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Laurence Noirez [a] & Alain Lapp [a]

[a] Laboratoire Léon Brillouin (CEA-CNRS), Ce-Saclay, 91191, Gif-sur-Yvette Cédex, France

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OBSERVATION OF THE STRUCTURE AND THE DEFORMATION OF A LIQUID-CRYSTALLINE POLYMER UNDER SHEAR FLOW

LAURENCE NOIREZ, ALAIN LAPP
Laboratoire Léon Brillouin (CEA-CNRS), Ce-Saclay, 91191 Gif-sur-Yvette
Cédex, France

Abstract We determined the evolution of the main-chain conformation and of the liquid crystalline structure of a liquid crystal polymethacrylate in the smectic phase, versus shear rate. It is shown that the macroscopic shear was transmitted to the smectic layers which ensured an efficient shear of the polymer main-chains. The outcome was a macroscopic orientation of the smectic monodomains with the smectic planes parallel to the shear plane. The polymer main-chains already confined by the mesogenic layers, were in addition, the more elongated along the velocity direction that the stronger, the shear was. These results were obtained *in situ* by the observations in the shear plane and in the vorticity plane.

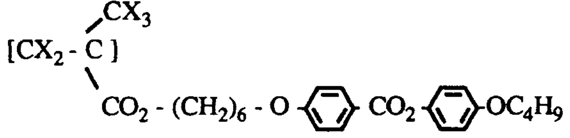
INTRODUCTION

The effects of a steady-state shear on the behaviour of liquid crystals or on the behaviour of "usual" polymers is well known, both from an experimental and a theoretical point of view [1]. In contrast, the behaviour of liquid crystal polymers under shear is yet far from being elucidated. Very interesting phenomena can be expected for liquid crystal polymers owing to the competition between the internal strain already provided by the side-chain mesogens on the polymer main-chain and the external strain brought by the shear process [2]. Neutron scattering techniques on partially deuterated polymers is the only method which can provide the bulk conformation adopted by the polymer main-chain. This method has been already employed with success in the case of the study of liquid crystalline polymers at rest [3]. The use of a cone-plate cell adapted to the observation of the shear plane together with the use of a new cell built for the observation of the vorticity plane, allows a complete description of the geometry adopted by the polymer under shear flow.

We propose to describe the informations carried out with these two devices and to give an interpretation of the results obtained with this method. The analysis concerns as well the conformation of the polymer main-chain (obtained from small-angle neutron scattering data) as structure of the phase obtained at larger angles.

EXPERIMENTAL

The liquid-crystalline polymer corresponds to the structural formula:



$$[CX_2-\overset{CX_3}{C}]-CO_2-(CH_2)_6-O-C_6H_4-CO_2-C_6H_4-OC_4H_9$$

with either X=H or X=D since the 1:1 isotopic mixture sample is needed to obtain the central scattering associated to the main-chain conformation.

The sample presents the following mesophases and transition temperatures: Tg - 35°C - SA1(smectic) - 99°C - N(nematic)- 104°C - I(isotropic). (values determined by DSC with a cooling rate of -5°C/mn).

The molecular weight has been determined by Gel Permeation Chromatography-Light Scattering on line before and after the shear experiment; the weight average is Mw=150000 with the polydispersity I≈2.8.

The two shearing devices are illustrated in figure 1.

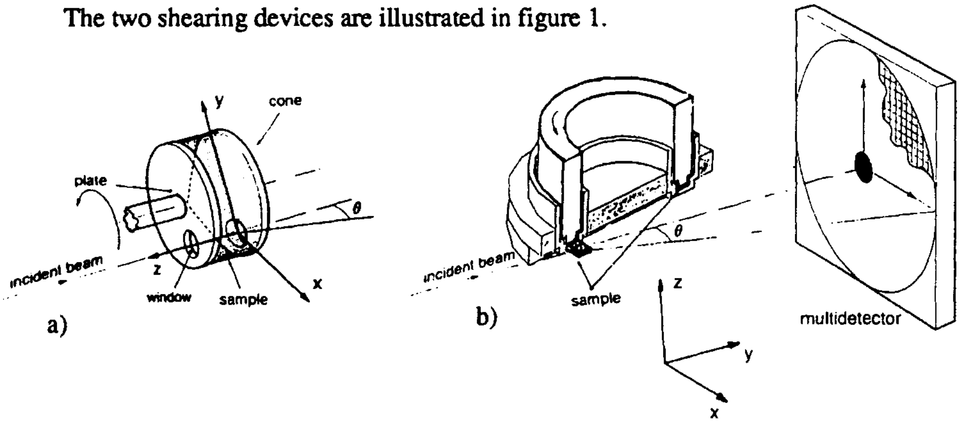


FIGURE.1: Schematic representation of the SANS device equipped:
a) with the cone and plate cell which plane is parallel to the 2d-multidetector plane. The neutron beam crosses the observation window placed at 4cm from the rotation centre.
b) with the new device which allows the observation of the vorticity plane. The neutron beam intercepts the tangent of one side of the ring over the 1mm hight and 7mm width.

The first one consists in a standard cone and plate device (Fig.1a) filled with five grammes of the 1:1 mixture of hydrogenated polymers and of polymers deuterated on the main-chain (prepared by evaporation from a chloroform solution). The mixture was heated to the isotropic phase and placed between the faces of a rotating Quartz window and a fixed cone of an aluminium alloy (which can be considered as transparent to neutrons as long as we do not take into account the very small angles of scattering) of angle $\alpha=3°$ (see figure 1a). 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 50rpm providing a maximum shear rate of $\gamma \approx 100\ s^{-1}$. The trajectory of the neutrons (beam diameter 7.6mm) intercepts the observation window of the shearing machine at around 4cm from the rotation centre so that the shearing lines can be considered in the window as a linear flow along the horizontal axis Oy.

The second device (Fig. 1b) consists of a thin hollow open Aluminium ring (3.5mm wide and 1mm deep). At the bottom of the well, the polymer was placed top a sample depth of 1mm. This part is the static one. Over this part, a filled ring of the same width and diameter is placed in contact with the polymer and ensures the shear by a steady-state rotation around the same axis. The set is tilted of 3-4° (from to the horizontal) in order to place only one side of the ring on the beam trajectory. The same system of small resistances and rotation ensures the heating of the set and the shear process of the material.

The scattered beam is collected on a x-y multidetector (PAXY of the Laboratory Léon Brillouin) of 128x128 cells. The data are normalized with an incoherent scatterer and the background noise of the empty set (without polymer) is subtracted from the signal. Two configurations have been choosen differing from the wavelength λ=10Å for the observation of the small-angle region, and λ=3.5Å for the observation of the 001 smectic reflection. In both cases, the multidetector-sample distance is 2 meters.

The scattering range corresponding to the small-angle conditions ($0.008\ Å^{-1} < q < 0.08\ Å^{-1}$ with $\vec{q}$ the scattering vector ($|\vec{q}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) where θ is the scattering angle and λ, the wavelength) justifies the Guinier approximation for which the scattered intensity $I(\vec{q})$ is proportional to the form factor $P(\vec{q})$ associated to the polymer main-chain :

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

where Rx, Ry, Rz are respectively the components of the radius of gyration following the Ox axis (parallel to the velocity direction), following the Oy axis (perpendicular to the velocity direction and parallel to the shear plane) and following the Oz axis (parallel to the velocity gradient).

RESULTS -DISCUSSION

We already know from previous studies on side-chain liquid-crystalline polymers that the main-chain conformation is a random coil in the isotropic phase, it becomes a slightly oblate in the nematic phase and adopts a strong oblate conformation in the smectic phase

[3]. In addition, we have demonstrated that the smectic corresponds to a microsegregation of the polymer main-chain in sublayers where the main-chains are more numerous between two adjacent mesogenic layers [4]. These results have been obtained on samples at rest aligned by a magnetic field in order to provide a monodomain sample. What happens now if a new caracteristic time is introduced via the shearing ? It is necessary to have a significant effect to apply the shear not far from phase transition temperatures. The experiments under shear flow which are described here, are carried out in the high temperature smectic phase (93±2°C) close to the nematic-smectic transition, on a melt of liquid-crystalline polymer without any specific orientation.

Observation of the main-chain deformation in the shear plane (xOy):

At the lowest shear rates ($1.5\ s^{-1}$), the xOy plane reveals that the main-chains begin to be elongated along the velocity axis (Ox). The absence of smectic reflections at larger angles together with the observation on quenched samples of well-oriented smectic reflections in the planes perpendicular to the xOy plane, are the first signs that the orientation of the smectic layers under shear, is carried out parallely to the shear plane[5]. Fig. 2 represents the small-angle scattering obtained in the xOy plane for a shear rate $5\ s^{-1}$.

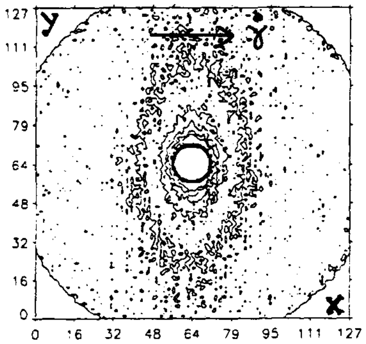


FIGURE 2: Isointensity lines associated to the SANS observed at 12Å, 2m in the shear plane (xOy) for the H/D mixture sheared at 93°C and $8s^{-1}$. The horizontal and vertical scales are given in cell units.

This shape remains approximatively the same whatever the shear rate above $4\ s^{-1}$ and corresponds to an anisotropy rate[5] of $\rho = Rx/Ry = 1/2$. However, at this temperature, once the shear is stopped the polymer main-chain recovers rapidly an isotropic conformation similar to what is found in the xOy plane for polymers aligned with a magnetic field (without shear). This behaviour is the indirect indication that the conformation adopted by the main-chains at rest in the smectic planes, is more consistent with a gaussian behaviour[3] than to a rod-like walk as it was theoretically suggested[6]. It is also important to notice that the anisotropy rate measured under shear in this plane is largely less significant than the anisotropy resulting of the establishment of the smectic layers. The same polymer aligned with a magnetic field, presents clearly a much stronger oblate shape with an anisotropy rate[3] of R(x,y)/R(z)=4. This comparison seems to indicate that the formation of mesogen layers exercices a stronger influence onto the main-chain deformation than the effect of a shear. However, it is then necessary to proove this statement to look directly, during the shear, in the plane xOz where the smectic reflections appear, which is perpendicular to the shear plane and parallel to the velocity direction (vorticity plane).

Observation of the scattering in the vorticity plane (xOz):

The device described in Fig.1.b gives rise to the observation of the vorticity plane. Fig.3 gives an illustration of the scattering observed at γ= 6 s^{-1} in the yOz plane.

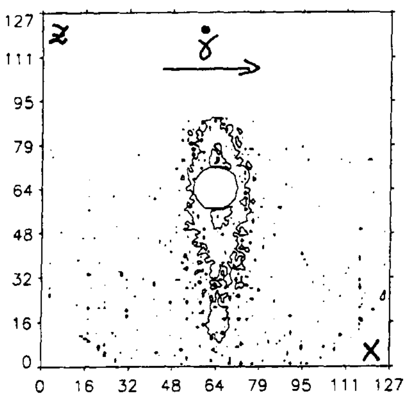


FIGURE 3: Isointensity lines of the scattering observed for γ=6s^{-1} at λ=3.5Å and d=2m, in the vorticity plane (xOz) at 93°C. The top of the figure is missing since the upper part of the device 1b matches the scattered beam. The spot located at the bottom of the figure corresponds to the 001 smectic reflection. The small angle scattering centred on the beam trapp is elongated along the Oz axis indicated that the main-chains are extended perpendiculary to the mesogen orientation.

The 001 smectic reflection is clearly seen at the bottom of the picture. The half width at half maximum of the peak indicates that the layers are established over a distance larger than 200Å, its position corresponds to a smectic thickness of 29±1Å. This value is similar to what is obtained at rest. The mesogens do not seem to be tilted during the shear process. It is also interesting to notice that the orientation takes place very abruptly as soon 1 s^{-1}, and seems to be destroyed for shear rates up to 14 s^{-1}. However, instabilities induced by the surface in motion or a change of orientation of the layers cannot be excluded, and have to be checked in the future. The central scattering is elongated along the vertical axis indicating that the polymer main-chain is effectively confined between the mesogenic layers during the shear process. The main-chain anisotropy, estimated when the smectic reflection takes its maximum value (for $4<\gamma<10$ s^{-1}), corresponds to values of radii of gyration Rx=80Å, Rz=25Å which is of the order of what it is usually measured in this plane for polymer at rest.

CONCLUSIONS

By combination of the analysis carried out on the two scattering planes (xOy and xOz), we can state that the shear has two effects on a desordered smectic phase. For shear rates included between $4<\gamma<10\ \text{s}^{-1}$, the liquid crystalline phase is aligned in a well defined monodomain whose smectic planes are oriented parallely to the shear plane. The smectic reflections are then visible in the vorticity plane (xOz). This plane reveals that the smectic layers are oriented along the velocity direction without any significant variation of the thickness. Also in this plane, we can confirm that the polymer main-chain is more extended following the Ox direction which is in agreement with a confinement of the main-chains between mesogen layers. This result is in contrast with the behaviour of usual polymers under shear which adopt a global tilted conformation in the velocity gradient[2]. In addition, the scattering plane (xOy) has revealed that the polymer main-chain is also elongated along the velocity direction. This means that main-chains sheared in the smectic phase, tends to adopt a one-dimensional walk along the velocity axis Ox. However, the walk is more restricted in the direction parallel to the mesogens than in the smectic phase. This result shows the dominating influence of the smectic strength over the shear constraint in this range of temperature and shear.

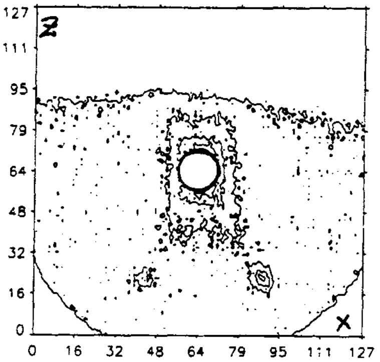


FIGURE 4: Relaxation figure observed in the same conditions as for Fig.4 obtained after a shear rate of 20s^{-1} and 2 hours at rest. The smectic reflection is splitted in to 2 spots tilted of 27° with the meridian and the central scattering indicates that the main-chains are tilted in the same way between the mesogen layers.

The relaxation phenomena are also very promising; At high temperature for low shear rates $(4<\gamma<10\ \text{s}^{-1})$, the relaxation process is rapid and the main-chains recover the gaussian conformation adopted at rest. However, for higher shear rates, the relaxation induces a tilt of the smectic layers. A similar tilt orientation occurs for the main-chains (Fig.4). This latter phenomenon is still to be elucidated.

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