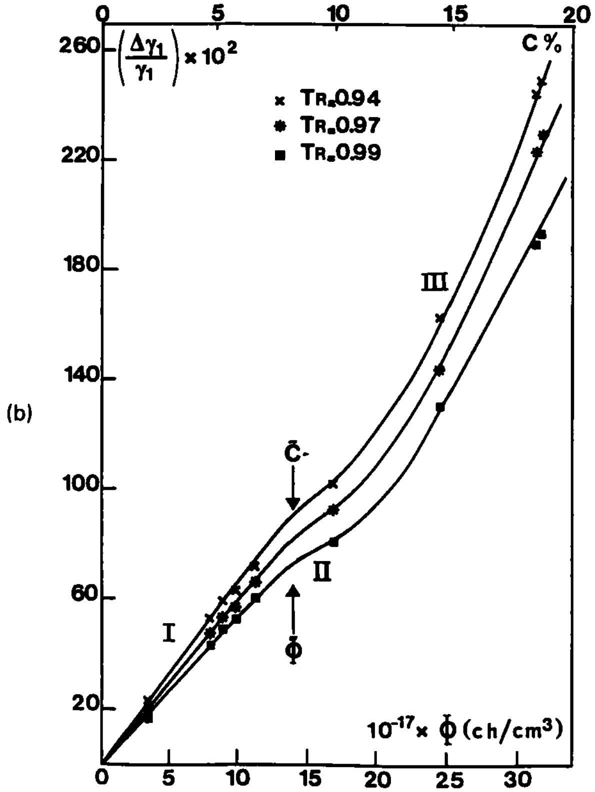

FIGURE 1 (*continued*)

than in the two previous cases. The experimental points are well described by a simple exponential law (Figure 2):

$$10^2 \times \left(\frac{\Delta\gamma_1}{\gamma_1}\right) = A \exp(\beta c) = A' \exp(\beta\Phi) \tag{1}$$

β is independent of the polymer P_n^{95} used (Table I). The net distinction between the two regimes (I and III) could also be easily pointed out on a simple viscosity increment ($\Delta\gamma_1$) versus c plot.[22]

Limiting ourselves to the linear region, we have reported the plot of $\Delta\gamma_1/\gamma_1\Phi$ versus T_R (Figure 3), where T_R designates the reduced temperature ($T_R = T/T_c(\Phi)$). The experimental data do not vary appreciably for either system: There is a continuous but weak decrease in ($\Delta\gamma_1/\gamma_1\Phi$) as T_R evolves, but still far from the clearing point for S.P.S. The data are virtually independent of T (T < Tc) for M.P.S. case (Figure 3b).

Remark: The elastic constant K_1 changes very little for S.P.S. in the range of concentrations scanned, while for M.P.S., K_1 and K_3 are largely affected by the presence of solute macromolecules.[22,23] This might reflect a difference in behavior

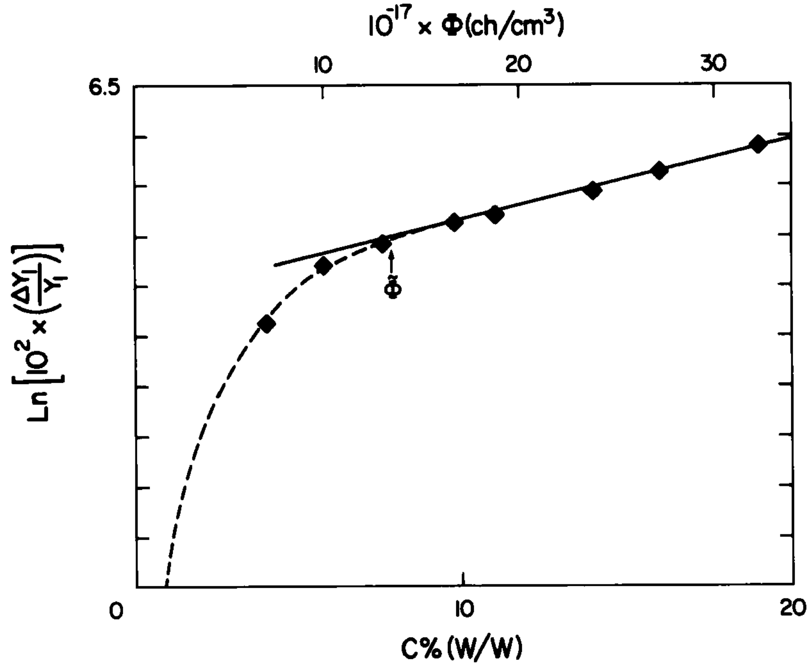

FIGURE 2 Semilogarithmic plot of the relative viscosity increment versus concentrations: $P_4 + M_2$ mixture; $T_R = 0.97$.

of the solutions, according to whether one studies static or dynamic properties of liquid crystal polymers.

2. Structural Measurements

The important findings of these measurements can be divided into two parts:

—The comb-like macromolecules have an anisotropy of conformation with $R_\parallel > R_\perp$.[9,22] The anisotropy ratio is quasi independent of the solute P_n^{95} used (n = 3; 4; 5; 6) (Figure 4). These two sizes (∥ and ⊥ to the nematic director) are weakly dependent on the reduced temperature, for $T_R < 1$.[9,22] The average sizes in the mesomorphic solvent are large compared to ordinary polymers (PDMS for instance), with similar polymerization index.[22,27] We have also always observed the inequality: $R_\perp < R_{iso} < R_\parallel$.

—In toluene the measurements have shown that the radius of gyration is concentration dependent with $R_G(c) < R_G(c = 0)$. In isotropic media the measured

TABLE I

A and β values for P_n^N components

Component	A	β
$P_3^{95} + M_2$	37	0.102
$P_4^{95} + M_2$	40	0.102
$P_5^{95} + M_2$	49	0.103

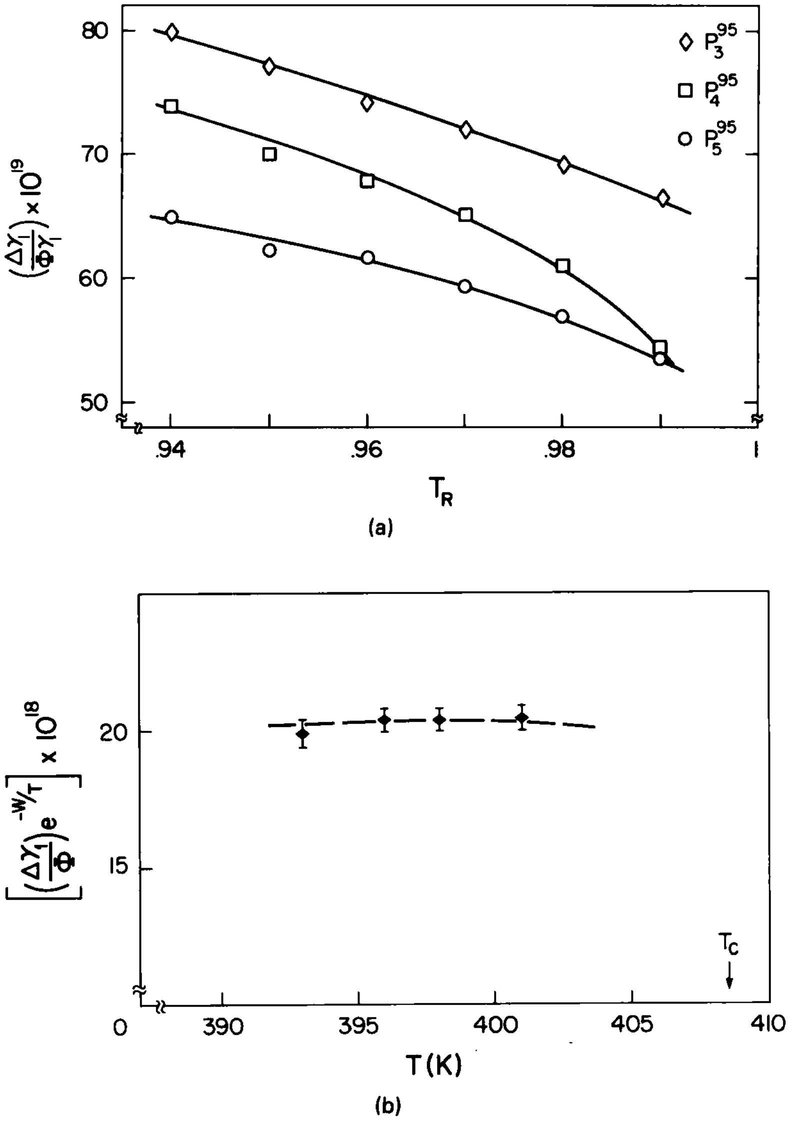

FIGURE 3 Slope of the relative viscosity increment versus reduced temperature T_R: a) P_n^{95} + M_2 mixture. b) copolyester + PPA mixture.

radius of gyration is similar at finite concentration, in both solvents. For instance, we have:

$$R_i \simeq 45\ \text{Å for } P_3^{95} \text{ at } c \simeq 5\%$$

The interactions between solute chains, as evidenced by concentration dependent sizes, could explain the fluctuations in the absolute dimensions $R_\parallel$, $R_\perp$ and R_{iso} in the nematic solvent for P_n^N.[22]

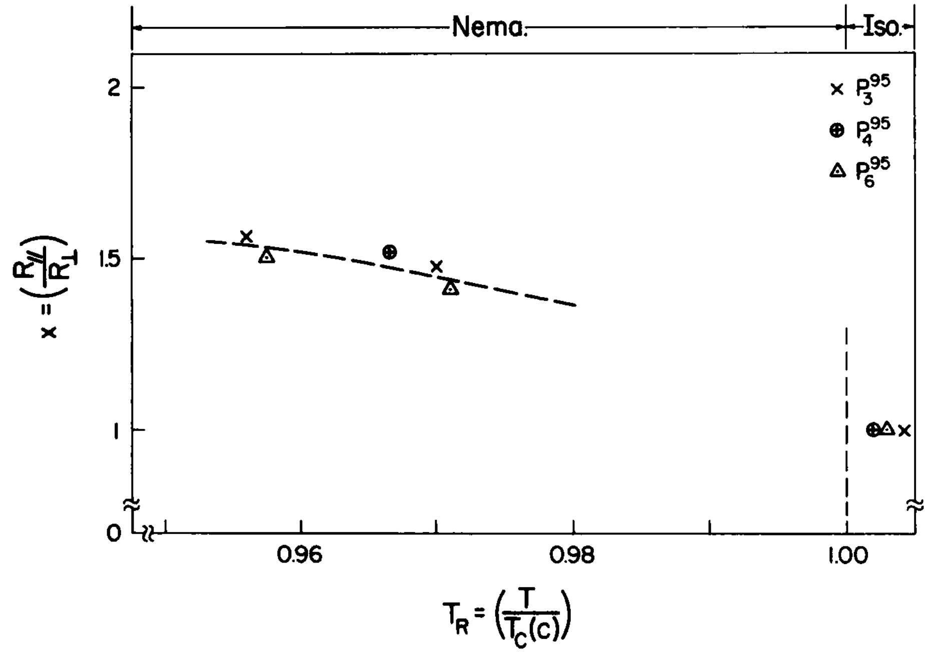

FIGURE 4 Characteristic behavior of the ratio ($x = R_{\parallel}/R_{\perp}$) versus reduced temperature T_R, deduced from X-ray study; $P_n^{95} + M_2$ at finite small concentration.

Remark Even though the anisotropy direction, with $R_{\parallel} > R_{\perp}$, is an intrinsec property for semiflexible liquid crystal polymers, it would be of great interest to determine the absolute values of these sizes in nematic solutions.

VI. DISCUSSION

1. Dilute Solutions

In the dilute solutions regime limit where we have performed measurements with the two kinds of solute chains, a comparison reveals different behaviors for the absolute increments: $(\Delta\gamma_1/\gamma_1)$ is, a priori, much more important for the main chain macromolecules than for the side chain case (Section II).

For both solutions, in this regime, the viscosity increase is qualitatively explained in the framework of the Brochard model which uses the hypothesis of anisotropic chains in such ordered media.[28] In fact, within this assumption, a rotation of the nematic director must be accompanied by a conformational adjustment of the macromolecules. This allows the chains to maintain their initial equilibrium. This motion is manifest in the supplementary viscosity increment which can be expressed as:* [28]

$$\Delta\gamma_1 = kT\,\Phi\,\tau_R\,h(x) \tag{2}$$

$^*\tau_R = \tau_{R0} \times \exp(W/T)$, W is the same activation energy which appeared in γ_1.

where kT and Φ designate respectively the Boltzman factor and the number of chains per unit volume (ch/cm^3). τ_R is the relaxation time expressed as function of two frictional coefficients $\lambda_\parallel$, $\lambda_\perp$ (parallel and perpendicular to the nematic director).[28] h(x) is the anisotropy factor:

$$h(x) = (x^2 - 1)^2/(x)^2 \text{ with } x = R_\parallel/R_\perp \qquad (3)$$

The first feature of this expression is the *linear dependence* of the relative viscosity increment on concentration, as observed for both solutions: S.P.S. (Zone I) and M.P.S. In the framework of this model one can extract the dependence on the polymerization index(N) and the anisotropy magnitude.

The effects of N are contained in the product ($\Phi \times \tau_{R0}$). For relatively short chains τ_{R0} could be expressed as the Rouse relaxation time: $\tau_{R0} \propto \xi N^2$; ξ is the frictional coefficient per monomer unit. On the other hand Φ is expressed as (c/N). With these substitutions Equation 2 becomes:

$$\frac{\Delta\gamma_1}{\gamma_1} \propto kT\, N\, c\, h(x) \qquad (4)$$

and the increment is consequently proportional to N. At a given concentration c, the effect on γ_1 for M.P.S. as compared to S.P.S. is less pronounced than what one would believe from a crude comparison which ignores the importance of the degree of polymerization (Figure 1a,b). In fact the values of N are different for the two solutes.[23,24]

$$N(\text{copolyester}) > 4 \times N\,(P_n^{95})$$

The anisotropic dumbell model of Brochard, together with the viscosity data do not enable us to deduce the direction of the anisotropy, since h(x) is symmetric in x and 1/x. However, one can extract the anisotropy ratio by making some rational assumptions. In fact τ_R could be estimated from Quasielastic Light Scattering in an ordinary solvent and with a raw correction to take account of the nematic solvent viscosity. For example, within these estimations, we have deduced the anisotropy magnitude for these solutes from the viscosity increment ($\Delta\gamma_1$) measurements:

$x = 1.54$ or 0.65 at $T_R = 0.94$ for S.P.S.

$x = 1.3$ or 0.78 at $T_R = 0.99$

$x = 1.75^*$ at $T_R = 0.97$ for M.P.S.

These anisotropy ratios indicate swelled chains in 3 dimensions for both cases. Therefore, the picture of an extended, one dimensional macromolecule for main chains is very seriously questioned, in nematic solutions.

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*$R_\parallel > R_\perp$ is an intrinsic property for semi-flexible polymers, and $x > 1$.

From X-ray measurements, we extracted, in the dilute solutions regime, values for the sizes in the S.P.S. case. The anisotropy hypothesis is thus experimentally confirmed. Moreover, we found that the direction is $R_{\parallel} > R_{\perp}$, and that the experimental values for the ratio are:

$$x \simeq 1.3 - 1.6 \text{ for } P_n^N \text{ components}$$

It is important to notice the excellent agreement between these values and those deduced from viscosity results above. The structural measurements confirm and complement the viscosity results and their interpretation.

The anisotropy evolution with reduced temperature T_R is shown on two different plots. From viscosity results, the plot for $(\Delta\gamma_1/\gamma_1\ \Phi)$ versus T_R (Figure 3a,b) represents the dependence of h(x) vs. T_R. On the other hand, Figure 4 shows the evolution of the ratio x versus T_R, deduced from X-ray study. For both cases there is a weak dependence, unless one goes very close to the clearing point where x and h(x) drop to 1 and zero, respectively. This behavior is comparable with that of the order parameter (S vs. T_R) in nematic media. The anisotropy ratio x (or function h(x)) is therefore a property of the liquid crystal order, and consequently follows the same principal dependences as this parameter, i.e., weak dependence of S on T_R for temperatures below the clearing point and its drop to zero in the isotropic state.

2. Intermediate Regime (Zone II) for S.P.S.

The inflection point in the relative viscosity vs. concentration increase marks a change from linear to exponential behavior. It occurs at the concentration $\Phi \simeq 14 \times 10^{17}$ ch/cm³. This value is very close to the overlap concentration Φ^* deduced from the radius of gyration (R_G) measurements (S.A.X.S.) in toluene:[29]

$$\text{For } R_G \simeq 55\text{Å} \ ; \ \Phi^* \simeq \frac{1}{\frac{4}{3}\pi R_G^3} \simeq 14.4 \times 10^{17} \text{ ch/cm}^3 \qquad (5)$$

The inflection point then coincides with a regime change in the ordinary polymer solutions sense. This change (inflection point) for the viscosity γ_1 vs. Φ behavior can be explained within the framework of the conformational anisotropy hypothesis (Brochard) in two ways:

a) When the concentration approaches the overlap value Φ^*, the interactions between solute macromolecules could cause a reduction of the anisotropy factor. This would be accompanied by a transient reduction of the increase in the viscosity increment, as Equation 2 would predict.

b) The second possible explanation is a change in the anisotropy direction as the solution goes through the overlap concentration. Starting from the Brochard approach, this should be accompanied by a sharp and local decrease of $\Delta\gamma_1$ when the anisotropy changes direction. This possibility is difficult to check; it requires a close investigation of Zone II with monodisperse and very well controlled systems.

The viscosity and X-ray measurements again provide us with consistent and complementary information.

3. High Concentrations Regime (Zone III) for S.P.S.

The viscosity increase in Zone III is more pronounced than in the two previous zones. It starts at the overlap concentration $\Phi = \Phi^*$. This is similar to the shear viscosity (η) behavior for ordinary polymer solutions.

We have studied relatively small macromolecules. The chains might interpenetrate but do not entangle for $N \simeq 100$. The rotational viscosity is a liquid crystal property. It is very difficult to have a clear description of the γ_1 vs. c (Φ) behavior in this domain from a simple comparison with the shear viscosity results. In addition, the theoretical approaches are still incomplete for η in the region of moderately concentrated solutions: $c^* < c \ll 100\%$. Nevertheless, we tried to fit our experimental data with various "classical" semi-empirical laws.[22] None of them were suitable. The best fit was obtained with a simple exponential law (Equation 1). This expression could also be written as:

$$\frac{\Delta\gamma_1}{\gamma_1} \propto A \exp \beta\,[c(\Phi) - c^*(\Phi^*)] \tag{6}$$

There is a concentration barrier above which the exponential law holds. This barrier is mass dependent. For higher molecule weight one would expect a lower onset for the exponential fit. The constant, β, is similar for the three P_n^{95} polymers we used, and does not depend on T_R. This property would suggest that β is mainly affected by molecular mass variation. We believe that β is larger for high N. It therefore turns out that β and Φ^* are directly dependent.

We now discuss the dependence of the viscosity increment on the reduced temperature T_R, as was done for the dilute solutions regime above. We have shown that in the high concentrations regime (Zone III), the relative viscosity increment is exponentially dependent on the solute concentration. From this and from Equation 1, one can isolate a temperature (T_R) dependence, by plotting the experimental data of $(\Delta\gamma_1)e^{-W/T}/e^{\beta c(\Phi)}$ (or $\Delta\gamma_1/\gamma_1\ e^{\beta c(\Phi)}$) vs. T_R. The corresponding curve, shown in Figure 5, has a weak decrease (for $T_R < 1$) similar to that observed in dilute solutions in the $(\Delta\gamma_1)/(\Phi\gamma_1)$ vs T_R plot (Figure 3). This behavior suggests the possibility that one can always discuss the viscosity increment data in the framework of the anisotropic "dumbell" model of Brochard. Therefore one can write this increment (Equation 1) as:

$$\frac{\Delta\gamma_1}{\gamma_1} \propto A(R_\parallel, R_\perp) \times \exp \beta\,(c - c^*) \tag{7}$$

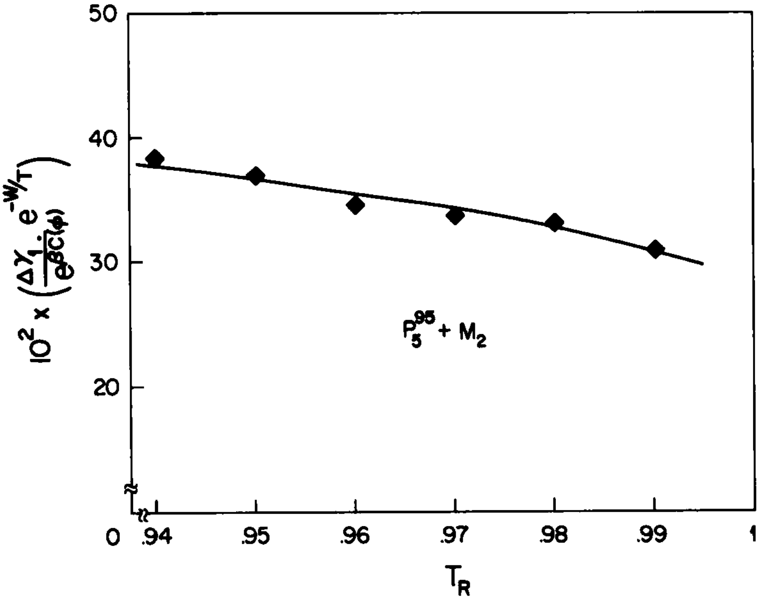

FIGURE 5 Experimental values of the expression $\Delta\gamma_1\ e^{-W/T}/e^{(\beta c(\Phi))}$ (or $\Delta\gamma_1/\gamma_1\ e^{(\beta c(\Phi))}$) versus T_R, in the regime III where the relative increment was found to increase exponentially with $c(\Phi)$; system $P_5^{95} + M_2$.

This indicates a separation of concentration c and temperature T_R dependencies of the viscosity increment in this regime, as was found for the dilute solutions regime (Zone I). Such a prediction is consistent with the following features:

—The exponential law with the registered values of A and β for P_4^{95} gives the same order of magnitude at c = 100% as P_4^{95} melt.[17] This law then seems to be valid throughout the whole concentration range going from solutions to pure melt systems:

$$\Delta\gamma_1(c = 100\%) \simeq \gamma_1(c = 100\%) = 5 \times 10^4 \text{ (poises)}$$

$$\gamma_1(P_4^{95}) \simeq 3.10^4 \text{ (poises)}^{17}$$

—The Brochard hypothesis is useful to interpret the rotational viscosity data for P_n^N melt case[10,17] (n = 4; 6; N = 95). The anisotropy of conformation has been experimentally checked using small angle scattering techniques, for comb-like nematic polymers in the melt phase.[7,8]

We have demonstrated the consistency of the viscosity (γ_1) results with the structural measurements in dilute nematic solutions. In addition we have checked the consistency of the viscosity results for relatively concentrated solutions with the pure melt case. These two points could provide a good starting tool for relating the structural measurements from small angle scattering on pure melts and concentrated solutions to those on dilute solutions presented here.

CONCLUSION

We have presented a combination of macroscopic and microscopic properties for comb-like liquid crystal polymers in nematic solutions. More precisely, we have correlated the typical nematic rotational viscosity behavior with the conformational anisotropy measured by small angle X-ray scattering. We have concurrently drawn a comparison between comb-like and semi-flexible liquid crystal polymers on the basis of viscosity studies.

For dilute solutions, the viscosity results for both kinds of solutes show consistent behavior. They are in good agreement with a phenomenological model due to F. Brochard. The size measurements for the side chain solute not only confirm the viscosity results and the corresponding explanation but also give the anisotropy direction and magnitude. This last value is in very good agreement with an estimation derived from the viscosity results and calculated from the anisotropic "dumbell" model (F. Brochard). Always for a comb-like solute, the transition from a simple linear increase of the viscosity increment ($\Delta\gamma_1$) to an exponential dependence on polymer concentration (Φ) coincides with the overlap process at Φ^* as deduced from size measurements in Toluene.

For high concentration regimes of comb-like macromolecular solutes, the exponential law is due to short range interactions, i.e. interpenetration between chains in solution. This exponential behavior seems to be a suitable law for all concentrations from c* to pure polymers, since at $c = 100\%$, the γ_1 obtained is consistent with the one directly measured for melt chains. Always in this regime, we have mentioned a separation between concentration $c(\Phi)$ and temperature T_R dependence of the viscosity increment, as was done for dilute solutions. This suggests the existence of an anisotropy factor which could be independent of the concentration parameter. This property agrees with the interpretation of the γ_1 results for pure chain polymer systems in the framework of the anisotropic "dumbell" model.

It would be very interesting to pursue a similar viscoelastic study on main chain liquid crystal polymers in a nematic solvent using a wide range of concentrations and several nematic skeletons. In fact it has been noticed that the nematic properties for this kind of component are very dependent on the structural details in the chains. A small angle neutron structural study on main chain polymers, analogous to the present achieved on comb-like polymers, could clarify these points. The corresponding results should also be closely correlated to the viscoelastic properties. The viscoelastic and structural studies should be tested on other comb-like macromolecules with different backbones and different pendent groups.

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