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DYNAMICS OF A FREDERICKS TRANSITION IN SIDE CHAIN NEMATIC POLYMERS : DETERMINATION OF THE VISCOELASTIC COEFFICIENTS K_1 AND γ_1

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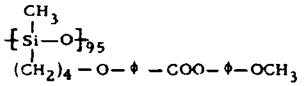
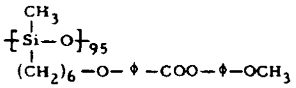
INTRODUCTION

We report here measurements of the splay elastic constant, K_1, and the twist viscosity coefficient, γ_1, of side chain mesomorphic polymers ; we compare them so the values obtained for certain low molecular weight compounds, similar to the nematic moiety of the polymers.

MATERIAL

All the compounds studied were synthesized at the "Institut für Physikalische Chemie", Clausthal. Their chemical structures and nematic to isotropic transition temperature T_c are given in table 1. The polymers are derivates of poly(methyl-siloxane) with a phenylbenzoate in the side chain, connected to the main chain by a spacer of four (P_4) or six (P_6) methylene groups. The average degree of polymerization is 95 (molar weight ≈ 35.000). The low molar weight compounds (P.m.w) are also phenylbenzoate, and differ by one of their end groups.

(x) Equipe de Recherche Associée au C.N.R.S. (E.R.A. n° 542).

	Formulaes		H_c/Gauss (d = 100 μ)	τ (0)	$K_1 . 10^7$ dyne	γ_1/poise
P_4	 $\left[\mathrm{Si(CH_3)}\!-\!\mathrm{O}\right]_{95}$, $(CH_2)_4-O-\phi-COO-\phi-OCH_3$	376	< 1500	0 min		
P_6	 $\left[\mathrm{Si(CH_3)}\!-\!\mathrm{O}\right]_{95}$, $(CH_2)_6-O-\phi-COO-\phi-OCH_3$	385	877			
M_a	$H_{13}C_6O-\phi-COO-\phi-OC_8H_{17}$	365	1250	0		
M_b	$H_{13}C_6O-\phi-COO-\phi-O-CH_2-CH{=}CH_2$	360	964	3		

CEDURE

transition, following the method of Piéransky and al(1) in the geometry "1". The sample is in a planar texture between two glass slides uniaxially polished with a diamond paste ; a magnetic field H is applied perpendicular to the slides, with $H > H_c$ when $H_c = \frac{\pi}{d}\sqrt{K_1/\chi_a}$; here d is the sample thickness (100 μ) and χ_a (C.G.S. cm^{-3}) is the diamagnetic anisotropy per unit volume. At time t = 0, H is rapidly decreased to $H_f < H_c$, causing the sample to relaxe to its planar initial state. In the limit of weak distortions, it can be shown(1) that the distortion exponentially relaxes, with a characteristic time τ, according to the relation

$$\tau^{-1}\ (H_f) = \frac{2\chi_a}{\gamma_1}\ (H_c{}^2 - H_f{}^2) \qquad [1]$$

By measuring τ^{-1} for several values of H_f, one gets, from equation [1], both the values of γ_1/χ_a and K_1/χ_a (via H_c). The diamagnetic anisotropy χ_a (C.G.S. G^{-1}) was measured at the C.R.P.P. (Bordeaux) with the collaboration of M.F. Achard(2). For both the monomers and the polymers, χ_a is of the same order of magnitude ($\simeq 10^{-7}$ C.G.S.) as usually found in nematics. The density was measured to be ρ = 0.95 ± 0.05 for the l.m.w. in the nematic phase, and ρ = 1.15 ± 0.03 for P_6(3) in the same conditions.

RESULTS AND DISCUSSION

Low molecular weight compounds M_a and M_b – as for the order of magnitude of the K_1 value as well as regarding the temperature dependence, M_a and M_b present a classical behaviour. K_1 is larger for M_a than for M_b (Fig. 1) as is generally observed when the length of the side chain increases. The temperature dependence of γ_1 (Fig. 2) is well fitted by the Arrhénius law proposed by Prost(4)

$$\gamma_1 \simeq \chi_a\ e^{W/T} \qquad [2]$$

with $W(M_a)$ = 4.300 K and $W(M_b)$ = 3.100 K.

Polymers P_4 and P_6 – a good quality of planar orientation (as juged by observation under the polarizing microscope) is obtained for these polymers by the same polishing method as for the l.m.w. compounds ; but the time for filling the cell

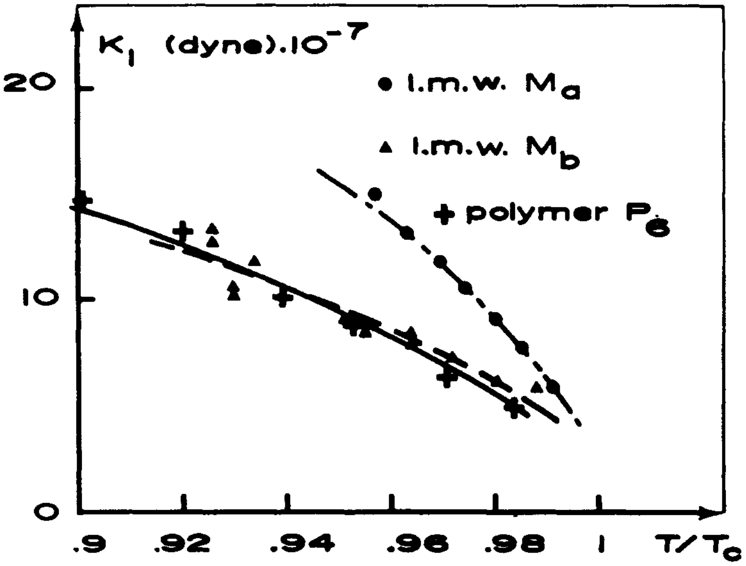
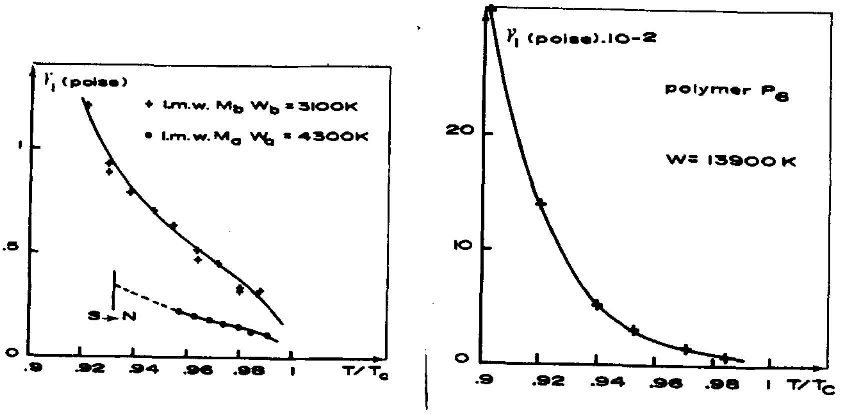


Figure 1

is considerable longer (several hours).

P6 - except for a considerable enhancement of the scale of time, the behaviour is quite similar to that for low molecular weights. Distortion of the alignment is observed when H is higher than a critical value H_c ; when H is then decreased to $H_f < H_c$, we verify an exponential relaxation which obeys the relationship [1] as expected for classical nematics(1). We note first that H_c has the same order of magnitude as for the l.m.w. nematics ; values of K_1 are reported in Figure (1) as a function of the reduced variable T/T_c. The values are very similar to that for the monomer M_b ; due to the difference in the terminal chain, which appears to be very effective (compare M_a and M_b), it is difficult to conclude about the effect of the siloxane chain on the splay elastic constant.



<u>Figure 2 and Figure 3</u>

By contrast, γ_1 (Fig. 3) is several orders of magnitude higher than for l.m.w. nematics, and increases more rapidly with temperature : an Arrhenius relation [2] is followed, with an activation energy W (P_6) = 13.900 K. Note that all measurements have been made within an aging of three days for the oriented sample in its nematic phase. In these conditions, γ_1 and K_1 values are fairly well reproducible.

<u>P_4</u> - for this shorter spacer polymer, the situation seems more delicate, although the oriented sample exhibits a Fredericks transition at a critical field H_c comparable to those previously observed. However (i) the relaxation times are huge (Table 1) : $\tau(0) \approx 90$ min., compared to 30 min. for P_6 and ~ 3 sec. for l.m.w. samples. It would have required several months to measure the temperature dependence of γ_1 and K_1, (ii) we observe an aging effect : starting with a freshly prepared cell (which appears well-oriented under the

polarizing microscope) and keeping constant the temperature, we observe first a relatively short relaxation time $\tau(0)$, which then increases and saturates to the values quoted in Table (1). These phenomena are not clearly understood and deserve further investigation. They may be explained by an influence of the polymer backbone : in filling the cell, the conformation of the siloxane chains is disturbed, and relax then very slowly towards equilibrium. Similar effect have been obtained by the optical properties of cholesteric polymers where the time required for the formation of the Grandjean texture depends on the length of the flexible spacer.

CONCLUSION

From measurements of K_1 and γ_1, we have found that the response times of the side groups in mesomorphic polymers are several orders of magnitude larger than in l.m.w. nematics, although their critical magnetic fields are very similar. These slow kinetics probably explain the effects observed when bulk samples are oriented in a magnetic field(2). On the whole, these results, including the aging effect, raise interesting questions about coupling between the dynamics of the main chain and of the side nematic groups.

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