INFLUENCE OF THE NEMATIC ORDER ON RHEOLOGY AND CONFORMATION OF STRETCHED COMB-LIKE LIQUID CRYSTALLINE POLYMERS.

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Thermotropic liquid-crystalline polymers combine the long-range orientation phases with the mechanical properties of polymers. We study **melts of comb-like liquid-crystalline polymers** in which the mesogenic part is linked as a side-chain on each unit of a flexible polymer (see Fig.1). The understanding of **the dynamics of these materials** in the nematic phase raises fundamental questions: what is the influence of the **comb-like structure?** And what is the specific effect of the **nematic interaction** on the dynamics?

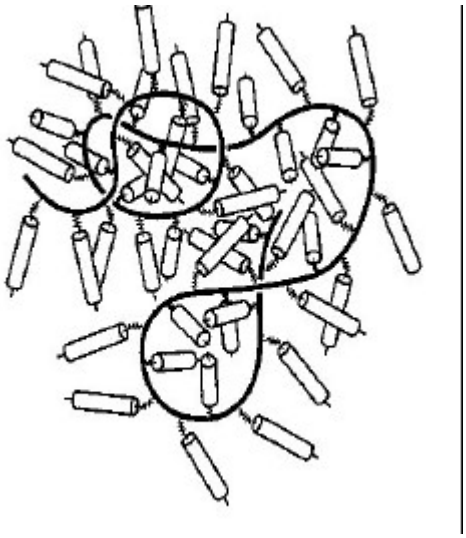

Figure 1. Schematic representation of a comb-like liquid crystalline polymer in an isotropic state.

For this purpose, we have synthesized **two isomers** of a comb-like polymetacrylate polymer (Fig.2). One polymer displays **a nematic phase** over a wide temperature range, between the glass transition temperature, T_g=44°C, and the nematic to isotropic transition temperature, T_{N-I}=83°C. Its isomeric form only has **an isotropic phase** above a glass transition temperature, T_g=32°C. The comparison of the dynamics of the nematic polymer with that of its isotropic isomer and that of the linear amorphous polystyrene allows us to dissociate the contributions due to the comb-like structure and to the nematic interaction.

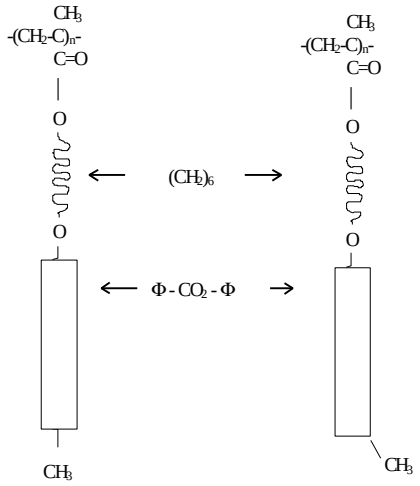

Figure 2. Chemical formula of the polymer and its isomeric form

For this study, we have associated :

- **classical rheology**, in order to obtain the characteristic times of the polymer chains both in the isotropic and nematic phases,
- **Small Angle Neutron Scattering** (SANS), in order to measure the chain conformation relaxation after an uniaxial stretching,
- **X-Ray scattering**, in order to obtain the average orientation of the mesogenic moieties in the nematic deformed samples.

Due to an important work of synthesis and fractionation of the polymers, such a study has been performed, for the first time, on polymetacrylate chains of **well-defined molecular weights.**

In the isotropic phase, our SANS study [(1)] shows that the conformation of the backbone of the comb-like polymers is similar to that of the linear polystyrene. Indeed, we have measured the variation of the radius of gyration, $R_g = 2.75N^{1/2}$, and the persistence length, $l_p \cong 10\,\text{Å}$. Thus, despite the presence of a hanging group of about 23 Å length every 2.5 Å of monomer, the **conformation of the polymetacrylate backbone is that of polystyrene**. The local rigidity due to the mesogenic group is not transmitted to the

backbone, probably because of the flexibity of the spacer $-(CH_2)_6-$.

For the dynamic study, our measurements[2] by classical rheology (a shear of small amplitude) confirm previous results[3] and show only little differences between the complex modulus curves (G', G'') in the isotropic and nematic phases. A time/temperature superposition can be established across the isotropic to nematic transition leading to unique master curves for the complex moduli (see Fig.3). The absence of a rubber plateau on these curves for polymers with degrees of polymerization N in between 40 – 1000, shows that **these comb-like polymers are not entangled**. For linear polystyrene, the average number of monomers between two neighboring entanglements is 180. Nevertheless, the observed dynamics is different from the Rouse dynamics expected for free chains. Indeed, the terminal times varies as $\tau_{ter} \propto N^{2.6}$ instead of $\tau_{ter} \propto N^2$ for a Rouse dynamics, the viscosity $\eta_0 \propto N^{1.3}$ and not $\eta_0 \propto N^1$. These results suggest a **more collective dynamics for the comb-like polymers than for linear polystyrene**.

The SANS experiments[4] allow us to describe the chain conformation of the deformed samples by two parameters: λ_p, the global chain deformation and p, the number of monomers of locally relaxed sub-chain. For a linear polymer in a Rouse regime, the chain deformation is affine (λ_p is equal to λ_s the deformation ratio of the sample) and p increases with the relaxation time t_R as $p \propto t_R^{1/2}$. For the isotropic comb-like polymer, the chain deformation λ_p remains constant, but is smaller than the sample deformation λ_s : **the chain deformation is pseudo-affine**. Meanwhile, the p values increases as $p \propto t_R$. To explain these results, we assume the existence of **living clusters** made of **temporary junctions between teeth of the comb**. The chain dynamics observed in the isotropic phase involves movements more rapid than a simple Brownian motion. If such effects probably come from specific interactions between teeth of the comb, their exact nature is still an open problem.

In the nematic phase, the chain deformation is also pseudo-affine as in the isotropic phase. But here, when the relaxation time increases, the chain deformation decreases as a stretched exponential function of the rheological terminal times (τ_{ter}) (see Fig.4). The p values are small, and remain constant; they only depend on the stretching temperature. We observe a slowing down of the chain dynamics. The **nematic interaction hindered the local relaxation of the chains**; the lifetime of the junctions is strongly prolonged. Therefore, the chain relaxation is the same at all scales.

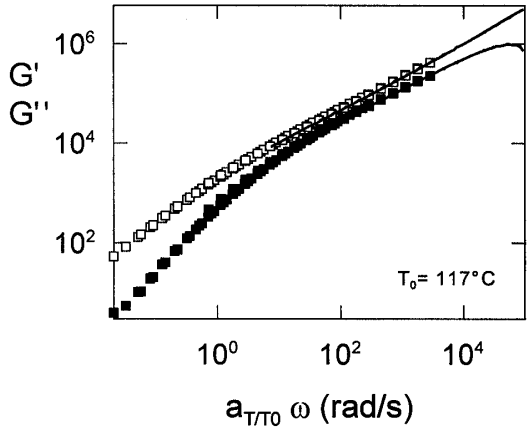

Figure 3. Master curves of the complex moduli G' G'' (unit : Pa) obtained from the time temperature superposition of the measurements obtained for the polymetacrylate polymer in the nematic phase (lines) and in the isotropic phase (G' (full symbols), G'' (open symbols). a_{T/T_0} *are the shift factors. The reference temperature* T_0 *is 117°C.*

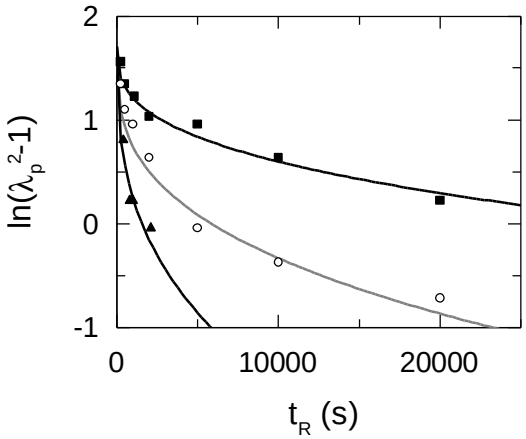

Figure 4. Relaxation of the global chain deformation of the nematic polymetacrylate of three different molecular weights. (square) M_w*=260 000 ; (o)* M_w*=130 000; (triangle)* M_w*=75 000. The full lines are the fits to a stretched exponential* $\exp[(-t/\tau_{ter})^{0.35}]$*. The exponent, 0.35, shows that the nematic interaction slows down the chain relaxation processes.*

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