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Steady-state shear experiments on a side-chain liquid-crystal polymer: Determination of the polymer conformation and liquid-crystal structure

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We consider the effect of shear on the structure and the conformation of the main chain of a side-chain liquid-crystal polymer. The liquid-crystalline polymer is sheared using a cone and plate device, and the effect of this shear is determined *in situ* by small angle neutron scattering. We find that, in the isotropic and the nematic phases, the main-chain extensions in the shear plane are invariant within the shear range studied. In the smectic phase, however, the main chain is elongated in the direction of the shear flow. This elongation is superposed to a confinement of these main chains between the mesogen layers. The mesogen layers exist in a well oriented mesophase parallel to the shear plane. [S1063-651X(96)11406-9]

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I. INTRODUCTION

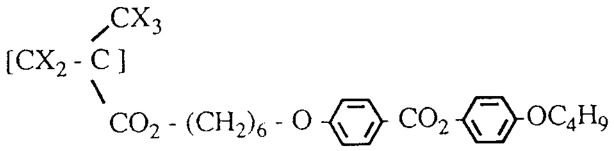
The obtaining of monodomains is a very important challenge in the field of liquid crystals or liquid-crystal polymers since microscopic properties can be related to macroscopic ones. The purpose of this paper is restricted to the study of the orientation of liquid-crystal polymers possessing a mesogenic group in the side chain, which are named side-chain liquid-crystal polymers

The orientation of the mesophase of such polymers is usually achieved by magnetic field [1], by film layering [2], or by stretching [3]. Although the shear flow process of orientation has been broadly studied for small molecules of liquid crystals [4], no similar study has been attempted concerning the orientation of side-chain liquid-crystal polymers in the bulk. Such experiments are important in the case of side-chain liquid-crystal polymers. The shear flow can act *a priori* on two different elements of the liquid-crystal polymer (the polymer conformation and/or the liquid-crystal phase orientation) and in particular we do not know what could be the influence of a deformed polymer on the mesophase. Indeed it is well known that a shear flow produces stretching of usual polymers (non-liquid-crystalline) and that side-chain liquid-crystal polymers are stretched in oriented mesophases, especially in the smectic phase [6], and there are, however, no data which demonstrate that preliminary sheared side-chain liquid-crystal polymers produce the orientation of the mesophase. It is important to note that the mechanism of shearing is different from that involved in a stretching. The symmetry of stretching is uniaxial whereas a shearing generally implies a planar geometry in which the polymer is placed at the interface of two plates, one mobile the other one fixed. The resulting motion can be considered as the superposition of a translation motion and a rotational motion. If the stretching is based on a process of chain disentanglements, the shearing depends also on the ability of the polymers to remain sticky on the surface. The shearing experiment proposed here is in contrast with what has already been done on similar stretched side-chain liquid-crystal polymers [5]. Moreover, it has the advantage of making possible the measurement in the isotropic state as well as in the nematic or smectic phase. In addition, the experiment is carried out *in situ* as a function of the temperature and the shear gradient, avoiding the difficulties present in the study of materials quenched under the glass transition.

We use neutron scattering on mixtures of labeled and unlabeled main chains of side-chain liquid-crystal polymers [7,6] to access the form factor of the main chain alone providing the average main-chain anisotropy and size during the shearing process.

II. MATERIALS AND METHOD: EXPERIMENTAL PART

The side-chain liquid-crystal polymer used in this work is a polymethacrylate, PMA-OC4H9, widely studied elsewhere [6,8,9] with the chemical formula:



$$\begin{array}{l}\qquad\quad CX_3\\ [CX_2 - C\,]\\ \qquad\quad CO_2-(CH_2)_6-O-C_6H_4-CO_2-C_6H_4-OC_4H_9\end{array}$$

with $X=H$ or D depending on whether the main-chain part is hydrogenated or deuterated.

The mixture has the following phase transition temperature (cooling rate −5 °C/mn):

$$I(\text{isotropic}) \underset{104\,^\circ\text{C}}{\longrightarrow} N(\text{nematic}) \underset{99\,^\circ\text{C}}{\longrightarrow} S_{\text{Al}}(\text{smectic}) \underset{35\,^\circ\text{C}}{\longrightarrow} T_g(\text{glassy}).$$

Five grams of the mixture of hydrogenated polymers and of polymers deuterated on the main chain have been prepared by evaporation from a chloroform solution. The mixture is heated to the isotropic phase and placed between the faces of a rotating quartz window and a fixed cone of an aluminium alloy (transparent to neutrons) of angle $\alpha=3°$ (see Fig. 1). Small resistances ensure the heater of the set and can provide a range of temperature between room temperature and 180 °C whereas the speed of the rotating window can vary from the static state to 100 rpm providing a maximum shear rate of $\dot{\gamma}\simeq 200\ \text{s}^{-1}$. The trajectory of the neutrons (beam diameter 7.6 mm) intercepts the top of the quartz window of

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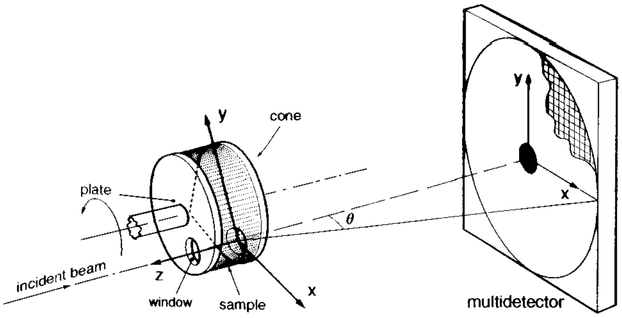

FIG. 1. Schematic representation of the SANS device equipped with the cone and plate cell whose plane is parallel to the two-dimensional multidetector plane. The neutron beam crosses the observation window which is placed at 4 cm from the rotation center.

the shearing matching at around 4 cm from the rotation center so that the shearing lines can be considered in the window as a horizontal flow.

The scattered beam is collected in the plane of the two-dimensional multidetector PAXY of the Laboratoire Léon Brillouin (Orphée Reactor, Centre d' Etudes de Saclay) which contains 128×128 cells of 5×5 mm each. The geometry adopted here corresponds to the observation of the shear plane xOy for which the flow is parallel to the Ox axis whereas the shear gradient in the plane xOz is parallel to the incident beam Oz. Two scattering ranges have been chosen: $0.03\ \text{Å}^{-1} < q < 0.3\ \text{Å}^{-1}$, which covers a scattering vector domain extended to the zone of the 001 smectic reflection corresponding to a layer distance of 29 Å, whereas $0.008\ \text{Å}^{-1} < q < 0.08\ \text{Å}^{-1}$ allows the measurement of the central scattering (where $\vec{q}$ is the scattering vector $[|\vec{q}| = (4\pi/\lambda)\sin(\theta/2)]$, θ is the scattering angle, and λ is the wavelength). This intensity $I(\vec{q})$ is proportional to the form factor $P(\vec{q})$ associated with the main-chain part of the polymer:

$$1/I(\vec{q})\,\alpha\,1/P(\vec{q}) = n\langle 1 + (q_x^2 R_x^2 + q_y^2 R_y^2 + q_z^2 R_z^2)\rangle.$$

n is the degree of polymerization and R_x, R_y, and R_z are the components following the three main directions Ox (parallel to the flow), Oy (neutral direction), and Oz (parallel to the velocity gradient) of the radius of gyration R_g ($R_g^2 = R_x^2 + R_y^2 + R_z^2$). This formula is applied assuming the small angle approximation ($\vec{q}_i \cdot \vec{R}_i \leqslant 2$) is fulfilled.

The distance chosen is 2 m and the wavelength can be switched from 3 Å to 12 Å to access each scattering range. The neutron measurements are normalized by an incoherent scatterer and corrected from the background noise by subtracting the intensity scattered by the empty shearing machine.

III. RESULTS

The molecular weight of the mixture has been determined by gel permeation chromafography light scattering on line (C. Strazielle at the ICS Strasbourg) before and after the experiment. Before the experiment, the weight average molecular weight was 212 000 and the polydispersity was $I = 2.92$, whereas after the shearing experiment the molecular weight was 154 000 and the polydispersity $I = 2.85$. This result indicates clearly a reduction of the chain length due to mechanical shear. On the other hand, no shift of phase transition temperature has been detected between the original sample and the sheared one on differential scanning calorimetry (DSC) thermograms (heating rate +5 °C/mn from room temperature up to 120 °C).

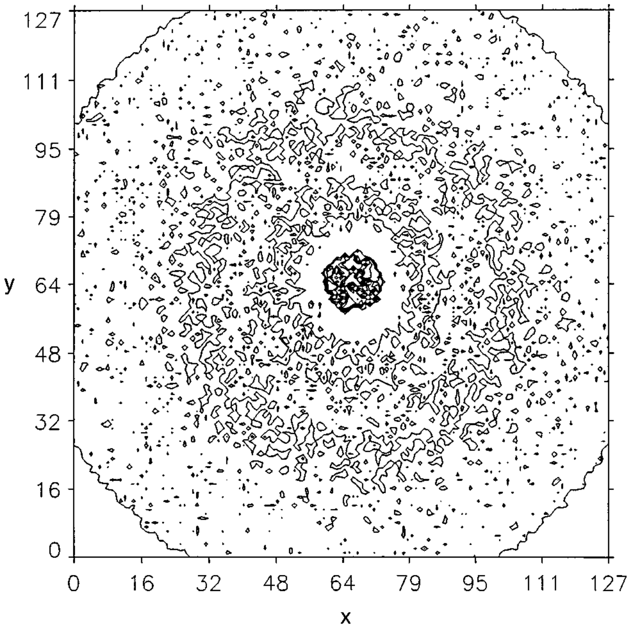

FIG. 2. Isointensity lines corresponding to the small angle scattering observed in the xOy plane ($\lambda = 12$ Å, $d = 2$ m) of the mixture PMA(H)-OC4H9–PMA(D)-OC4H9 at 117 °C.

A. Main-chain conformation of PMA-OC4H9 in the isotropic and nematic phases

As previously explained, the geometry of the device gives access to the xOy observation plane providing the measurement *in situ* of the components R_x and R_y of the radius of gyration of the polymer main chain. A first experiment has been carried out in the isotropic phase at 117 °C. Figure 2 gives a view of the small angle neutron scattering pattern associated with the form factor of the polymer backbone of PMA-OC4H9 at 117 °C under a shear gradient of $\dot{\gamma} = 20\ \text{s}^{-1}$. No difference in the polymer main-chain shape or size can be observed compared to the isotropic phase at rest. The main-chain conformation is invariant in the xOy plane [within the accuracy of the measurements $R_x = R_y = R$ (at rest)] whatever the value of the shear gradient between 0 and 20 s^{-1} (Fig. 3). Higher shear gradients induce a loss of the surface adherence of the polymer.

The nematic phase of PMA-OC4H9 corresponds to a very narrow temperature range (≈5 °C). X-ray and neutron measurements revealed the presence of smectic fluctuations on samples aligned with a magnetic field [6a,b]. This phase is reached by decreasing the temperature down to 101±2 °C either from a sheared isotropic phase or from the isotropic phase at rest obtained after annealing the thermal history (heated 4 h at 140 °C).

In the first case, the sample keeps its transparency when passing from the isotropic phase down to temperatures corresponding to the nematic phase under a shear gradient of 1.5 s^{-1}. Different shear gradients have been applied, varying be-

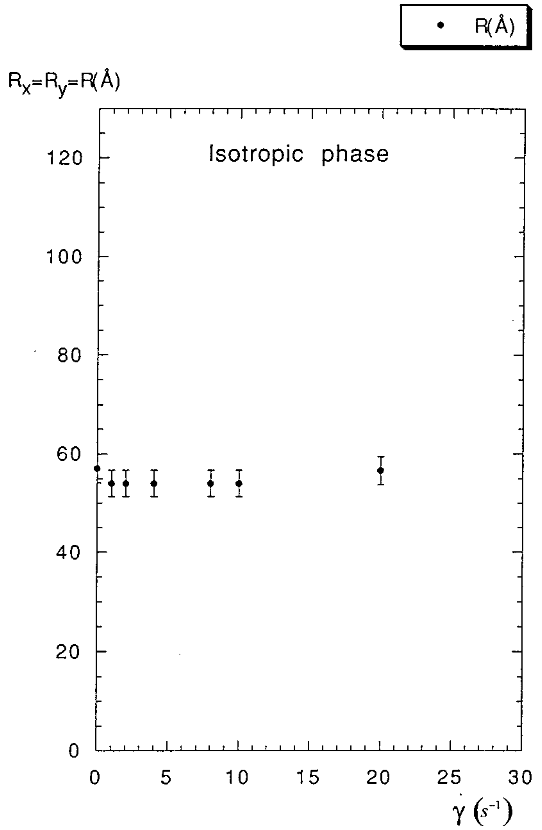

FIG. 3. Experimental values of the components $R(\text{Å})=R_x=R_y$ of the radius of gyration of the polymer main chain as a function of the shear gradient at 117 °C in the isotropic phase.

tween $0.1<\dot{\gamma}<4$ s^{-1}. No modification of the shape of the polymer main chain or optical transparency (which cannot fit with the presence of large disoriented nematic polydomains) can be detected in this shear range.

In the second case, the initially dark sample (presence of polydomains) rapidly becomes transparent as soon as the shearing process starts. In both cases, the sample is, or becomes, transparent which is compatible with the establishment of a macroscopic oriented monodomain. Moreover, the observation of the scattering domain at large angles indicates that there are no smectic fluctuations in this plane which are coherent with the existence of a well-oriented phase. On the other hand, the *x-y* dimensions of the main chain measured at this temperature in the *xOy* plane remain unchanged in this phase (similar to the values obtained in the isotropic phase).

B. Main-chain conformation of PMA-OC4H9 in the smectic-*A* phase

1. Observation in the xOy plane

The measurements were first carried out at 93±2 °C which corresponds to the high temperature smectic phase. Two experiments as a function of thermal story have been achieved at this temperature depending on whether or not the polymer has been previously submitted to shearing in the isotropic and the nematic phases. Both experiments started with the polymer at rest. A progressive main-chain deformation is observed in the *xOy* plane as a function of the increase of shear rate which occurs at shear gradients between 0.5 s^{-1} and 1.4 s^{-1} (reciprocally the coil deformation is observed from 93 °C by decreasing the temperature from the nematic-smectic transition while keeping a constant shear rate of 1.4 s^{-1}). The evolution of R_x versus shear values (Fig. 4) indicates that the dimension of the polymer main chain in the direction of the flow first grows rapidly and then almost saturates for shear gradients $\dot{\gamma}>4$ s^{-1}. The accuracy of these first measurements do not allow a determination of a critical shear rate which occurs at a very small rate at this temperature. The perpendicular component R_y of the main chain remains unchanged (within error) whatever the shear gradient. The initial values of R_x and R_y are almost completely recovered once the shearing is stopped (we can estimate that the ratio R_x/R_y decreases from 1.8 to 1.2 after 800 s at 93 °C; however the acquisition time is a severe restriction for such measurements). The observation at large angles indicates that there is no extra scattering in the *xOy* plane whatever the temperature or the shear gradient used.

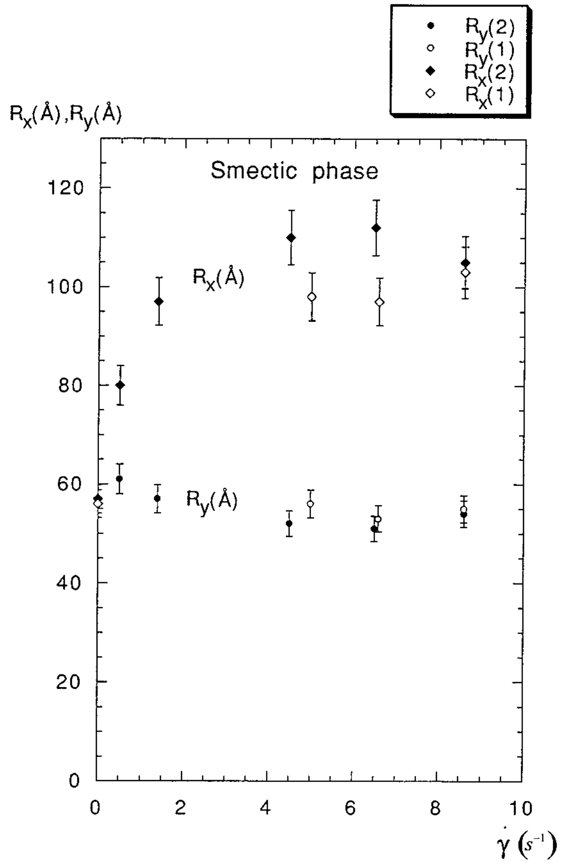

FIG. 4. Experimental values of the components R_x and R_y of the radius of gyration of the polymer main chain as a function of the shear gradient at 93 °C in the high temperature smectic phase. Open symbols are related to the sample previously sheared at higher temperature and filled symbols denote the experiment starting with a polymer at rest (a possible shift of temperature exists between the two experiments and can be estimated to ±2 °C).

2. Observation at room temperature of the xOy, xOz, and yOz scattering planes

The same sample is slowly cooled under shear until 80 °C and rapidly cooled down to room temperature which is be-

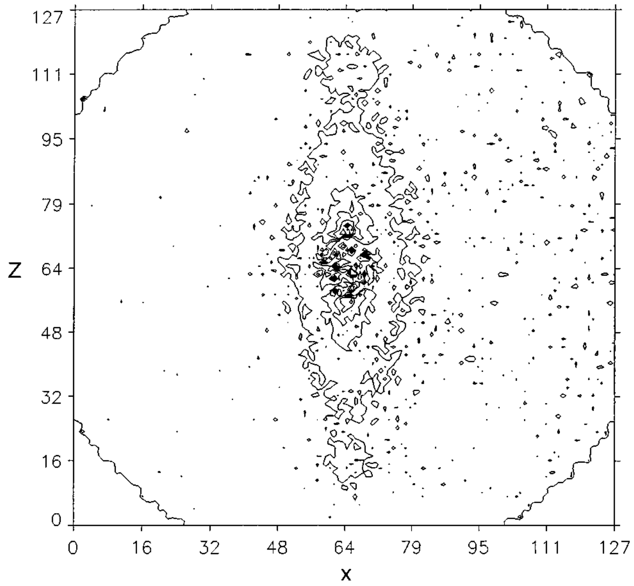

FIG. 5. Picture of the scattering observed at room temperature in the *xOz* plane ($\lambda=3$ Å, $d=2$ m) on the sample previously sheared at high temperature. The 001 smectic reflections at the top and at the bottom of the pattern border the anisotropic small angle scattering.

low the glass transition temperature. During the cooling process, the optical transparency of the sample was preserved and it can be assumed that the structure then observed at low temperature corresponds to a state similar to the structure at 80 °C. Small slices of oriented polymers are cut in order to prepare three samples corresponding, respectively, to the observation of the structure and conformation of the main chain in the three principal planes *xOy*, *xOz*, and *yOz*. In the *xOy* plane the same observation as previously done *in situ* at higher temperatures can be done at room temperature; there is no other extra scattering except for the central scattering. This information has been confirmed on x-ray pattern.

The observation in the *xOz* plane shows on each side of the anisotropic central scattering the 001 smectic reflection indicating that smectic layers have been developed parallel to the *xOy* plane (Fig. 5). The central scattering confirms that the polymer main chains are confined perpendicular to the mesogen direction as has already been observed for smectic liquid-crystal polymers at rest [6]. The normal axis to the layers is parallel to the *z* axis. The width of the smectic spots (half width at half maximum approximately equal to 10^{-2} Å^{-1}) indicates that the order range is equivalent to what is usually obtained in the case of alignment with a magnetic field. X-ray patterns obtained at higher angles in this scattering plane show three smectic orders identical to those previously observed for samples oriented with a magnetic field [9]. The transparency of the sample previously observed at higher temperature in the nematic or in the high temperature smectic phase indicates the alignment of the monodomains. We have also determined that the three smectic reflections exist in the direction corresponding to the observation of the *yOz* plane (shear front).

IV. DISCUSSION

The polymer studied here, PMA-OC4H9, was previously investigated from a rheological point of view. These preliminary measurements carried out with a Rheometrics RMS 605 rheometer (EAHP, Strasbourg) have revealed a non-Newtonian behavior with a viscosity law $\eta^* \alpha \dot{\gamma}^{-0.5}$, in a temperature range between 120 °C and 65 °C for a frequency interval between 10^{-2}–10^{2} s^{-1}, but no large characteristic time was found. The inability to determine any characteristic mode τ for the polymer makes it difficult to determine a shear regime corresponding to $\dot{\gamma}\tau \geqslant 1$ for which an eventual observation of the isotropic coil-stretch deformation of the polymer main chain is possible [10].

In the isotropic phase, no change in the main-chain dimensions nor in the coil isotropy has been observed from the smallest shear gradients up to 20 s^{-1}. On the other hand, the persistence length of the polymer main chain has been estimated to be about 20 Å in the isotropic phase [6] indicating a chain flexibility close to that of a polystyrene chain. From the relative high flexibility of the chain together with the absence of deformation under shear in the isotropic phase, it can be concluded that the internal mobility of the chain is higher than the velocity gradient induced by friction with the neighbor streamed polymers. As a consequence, the average polymer conformation is not altered in the isotropic phase. This result is not in contradiction with the rheological observations, if we consider the non-Newtonian behavior as a result of a side-chain contribution rather than that of the main chain.

It can be interesting to attempt a comparison between the behavior of the liquid-crystal polymer in the isotropic phase (80 °C above the glass transition temperature) with the behavior of a usual polymer heated at 80 °C above its glass transition. The polystyrene reported in [11] can be considered as a reference since it presents a flexibility similar to the liquid-crystal polymer studied here. It is reported that this polystyrene chain of degree of polymerization (DP) 900 already presents a deformation of about 18% for shear rates of the order of $\dot{\gamma}=10^{-4}$ s^{-1} at a temperature of 23 °C above the glass transition temperature of 100 °C. Using the Williams-Landau-Ferry equation to calculate the variation of viscosity between 123 °C and 180 °C and estimating the shear rate γ for a polymerization degree equivalent to that of the liquid-crystal polymer (DP of 350), we expect a deformation for shear gradients equal to or higher than $[\eta(180\ ^\circ\mathrm{C})/\eta(123\ ^\circ\mathrm{C})]10^{-3} \approx 10$ s^{-1}. The absence of main-chain deformation for gradients up to 20 s^{-1} indicates that the liquid-crystal polymer, even in a nonliquid crystalline phase, remains different from an ordinary polymer (assuming that the laws of viscosity-temperature equivalence are valid).

In the nematic phase, the shear gradient used here was not sufficiently high to deform the polymer coil. However, the same gradients were sufficient to induce the orientation of the nematic monodomains since the sample became transparent almost as soon as the shear was applied. Under the influence of shear flow, liquid crystalline orientation and/or polymer stretching can occur and it appears here, for this shear range, that the process of phase orientation overrides the polymer deformation.

The situation in the smectic phase is similar to that of the nematic phase. The transparency of the sample indicates that the smectic monodomains are first aligned at a low shear rate before any deformation of the main-chain extensions R_x and R_y in the shear plane [whereas R_z is considerably reduced because of the compression induced by the mesogenic layers [6,8], the figure observed at low temperature (Fig. 5) demonstrates *a posteriori* that this phenomenon had effectively taken place]. The smectic layers are oriented parallel to the shear plane which explains why no smectic reflection was visible in that plane. Such an arrangement allows an internal slit of the mesogen layers on each other but this slitting is hindered by the entangled main chains confined between mesogen layers (Fig. 5) and also by the polymers crossing the layers. The confinement of the main chains between smectic layers formed by the side chains starts as soon as the nematic-smectic transition occurs, whereas a certain proportion of main chains cross the side-chain layers [6]. The population of confined main chains and main chains crossing the layers is a dynamical process which varies as a function of the temperature [6]. In the low shear regime, the flow acts only at the level of the monodomains and a number of layers move together. As a result, the main chains are not sheared and the conformation remains, on average, isotropic. However, at higher shear gradients, the velocity of each smectic layer becomes sufficiently different from one layer to the other to induce an effective plane-plane shear at the scale of the layer. As a consequence, the main chains at the interfaces of the mesogen layers are now sheared by the layers following the Ox direction (which is different from the effect of a shear flow which would induce a tilt of the polymer in the xOz plane [11]). One can easily imagine that the main chains opposed to the slit motion of the smectic planes such as polymers participating in two successive layers are the first to be strongly drawn in the Ox direction. This process will also affect the other chains because of the numerous entanglements which bind the main chains to each other. This results in, as has been observed here, an elongation of the main-chain extension R_x which is all the more strong when the shear gradient is high. The gradual evolution of R_x versus $\dot{\gamma}$ is in agreement with theoretical predictions for usual polymers under constant shear [10]. The main-chain stretching (for $\dot{\gamma}=4\ \mathrm{s}^{-1}$: $R_x/R_y \approx 2$) of the shear flow remains less important than the main-chain confinement produced by the side-chain smectic layers [at rest, $R(x,y)/Rz \approx 4$ [6]). It is also interesting to remark that the perpendicular extension R_y of the main chain in the smectic plane (neutral direction) remains constant. This observation has also reported for usual polymers (polystyrene) [11].

V. CONCLUSIONS

This experiment demonstrates the difference in behavior between a liquid-crystalline polymer and a usual polymer under shear flow. Surprisingly, the main-chain conformation remains isotropic, in the isotropic phase, under shear gradients of up to 20 s^{-1}. Since the main chains are not sensitive to a shear effect in this regime, it seems that the non-Newtonian behavior observed by rheological measurements is likely related to a complex side-chain contribution than to the main-chain behavior itself. By decreasing the temperature, the effect of shearing favors first the orientation of the mesophase with, in particular, the orientation of the smectic planes parallel to the plate planes.

The second effect is indirect since the shear process is ensured by the smectic layers which stretch the main chains in the direction of the layer displacement. This is somewhat in contrast with the effect of a shear flow on ordinary polymers which produces a tilt of the molecule in the zOx plane. The tendency to align the monodomains before stretching the polymer main chain together when obtaining, at higher shear gradients, a weak main-chain deformation $(R_x/R_y=2)$ in the xOy plane is the obvious demonstration of the dominating influence of the liquid-crystalline order on the mechanical properties on the polymer. However, many questions remain unanswered since we could only observe the xOy plane as a function of the temperature and not the vorticity plane (zOx) which would certainly provide more information on the process of orientation of the mesogen layers and of the stretching of the polymer due to the slitting of these layers. On the other hand, it would be of interest to know if by increasing the shear gradient more we could encourage the stretching of the polymer relative to the orientation of the liquid-crystal phase. What would be the resulting mesophase? This work is in progress.

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