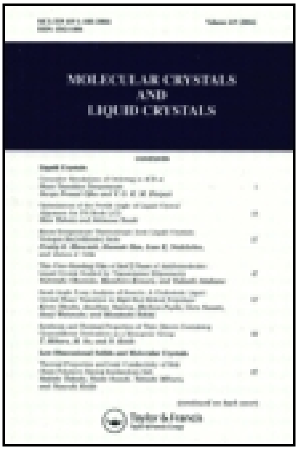

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The Role of the Smectic Layer Crossings in the Rheology of Side-Chain Liquid Crystalline Polymers

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The Role of the Smectic Layer Crossings in the Rheology of Side-Chain Liquid Crystalline Polymers

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Different behaviours have been observed by shearing the smectic phase of side-chain polymers. They present under shear flow, either a parallel layer orientation, a perpendicular layer orientation or a multilamellae cylindrical geometry. These different behaviours are analysed on the basis of a comparative description of the conformational architectures at equilibrium. They differ either by the molecular weight or by the flexibility of the main-chain of the mesomorphic polymer. It will demonstrated that the main-chain characteristics allow to explain the different orientations adopted under shear flow.

Keywords: non-equilibrium states; smectic phase; liquid-crystalline polymer; neutron scattering; diffraction

INTRODUCTION

Side-chain liquid crystalline polymers (SCLCPs) are well-known to gather, at least at equilibrium, both liquid crystalline and polymer features. Shear is often considered as an easy way both to align mesophases and to remove defects into the bulk. The first studies on non-equilibrium states of SCLCPs go against this intuitive result[1]. Because of the antagonistic nature of the viscoelastic properties of the polymer and of the mesophase, completely new behaviours are expected to occur in the non-equilibrium state. This paper focus on the response of the smectic phase of SCLCPs submitted to a simple steady-state flow far from a phase transition and in the low shear regime (further structural transitions due to shear increase are not considered here). Recently, three different orientations have been found in the sheared smectic phases of SCLCPs[1-3]. A description of the experimental method is first briefly exposed, then the equilibrium conformation displayed by the side-chain polymer in the smectic phase is presented introducing the discussion on the three different orientations adopted by the smectic layers under shear flow.

EXPERIMENTAL

The results exposed here have been obtained using the properties of neutron scattering which allows to determine the conformation of the main-chain alone at small-angles (the neutron scattering conditions were a wavelength of λ=8Å and a multidetector-sample distance of d=2m) and/or the orientation of the director determined at larger angles (the diffraction conditions were of λ=4Å and d=1.5m or 2m). These experiments have been carried out on the PAXY spectrometer of the Lab. Léon Brillouin (CEA-CNRS). The details of the procedure are exposed in other references[4,5,1]. The conformation at equilibrium is deduced from measurements carried on samples containing a melt of hydrogenated SCLCPs with SCLCPs deuterated on the main-chain alone, and aligned with a magnetic field. Two components of the radius of gyration of the main-chain, $R_{//}$ and $R_{\perp}$, respectively parallel and perpendicular to the director are thus deduced. Shear flow experiments were carried out in specific neutron shear cells[1] to access to the three main observation planes containing either: the velocity and the velocity gradient $(v, \nabla.v)$, the velocity and the neutral axis (vorticity) (v,z) or the neutral axis and the velocity gradient (z,v).

RESULTS – DISCUSSION

At equilibrium, for enthapic reasons, the main-chains are driven to separate from the smectic side-chain graftings. This periodic microphase separation gives to the SCLCP, a “sandwitch-like” aspect (Figure 1). Scaling laws have been determined in the smectic phase of SCLCPs[6]. They reveal a gaussian trajectory of the main-chains in between two successive mesogen layers ($R_{\perp} = \alpha_{\perp} . Mw^{0.50\pm0.02}$) where Mw is the molecular weight and α a prefactor containing the persistence length. In the direction parallel to the director, the main-chain trajectory follows a rod-like behaviour ($R_{//} = \alpha_{//} . Mw^{0.85\pm0.04}$) confirming the assumption of "rapid" main-chain crossings (layer hopping model[7]) through the smectic lamellae but contrasts with a random distribution theoretically expected[7].

Experimentally, all the SCLCPs known up to now display a strong oblate main-chain anisotropy in the smectic phase, which means that in all the cases, $\alpha_{//} << \alpha_{\perp}$. (By applying the critical exponents[6], the polymer described below (Figure 2) is characterised by $\alpha_{//} = 5.10^{-5}$ and $\alpha_{\perp} = 0.18$). An interesting extension of these scaling laws is their extrapolation at $Mw \rightarrow \infty$. Indeed, the critical exponents of the scaling laws indicate that when the molecular weight has reached a sufficient value (corresponding to $Mw^{*}=(\alpha_{\perp}/\alpha_{//})^{2.86}$, an inversion of the anisotropy, from an oblate to a prolate main-chain conformation should occur (Figure 1).

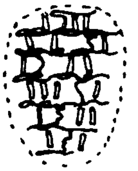
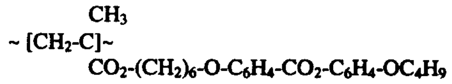


FIGURE 1: Supposed LC-polymer architecture extrapolated to the high molecular weight limit, in the smectic phase.

This curious anisotropic evolution of the conformation versus molecular weight evidences the rapid extension of the crossings through the layers, keeping locally the main-chains confined between the smectic layers. Such an evolution has strong implications under shear flow.

The comparison of the shear induced smectic behaviour of two chemically identical side-chain polymethacrylates (Figure 2) of different molecular weights $Mw1$=140000 and $Mw2$=610000 (the polydispersity are 2.8 and 2.7 respectively) provides the demonstration.

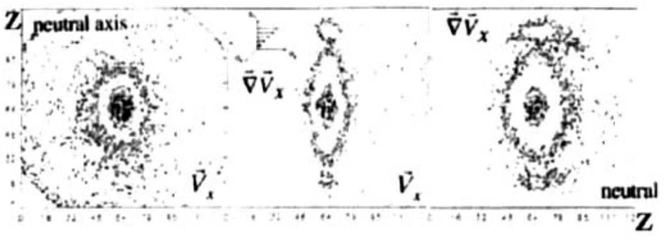
FIGURE 2 :



$$\sim[CH_2\text{-}\overset{CH_3}{\underset{CO_2\text{-}(CH_2)_6\text{-}O\text{-}C_6H_4\text{-}CO_2\text{-}C_6H_4\text{-}OC_4H_9}{C}}]\sim$$

Indeed, the low molecular weight $Mw1$ displays a parallel orientation as soon as applying a shear flow. The director is parallel to the velocity gradient and thus the smectic layers slip parallel to the plane (v,z) as long as the shear rate $\dot{\gamma}$ remains below 20s^{-1} at ΔT=10° below the nematic-smectic transition[2]. The high molecular weight $Mw2$ displays in contrast a perpendicular orientation; i.e. the director points along the vorticity (neutral axis) and the layers slip parallel to the $(v, \nabla v)$ plane, from the lowest shear rates and independently of the temperature. At equilibrium, the main-chain anisotropy in the smectic phase of the molecular weight *Mw1*, is about $\rho_{Mw1} = R_{\perp}/R_{/\!/} \approx 5.7$ whereas ρ_{Mw2} decreases down to 3.4 for the high molecular weight *Mw2* (calculated from the critical laws[6] on the basis of experimental measurements[5,2]). Because of the rod-like walk of the crossings, the ratio $\tau = R_{/\!/} / d$ where d the layer distance, is directly proportional to the number of crossings, and also to the extension of these crossings along the director. The effect of a molecular weight increase is thus a linear increase of the propagation of the layer crossings τ and a decrease of the previously defined anisotropy rate ρ_{Mw}.

In the shear induced parallel orientation, the smectic layers are supposed to slip over each other. Such a slip motion is not favoured by the main-chain elasticity if the anisotropy is weak (ρ_{Mw} small) or probably even completely forbidden in the case of a prolate anisotropy (shape extrapolated at large molecular weight). In such a case, to maintain the cohesion of the smectic layers, and to minimise the chain deformation, the only solution consists in adopting the perpendicular orientation. It is interesting to observe that the low molecular weight *Mw1* presents already the sign of instabilities which tend to rotate the layers from the parallel to the perpendicular orientation (the widths of the smectic reflection indicate than the mosaicity is about three times larger in Figure 3.c than in Figure 3.b). This behaviour is consistent with the existing models describing small LC-molecules[8]. In the case of these small LC-molecules, both parallel and perpendicular orientations coexist[9]. The parallel orientation displayed by the LC-polymer seems to be more stable than for small liquid crystalline molecules. It can be understood that a strong main-chain anisotropy and a relatively low molecular weight, as for *Mw1*, could contribute to a better stabilisation of the smectic interlayer against these undulation instabilities, at least as long as the extension of the layer crossings is weak.



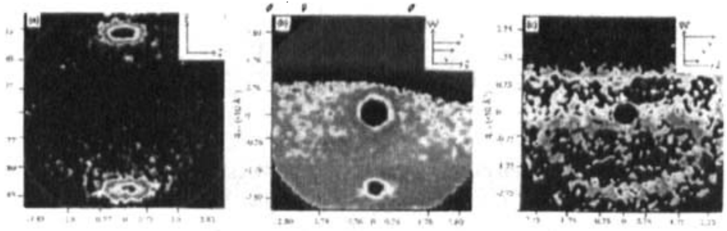
a) b) c)

FIGURE 3 : Neutron diffraction patterns (2m, 4Å) displayed in:
a) the (z,v) plane, b) the (∇v, v) plane, c) the (∇v,z) plane by the LC-polymethacrylate of molecular weight *Mw1* (on a quenched sample). The anisotropic shape centred on the direct beam is the form factor of the main-chain. The smectic spots are localised on both sides of the central scattering.

CONCLUSIONS

We have here demonstrated that the molecular weight of SCLCPs is a key parameter which governs the rheological behaviour in the smectic phase. Through the influence of the molecular weight, is revealed the crucial role of the main-chain layer crossings. If the main-chains contribute to the stability of the parallel orientation, the crossings constitute dynamic defects which penalise the flow symmetry when the main-chains is expanded over several layers. They correspond thus to a characteristic microstructural time of the system. Their time scale can be estimated to about $\nu = 0.05$s, 10 degrees below the N-S_A transition. Finally, an additional argument in favour of the determining influence of the crossings as characteristic time scale governing the non-equilibrium smectic state of SCLCPs, is the observation of a coexisting parallel and perpendicular orientations in the case of very low molecular weight LC-polyacrylate (*Mw3* = 25 000) displaying at equilibrium a large anisotropy rate $\rho \approx 3$[3,5] and an extension $R_{//} \cong 15$Å smaller than the smectic layer thickness (25Å). This LC-polymer differs from the previous one by the nature of the main-chain (polyacrylate chain) and by a methyl mesogen extremity (instead of a butyl). It presents several analogies with small liquid crystalline molecules because of its low molecular weight, its high anisotropy which indicates a very low rate of crossings if none, and finally a higher main-

chain flexibility which decreases the elastic contribution. This LC-polyacrylate shows indeed the typical behaviour of small LC-molecules with the formation of multilamellae smectic cylinders (Figure 4)[3].



a) b) c)

FIGURE 4: Neutron diffraction patterns displayed in the smectic phase of the LC-polacrylate of molecular weight *Mw3* a) in the *(v,z)* plane, b) in the *(∇v,v)* plane, c) in the *(∇v,z)* plane (reproduced from reference[3]). The upper part of Figures 4 b and c are shadowed by the absorbing part of the shear cell and by a multiple scattering phenomenon respectively.

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