

Elastic Coefficients and Twist Viscosity in Side-Chain Mesomorphic Polymers

P. Fabre, C. Casagrande, and M. Veysié

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

and

H. Finkelmann

Institut für Physikalische Chemie, D-3392 Clausthal,
Zellerfeld, West Germany

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The splay and bend elastic constants and the twist viscosity coefficient γ_1 have been measured for a series of side-chain nematic polymers. While the static properties are close to those of conventional liquid crystals, the hydrodynamic behavior resembles that of ordinary flexible polymers in the melt state. Furthermore, the results indicate an anisotropic conformation of the main chain as well as a coupling between the director rotation and the motion of the backbone.

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During the past several years, there has been increasing interest in the properties of thermotropic mesomorphic polymers.¹ However, relatively little is known about the typical mechanical liquid-crystal properties of these systems.^{2,3} We present here what we think to be the first comprehensive experimental study of the Frank elastic coefficients and of the twist viscosity constant γ_1 for side-chain nematic polymers. Extremely high values of γ_1 are found which may be associated with an effect of backbone reorientation under nematic torques. These results are discussed in terms of the relevant parameters of the system, schematized below (Fig. 1), i.e., the total length of the chain N , the degree of coupling n between the main polysiloxane chain and the mesomorphic moieties, and the temperature. The synthesis method⁴ ensures a well-defined value of the

chain length N , which allows a reliable determination of the physical constants. In Table I are presented the different polymers studied, their nematic-to-isotropic transition temperatures T_c , and their glass-transition temperatures T_g as defined by differential scanning calorimetry analysis. The viscoelastic coefficients of two analogous low-molecular-weight (lmw) liquid crystals have also been measured for comparison: M_2 ($C_6H_{13}-O-\phi-COO-\phi-O-C_2H_5$) and M_8 ($C_8H_{17}-O-\phi-COO-\phi-O-C_6H_{15}$), where ϕ represents a benzene ring.

The experimental procedure is the study of the dynamics of a Fréedericksz transition,⁵ in two different geometries: From the planar geometry, we get the splay elastic constant K_1 and the twist viscosity coefficient γ_1 ; from the homeotropic case, we obtain the bend elastic constant K_3 .⁶ In both cases, the principle of the method is the same: A magnetic field $H > H_c$ is applied perpendicular to the orientation of the director: $H_{c1,3}^2 = (\pi/d)^2 K_{1,3}/\chi_a$, where d is the sample thickness (20 to 100 μm) and χ_a the diamagnetic anisotropy per unit volume.⁷ At time $t=0$, H is rapidly decreased

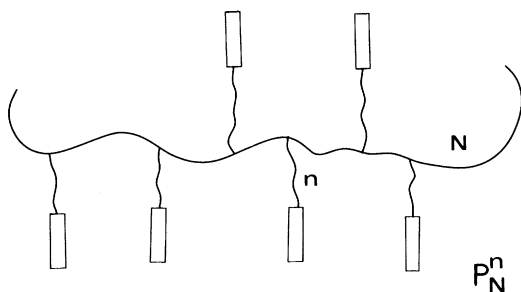
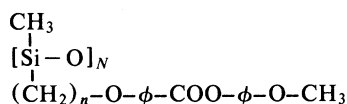


FIG. 1. Schematized representation of polymers P_N^n :



(ϕ represents a benzene ring).

TABLE I. Physical characteristics of the polymers P_N^n .

Name	T_g (K)	T_c (K)	A (10^{-6} cgs)	E^* (10^{+3} K)
P_{50}^6	≈ 280	379	0.58	13
P_{95}^6	278	385	1.43	13
P_{95}^4	287	376	30.6	11.8

to $H_f < H_c$, causing the sample to relax to its initial alignment. In the limit of weak distortion, it has been shown in conventional liquid crystals⁵ that the distortion relaxes exponentially with a characteristic time τ , according to the relationship

$$\tau_{1,3}^{-1}(H_f) = \frac{2\chi_a}{\eta(H_f)} (H_{c1,3}^2 - H_f^2), \quad (1)$$

where $\eta(H_f)$ is independent of H_f and equal to γ_1 in the planar case, where backflow effects are negligible. In consequence, by measuring τ_1^{-1} for several values of H_f , one gets γ_1/χ_a and K_1/χ_a (via H_{c1}); from τ_3^{-1} , one gets only the elastic term K_3/χ_a .

The experimental results show, first, that the behavior of the polymers is quite similar to that of lmw compounds, exhibiting a critical field H_c and a unique relaxation time τ which obeys Eq. (1). As for the elastic constants K_1 and K_3 , the striking result is that they are the same order of magnitude as those found in conventional liquid crystals (Fig. 2), in contrast to the case of main-chain systems.³ A more detailed analysis of the complete results as a function of N (total chain length) and n (length of flexible spacers) shows the following.

(i) The length of the chain has only a small influence: Going from P_{50}^6 to P_{95}^6 slightly increases (factor of $\approx 1, 2$) both K_1 and K_3 (Fig. 3). This would imply either a low exponent in a molecular-weight power law or a saturation effect.

(ii) The length of the spacer plays a more pronounced role in the Frank elasticity. In particular, the anisotropy of the splay and bend elastic constants, defined by K_3/K_1 , is inverted when going from $n = 6$ to $n = 4$, mainly due to a large increase

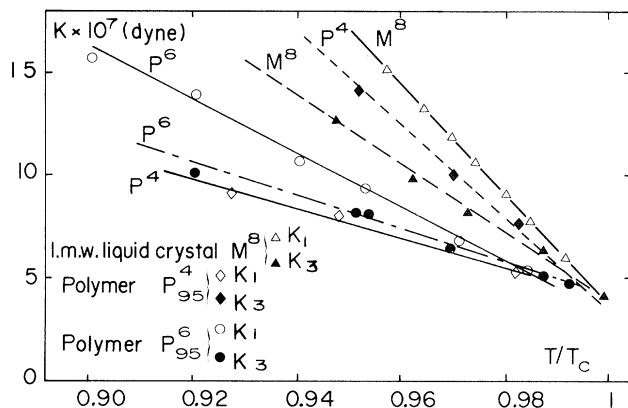


FIG. 2. Splay and bend elastic constants of some typical compounds as a function of the reduced temperature T/T_c .

of the bend constant K_3 (Fig. 3). This would be consistent with the existence of cybotactic groups, but no smectic phase is evidenced for P_{65}^4 . However, this suggests an interpretation which is not fundamentally different from the cybotactic hypothesis, but at a more local scale; it relies on the idea that the backbone does not have a spherical conformation, but resembles rather an elongated ellipsoid, and that this anisotropy increases with shortening of the spacer. The fact that a bend distortion for the director corresponds to a splay distortion of the backbones makes this difficult for flat main-chain conformation, leading to an increase for K_3 . This anisotropic model is supported by the results concerning the dynamics of these systems, as discussed below.

Considering now the twist viscosity coefficient γ_1 , it has to be emphasized that, for all the polymers studied, γ_1 is larger by several orders of magnitude when compared to analogous lmw compounds: At $T/T_c = 0.957$, $\gamma_1(M_8) = 0.88$ P and $\gamma_1(P_{95}^6) = 255$ P. Also γ_1 sharply increases when the temperature is lowered.

In order to analyze the data in more detail and to determine the effect of N and n , we first have to discuss the temperature dependence of γ_1 , which is a delicate problem. Recall that this coefficient describes the viscous coupling between the rotation of the director and the fluid, being thus specific to the nematic state; it therefore depends both on the absolute temperature T and on the reduced temperature T/T_c , which controls the order parameter of the nematic phase. To take into account the in-

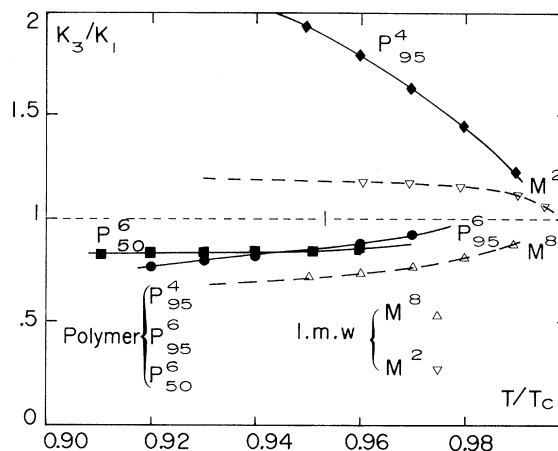


FIG. 3. Anisotropy K_3/K_1 of the elastic constants, as a function of the reduced temperature for polymers and lmw liquid crystals.

fluence of the order parameter, one may assume for γ_1 the relationship $\gamma_1(T, T/T_c) = \chi_a(T/T_c)f(T)$, which holds for conventional liquid crystals.⁸ With γ_1/χ_a then plotted as a function of the temperature for the three polymers (Fig. 4), it appears that the experimental curves are well fitted by an exponential law

$$\gamma_1/\chi_a = A(n, N)e^{E^*/T}, \quad (2)$$

where E^* , of the order of 10^4 K, depends on the spacer length, but not on the degree of polymerization (cf. Table I). We emphasize that, because of the proximity of the glass temperature T_g , E^* does not represent an activation energy, but has to be interpreted as an average value, on our temperature interval, of the exponent appearing in free-volume models, such as that in a William-Landel-Ferry-type equation;⁹ this interpretation is consistent with the numerical values of E^* and its variation with the spacer length.

If we turn now to the prefactor A in Eq. (2), which bears the dependence with the main-chain length N , it is observed that it varies nearly proportionally to N . It thus appears that, although γ_1 is specific to the nematic phase, its behavior is very similar to that of shear viscosity in ordinary nonentangled melt polymers. This suggests that, in this particular nematic phase, the rotation of the director involves a cooperative motion of the main chain, accompanying the turn of the mesogenic moieties. This leads us to rely, for discussing the results, on a model set up by Brochard for dilute chains in a nematic solvent, which may also be valid for nonentangled melts.¹⁰ The basic idea is that an anisotropic conformation of the backbone requires a readjustment of the whole chain when changing the orientation of the director, causing a polymer-type dissipative effect. The chain is then described as an

“anisotropic dumbbell” with two size parameters R_{\parallel} and R_{\perp} and two friction coefficients λ_{\parallel} and λ_{\perp} , leading to the expression

$$\gamma_1 = kT\tau_R [c/N] (R_{\perp}^2 - R_{\parallel}^2)^2 / R_{\parallel}^2 R_{\perp}^2,$$

where c is the number of monomers per unit volume and τ_R is a characteristic relaxation time of the chain, expressed by

$$\tau_R = (1/kT) \lambda_{\parallel} R_{\parallel}^2 \lambda_{\perp} R_{\perp}^2 / (\lambda_{\perp} R_{\perp}^2 + \lambda_{\parallel} R_{\parallel}^2).$$

In this formula, the temperature dependence of γ_1 is included in the friction coefficients λ_{\parallel} and λ_{\perp} . Neglecting the anisotropy influence in τ_R in a first approximation, one expects τ_R to scale as $N^{2\nu+1}$ with $\nu = 0.5$; this corresponds to the classical Rouse model, which is valid for moderate chain length in the melt state, and leads to the prediction of a linear dependence of γ_1 with N . This is close to the experimental results, as previously noted. The somewhat larger increase from $N = 50$ to $N = 95$ (cf. Table I) may be understood by an additional effect due to an increase of the anisotropy factor $F = (R_{\perp}^2 - R_{\parallel}^2)^2 / R_{\perp}^2 R_{\parallel}^2$ when the chain is lengthened. Furthermore, the large variation of A when changing n (N being constant) may also be interpreted in the same way: A stronger coupling between the main chain and the mesogenic moieties leads to a more anisotropic conformation chain, hence, to a larger value of F . More precisely, calculating the variation of F when deforming a sphere of size R to an ellipsoid, with the additional condition of constant volume ($R_{\perp}^2 R_{\parallel} = R^3$), one finds that an increase of R_{\perp}/R of 0.14 is sufficient to multiply F by a factor equal to 25; this is very consistent with the results obtained for $A(n)$ in P_{95}^6 and P_{95}^4 . A more accurate description of the anisotropy would require either an independent measurement of τ_R , or a direct determination of R_{\parallel} and R_{\perp} , by small-angle x-ray or neutron scattering. At the present state, the analysis of the whole experimental results of the twist viscosity coefficient in terms of T , n , and N is in agreement with the “anisotropic dumbbell” model. This implies both a nonspherical conformation of the main chain, as indicated also by the elastic constant study, as well as a cooperative motion of the flexible chain when rotating the director.

It thus appears that certain of the properties of the side-chain nematic polymers are very close to those of conventional low molecular weight liquid crystals: This is the case of K_1, K_3 and of the order parameter.¹¹ On the other hand, as for the viscosity, the behavior is dominated by the flexible chain aspect, which also appeared in the miscibility diagrams.¹² However,

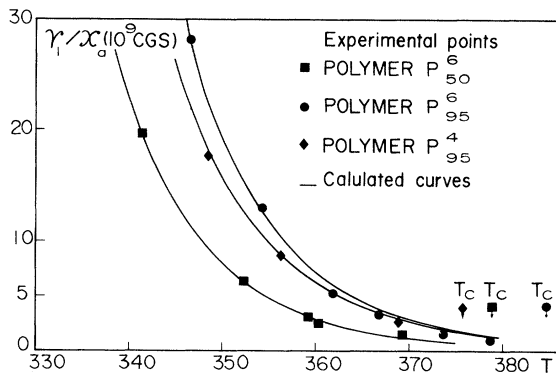


FIG. 4. Temperature dependence of the twist viscosity coefficient for the polymers.

the coupling between the two parts of this composite object is evidenced both in the static and dynamic properties, implying an anisotropic conformation of the backbone.

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⁶The planar alignment was obtained easily by uniaxial rubbing of two glass slides. The homeotropic texture was more difficult to realize for the polymers: The glass slides had to be treated by hot sulfochromic acid and the sample had to be slowly cooled in a magnetic field. The quality of this anchoring seems reasonably good, because samples of different thickness lead to the same results for the physical constants.

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