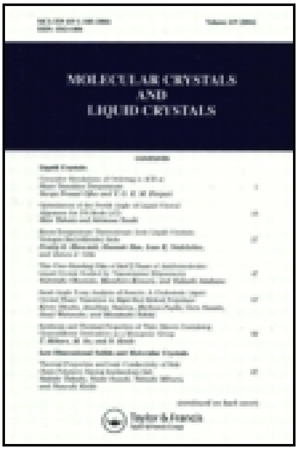

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VISCOELASTIC PROPERTIES OF SIDE CHAIN MESOMORPHIC POLYMERS IN NEMATIC PHASE : MELT AND SOLUTIONS

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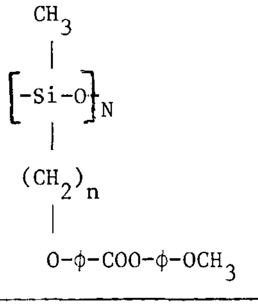
Abstract We have measured the Franck elastic coefficients and the twist viscosity constant for thermotropic side chain mesomorphic polymers, in melt and in solutions. The results are in agreement with a theoretical model based on an anisotropic conformation of the main chain.

INTRODUCTION

During these last years, an increasing interest has been devoted to thermotropic side chain mesomorphic polymers. However, relatively little is known about the typical mechanical liquid crystal properties of these systems. We present here measurements of Franck elastic coefficients and the twist viscosity constant for a series of this kind of polymers, either pure or in dilute solutions.

The relevant parameters of the system are N, the degree of polymerization of the backbone, n the number of methylene groups between the main chain and the mesomorphic moities, T the absolute temperature and $T_R=T/T_c$ the reduced temperature. The formulae, the glass temperatures T_g of the polymers, and the clearing temperatures T_c of polymers and the low-molecular-weight liquid crystals (l.m.w.) we have studied are summarized in Table I.

TABLE I

FORMULAE	Name	T_c(K)	T_g(K)	N	n
 $\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle (CH_2)_n-O-\phi-COO-\phi-OCH_3}{Si}}-O-\right]_N$	P^4_{95}	376	287	95	4
	P^6_{95}	385	278	95	6
	P^6_{50}	378	282	50	6
$H_{13}C_6O-\phi-COO-\phi-OCH_2-CH=CH_2$	M_{11}	360			
$H_{17}C_8O-\phi-COO-\phi-OC_6H_{13}$	M_8	365			
$H_{13}C_6O-\phi-COO-\phi-OC_2H_5$	M_2	368			

EXPERIMENTAL PROCEDURE

We determined the splay (K_1) and bend (K_3) elastic constants and the twist viscosity coefficient γ_1, from the study of a Fredericks transition. For measuring K_1 and γ_1, the samples are oriented between two glass slides in a planar texture, and for measuring K_3, in a homeotropic texture. A magnetic field H is applied perpendicular to the initial orientation. When H is larger than a critical value H_c, a distortion appears. It is related to the elastic constants by

$H_{c1,3} = (\pi/d)(K_{1,3}/\chi_a)^{1/2}$ where d is the sample thickness and χ_a the anisotropy of the diamagnetic susceptibility[1]. H is then rapidly decreased to a value $H_f < H_c$, causing the sample to relax to its initial texture. In the weak distortion approximation, the relaxation time is given by[2]

$$\begin{aligned} \tau_1^{-1}(H_f) &= 2\,\chi_a/\gamma_1\,(H_{c_1}^{\;2} - H_f^{\;2}) \\ \tau_3^{-1}(H_f) &= 2\,\chi_a/\gamma_1^{*}\,(H_{c_3}^{\;2} - H_f^{\;2}) \end{aligned} \tag{1}$$

Thus, by measuring τ_1^{-1} for several values of H_f, one gets γ_1 and K_1 ; from τ_3^{-1}, one gets K_3, with a good accuracy. The measurements have been performed on pure polymers P^4_{95}, P^6_{95} and P^6_{50}, on l.m.w. M_{11}, M_2 and M_8, and on dilute solutions of these three polymers in a l.m.w. solvent.

EXPERIMENTAL RESULTS

DILUTE SOLUTIONS

Phase diagram studies have shown that the nature of the l.m.w. compounds considerably affects the miscibility of the polymers in the nematic range[3-4] ; since as for M_{11} the miscibility is complete in the entire temperature range, we have chosen this compound as the solvent for the polymers. We characterize the solution by the chain concentration ϕ_{ch} (number of chains per cm^3), which was varied in the range 0-10^{16} ch/cm^3 ($\simeq$ 5 % in weight).

The main results are summarized below[5] :

1) While the static constants are the same as in the pure l.m.w. M_{11}, the viscosity coefficient γ_1 is modified, even in the very dilute regime, increasing by the quantity $\delta\gamma_1$.

2) $\delta\gamma_1$ varies linearly with ϕ_{ch}, as expected in the dilute regime ; comparing P^6_{95} and P^6_{50} shows that the effect decreases when N increases (figure 1).

3) Comparing P^4_{95} and P^6_{95} shows that the effect is increased when the coupling between the main chain and the nematic moities is increased.

4) Dependence on T_R : $\delta\gamma_1$ increases when T/T_c decreases, i.e. when the order parameter $S(T/T_c)$ increases (figure 2). In figure 2 we also see a change in the temperature dependence for the highest concentration $\phi_{ch} = 9.10^{17}$ ch/cm^3, that we interpret as the change from the dilute to the semi-dilute regime.

All these results are in agreement with a theoretical model of F. Brochard[6], who has calculated the increment of the twist viscosity coefficient γ_1 in a dilute solution of polymers in a nematic solvent.

If $\vec{n}$ is the director of the nematic medium, parallel to the Z axis

$$\delta\gamma_1 = \phi_{ch}.kT.\tau_R.\left(\frac{(R_\perp^2 - R_\parallel^2)^2}{R_\perp^2 . R_\parallel^2}\right) \qquad (2)$$

Where $R_\perp^2 = \langle x^2\rangle = \langle y^2\rangle$ and $R_\parallel^2 = \langle Z^2\rangle$ are the size parameters of the backbone, and τ_R is a characteristic relaxation time of the chain.

From these formulae, we can see that the existence of a non-zero viscosity increment $\delta\gamma_1$ implies an anisotropic shape of the polymer backbone : $R_\parallel \neq R_\perp$. This anisotropy was confirmed by direct measurements of $R_\parallel$ and $R_\perp$ on magnetically oriented samples of dilute and semi-dilute solutions of P^4_{95} and P^6_{50} in $M_\parallel$: by small-angle X-ray scattering with the $\vec{q}$ vector parallel and perpendicular to the director.

PURE POLYMERS

The elastic constants K_1 and K_3 are of the same order of magnitude for all the polymers and the l.m.w. compounds.

Comparing the polymers, we observe that both K_1 and K_3 increase with N, but very slightly.

The dependence with n is more pronounced (Table II) : because of the large increase of K_3 when going from n = 6 to n = 4, the anisotropy of the elastic constants represented by K_3/K_1 is significantly increased between the two polymers, as evidenced by the influence of the backbone on the Franck elasticity.

Considering now the twist viscosity coefficient γ_1, we found that it was about three orders of magnitude larger for polymers than for the analogous l.m.w., and that it increased faster with decreasing temperature.

Plotting $\gamma_1(T,T_R)/\chi_a(T_R)$ as a function of absolute temperature, we find that the experimental curves are reasonably fitted by an exponential law.

$$\frac{\gamma_1}{\chi_a} = C\, e^{E^{\star}/RT} \qquad (3)$$

The values of C and $E^{\star}$ are reported in Table III.

TABLE III

	C(c.g.s.)	$E^{\star}$(kJ/mole)
P^6_{50}	$0.58.10^{-6}$	108
P^6_{95}	$1.43.10^{-6}$	108
P^4_{95}	$30.6\ .10^{-6}$	98

The fact that E^{*} remains constant when N varies ($P^{6}_{50} \rightarrow P^{6}_{95}$), but increases with the size of the side-groups ($P^{4}_{95} \rightarrow P^{6}_{95}$) support this free-volume interpretation. The pre-factor C may then be discussed in terms of Brochard's theory, which is also valid for melts[9]. It appears in particular that, n being constant, C is nearly proportional to N, in agreement with the Rouse model, which seems reasonable for these rather small values of the chain length (no entanglement).

CONCLUSION

Viscosity and X-ray scattering measurements of side chain mesomorphic polymers in a nematic solvent indicate an anisotropy of the conformation of the main chain. Our experimental results show that in the melt the elastic constants of side chain polymers are very close to those of the analogous low-molecular weight nematics. However, the effect of the backbone is evidenced by the variation of the elastic anisotropy with the strength of the coupling. On the contrary, the twist viscosity coefficient, although it is specific to the nematic phase, behaves like the ordinary viscosity in conventional polymer melts.

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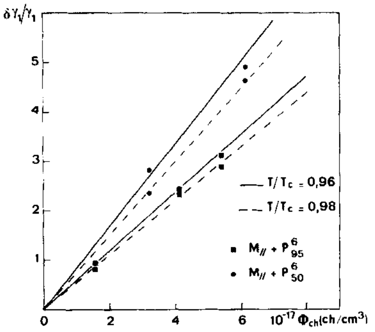

FIGURE 1

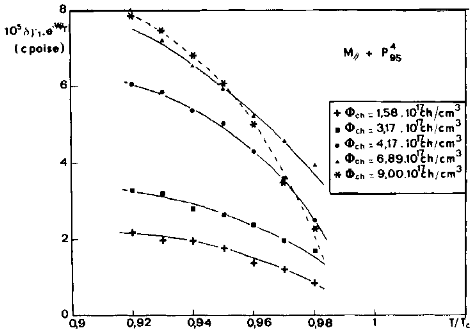

FIGURE 2

NAME	ν	K_1	K_3	K_3/K_1
		(10^{-7}dyne)		
M^8	14	14	10	0.8
M^2	8	9	10	1.2
P^6_{95}	7	8	7	0.9
P^4_{95}	5	7	13	1.8

TABLE II : Variation of K_1,K_3 and K_3/K_1 with the total number ν of C atoms in the alkyl chain for polymers and l.m.w. compounds.

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