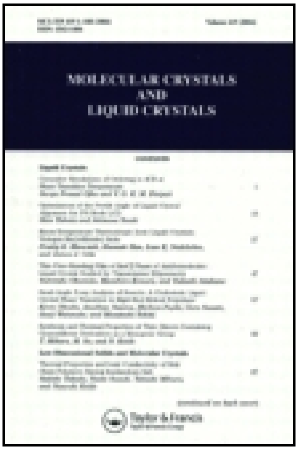

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Neutron Scattering Study of the Shear Induced Behaviours of the Smectic Phase of a Side Chain Liquid Crystal Polymers

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Neutron Scattering Study of the Shear Induced Behaviours of the Smectic Phase of a Side Chain Liquid Crystal Polymers

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We study the shear induced behaviour of a side-chain liquid crystal polymer, PA-OCH_3, within the smectic (S_A) phase using small angle neutron scattering technique. We show that the formation of multilayer cylinders oriented along the velocity direction is a stable geometry which can be observed at different shear rates and temperatures in the S_A phase. A careful examination of the scattering intensities displayed on both $(\vec{z},\vec{v})$ and $(\vec{v},\vec{\nabla}v)$ planes indicates that the population of layers is higher along the neutral axis $\vec{z}$. The perpendicular orientation is thus more favoured than the parallel one. In the vicinity of the nematic (N)- S_A phase transition a shear induced S_A phase is observed, followed by a shear induced nematic phase reentrance at higher shear rates. A comparison with low molecular weight liquid crystals is carried out. Ms number DV3663. PACS numbers: 10.10.+q, 12.15.Ji,14.80.Ef, 14.80.Gt

I. INTRODUCTION

The study of layered materials under shear constraint has been the subject of several theoretical and experimental works during the last years.[1–7] Thermotropic smectic (S_A) phases of liquid crystals (LC) and side-chain liquid crystal polymers (SCLCPs) are some of the layered systems studied under shear flow [1–7].

SCLCPs are made by a main chain, which can be a flexible polymer chain as here and by mesogens laterally attached onto the main chain. The director of the liquid crystal phase, $\vec{n}$, is given by the average orientation of the mesogenic

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* Corresponding author.

groups.[5–7] In the S_A phase, in the absence of external constraints, the mesogens are aligned in smectic layers and the polymer main chains preferentially occupy the space available between the layers.[8] In contrast to LCs, the shear flow can exacerbate in different degrees each one of the main basic elements of SCLCPs: the polymer conformation and/or the LC phase orientation.[5–7]

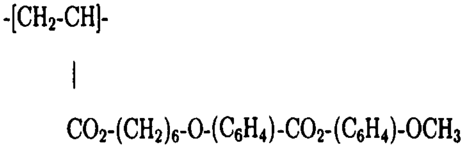
The variety of orientations and structures exhibited by smectic LCs and SCLCPs under shear flow, is a complicated function of the temperature T and the shear rate $\dot{\gamma}$. [1–7] In particular, although there is no theory available to explain SCLCPs behaviour under shear flow, results on LC under shear constraint could be successfully explained by theoretical models based in terms of the study of thermal fluctuations of the smectic layers [3] and also in terms of the critical smectic fluctuations on the hydrodynamics of the system in the vicinity of the Nematic (N) – S_A phase transition.[1]

In a previous work we gave, using neutron scattering technique,[7]a very accurate description of the evolution of the conformation displayed first at rest by the SCLCP called PA-OCH_3, and then under a steady state shear flow in the N phase. The behaviour in the N phase revealed a shear induced transition from a flow aligning ($\vec{n}$ parallel to $\vec{v}$) to a non-flow aligning regime ($\vec{n}$ becomes parallel to $\vec{z}$) by decreasing the temperature. This transition is related to a change, at rest, from prolate to oblate main chain conformation. Very first results on the S_A phase showed that the smectic layers form multilayers cylinders which axis are oriented along the shear flow direction. It was open to question if the multilayer cylinders are the definitive shear induced smetic geometry or if they correspond to an intermediate state. A parallel orientation was indeed found in the case of higher molecular weight SCLCPs,[5–6] in agreement with what was also observed in the frame of block copolymers.[2] In contrast, our early experiments have shown that PA-OCH_3 behaves under shear flow similarly to small molecular weight LCs,[1,4] thus screening the polymeric nature of SCLCPs. Therefore, it appears necessary to go further insight in the description of the shear flow behaviour in particular by applying higher shear rates within the S_A phase.

Due to the lack of theories specially developed for SCLCPs under shear flow, we will interpret our results in the frame of models already developed for LCs.[1,3] We will also establish the parameters of the answer to the external shear constraint which denote the polymeric nature of PA-OCH_3. After this goal, we will consider measurements made *in situ* for different temperatures and shear rates, using neutron scattering, and we will also use our preliminary results on the S_A phase under shear flow,[7] as a context for the interpretation of our data.

II. EXPERIMENTAL

The PA-OCH_3 SCLCP polyacrylate used in this study, corresponding to the chemical formula:



$$\begin{array}{c}-[CH_2\text{-}CH]- \\ | \\ CO_2\text{-}(CH_2)_6\text{-}O\text{-}(C_6H_4)\text{-}CO_2\text{-}(C_6H_4)\text{-}OCH_3\end{array}$$

has a molecular weight Mw~ 27600 and the polydispersity Ip~ 1.7.

In this work we will investigate the structure of the S_A phase under shear flow, through the study of the diffraction pattern obtained by neutron scattering.

The phase transition temperatures were determined using Differential Scanning Calorimetry. PA-OCH_3 presents the following sequence of temperatures: glassy state – 22°C – S_A – 89°C – N – 116°C – I (isotropic). The S_A phase is characterised by the presence of the 001 smectic reflection at q= 0.256 ± 0.001Å^{-1} (accurate value measured on 3-axis spectrometer at room temperature with $|\vec{q}|$: scattering vector= $4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength radiation). This reflection corresponds to a monolayer structure of interlayer distance ~ 25 Å which does not present any significant evolution versus temperature or shear rate.

Our study was made using the small angle neutron scattering 2d-multidetector (PAXY) of the Laboratoire Léon Brillouin (CEA-CNRS). A wavelength λ= 4 Å and a sample-multidetector distance D= 1.5 m were chosen in order to measure the first smectic reflection.

Two different shear devices were used to study *in situ* the $(\vec{v}, \vec{z})$ or the $(\vec{v}, \vec{\nabla} v)$ shear planes, with associated coordinates (q_v, q_z) and $(q_v, q_{\nabla v})$ respectively.

The observation of the $(\vec{v}, \vec{z})$ plane was obtained with a cone-plate shear cell.[5] This device consists of a thin circular cone made of Aluminium and a quartz plate of same diameter. A 1 mm thick layer of sample is deposited on the cone. The quartz plate is put in contact with the polymer. The cone-plate shear cell rotates around the $\vec{\nabla} v$ axis, its plane being parallel to the multidetector and to the $(\vec{v}, \vec{z})$ planes. The incident neutron beam, parallel to $\vec{\nabla} v$, insides at 4 cm away from the rotation centre.

The other shear device allows the study of the $(\vec{v}, \vec{\nabla} v)$ plane of observation.[6] The static part consists of a thin hollow open ring, made of Aluminium, containing 1 mm of thickness sample. The longitudinal plane of the hollow ring is tilted at (2–3)° to the horizontal plane, which is parallel to the $(\vec{v}, \vec{z})$ plane, in order to place only one side of the ring on the beam trajectory. The incident neutron beam, parallel to the $\vec{z}$ axis, insides on the exposed side of the fixed hollow ring. A solid ring of the same width and diameter is placed over the hollow ring, in contact with the polymer, and enables the steady-state rotation.

The scattered intensity, $I(q)$, was normalised by the scattering of an incoherent sample (plexiglass in our experiment). Neutron scattering measurements showed that the contribution due to the shear cells alone can be neglected at the considered scattering angles. Therefore, if we neglect multiple scattering effects (supposed to be weak), the scattered intensity can be decomposed in the coherent contribution, corresponding to the diffraction pattern of the sample, and the incoherent contribution, corresponding to a constant background proportional to the number of scatterer in the sample.[9]

The scattered intensity, $I(q)$, has been normalised on each observation plane in order to have the same incoherent background. This enables us to make a direct confrontation of the intensity of the 001 reflection, I_0, measured on the $(\vec{v}, \vec{z})$ plane with that measured on the $(\vec{v}, \vec{\nabla}v)$ plane.

III. RESULTS AND DISCUSSION

As stated in the Introduction we will test the stability of the multilayer cylinders structure by applying different shear rates up to 18 s^{-1}. Different temperatures are considered.

At high temperature (T= 90°C), close to the $N - S_A$ phase transition, the observation of a diffuse peak centred in (q_z= 0.26 Å^{-1}, q_v= 0 Å^{-1}) with a length of correlation $\xi_\parallel \sim$ (190 ± 10) Å shows the presence of smectic fluctuations aligned with $\vec{n}$ parallel to $\vec{z}$ for $\dot{\gamma} < 1\ s^{-1}$. For higher shear rates, the smectic reflection can be observed in the $(\vec{v}, \vec{z})$ plane, as well as in the $(\vec{v}, \vec{\nabla}v)$ plane, indicating that the layers are oriented with $\vec{n}$ simultaneously parallel to $\vec{z}$ and $\vec{\nabla}v$. The presence of this scattering on both planes is the signature of the existence of multilayer cylinders oriented along $\vec{v}$. Figure 1 shows the dependence with the shear rate of the maximum of intensity of the smectic peak I_0, the mosaicity ϖ and the correlation length $\xi_\parallel$ along the directions parallel to $\vec{z}$ and $\vec{\nabla}v$. The increment of the correlation length which reaches (230 ± 10) Å, reveals a shear induced appearance of the S_A phase for $\dot{\gamma} > 2\ s^{-1}$. Therefore, the intensity I_0 and the mosaicity ϖ reported in Figure 1.a-b, characterise the evolution of the shear induced S_A phase. It is possible to deduce from the evolution of I_0 and ϖ that the shear induced orientation of the layers is much well defined in the $(\vec{v}, \vec{\nabla}v)$ plane compared to the $(\vec{v}, \vec{z})$ plane. The smectic planes oriented with $\vec{n}$ parallel to $\vec{\nabla}v$ are much more stable in orientation (lower mosaicity). The intensity dis-

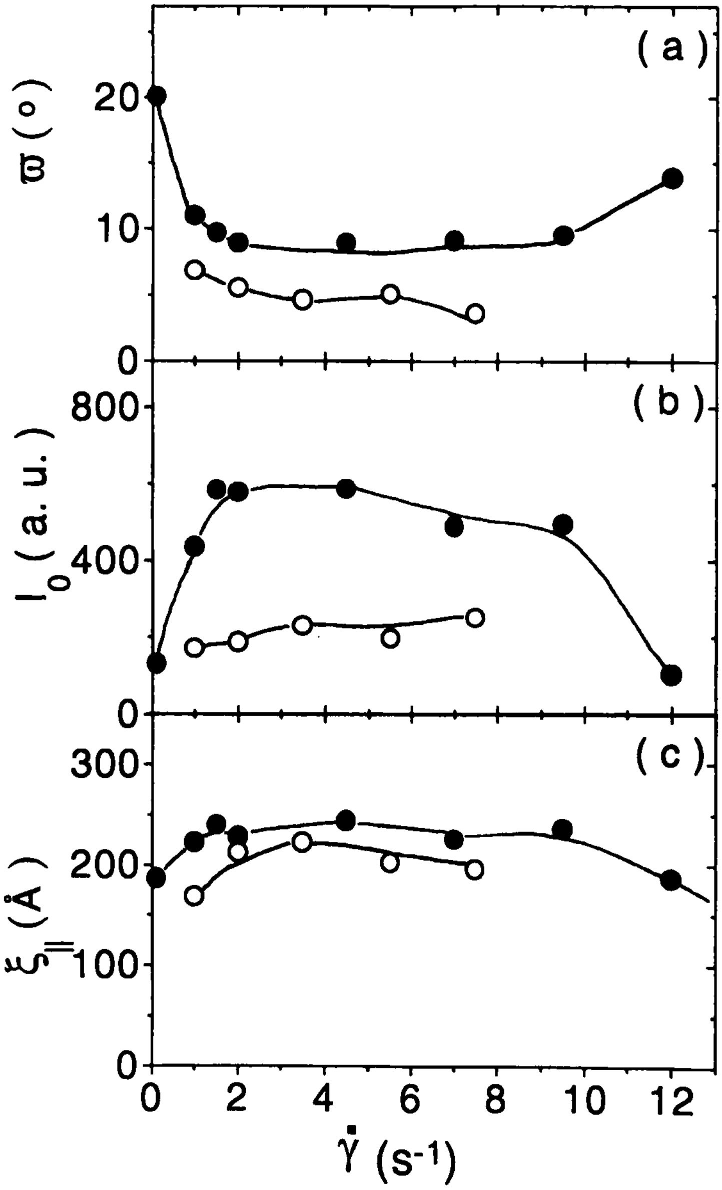


FIGURE 1 Dependence of the smectic 001 reflection versus shear rate $\dot{\gamma}$; at 90°C, (•) in the $(\vec{z},\vec{v})$ plane and (o) in the $(\vec{\nabla}v,\vec{v})$ plane. (a) Mosaicity ϖ. (b) Intensity maximum I_0. (c) Length of correlation $\xi_\parallel$. The errors in I_0, $\xi_\parallel$ and ϖ are estimated to be ± 2°, 5% and ± 20 Å respectively. Full lines are a guide for the eyes

played is in contrast lower in the $(\vec{v}, \vec{\nabla} v)$ plane compared to the the $(\vec{v}, \vec{z})$ plane. The smectic layers are indeed distributed with a cylindrical symmetry, however the number of layers contributing to the cylinder is much weaker along the $\vec{\nabla} v$ direction compared to the $\vec{z}$ direction. Finally, when the shear rate is increased up to $\dot{\gamma} = 12s^{-1}$, the correlation length surprising decreases towards the unsheared value. Simultaneously a strong reduction of I_0 and a visible increment of ϖ are observed (Figure 1). This result suggests that $\dot{\gamma} = 10s^{-1}$ is a critical shear rate above which the smectic orientation created within $2< \dot{\gamma} < 10$ s^{-1} is no longer stable. The system is driven back to the same orientation observed for $\dot{\gamma} < 1$ s^{-1}, with the smectic fluctuations oriented perpendicularly to the $(\vec{v}, \vec{z})$ plane. Therefore at 90°C, for intermediate shear rate $\dot{\gamma}$, the shear flow rises the $N - S_A$ transition temperature because it induces the long range alignment of the pretransitional smectic fluctuations. But when sufficient high shear rates are applied, a breakup of long range smectic order takes place, and the thermodynamic barrier which separates long range from local smectic order is overcome. Since this barrier is lower close to the $N - S_A$ phase transition temperature, the reentrant effect in the N phase is favoured at 90°C. The driving component of this instability is the torque produced by the velocity gradient on the lamellar interface. Under this voiticity effect, the smetic layers become bent leading to a rotation of the normal to the lamellae from $\vec{n}$ parallel to $\vec{\nabla} v$, to $\vec{n}$ parallel to $\vec{z}$.

At lower temperature (T= 84.5 °C), within the S_A phase, the correlation lengths (Figure 2.c) do not present, in the whole shear range, any particular evolution compared to the value displayed at rest ($\xi_{\parallel} \sim 230 \pm 15$ Å). The presence of smectic peaks on both $(\vec{v}, \vec{z})$ and $(\vec{v}, \vec{\nabla} v)$ planes confirms the relative stability of the multilayer cylinders at higher shear rates, up to $\dot{\gamma} = 18s^{-1}$. In contrast, the modelling of the smectic reflection on the $(\vec{v}, \vec{z})$ plane has revealed the superposition of two peaks centred in (q_z= 0.26 Å^{-1}, q_v= 0 Å^{-1}) and (q_z= 0.26 Å^{-1}, q_v= −0.03 Å^{-1}) (Figure 3), which corresponds to two slightly different orientations of smectic layers. The two different main populations of layers are oriented with $\vec{n}$ approximately parallel to $\vec{v}$ or making an angle of *arcsin* (0.03 Å^{-1} / 0.26 Å^{-1})= 7° with $\vec{v}$. The fact that the intensity of the peak in (q_z= 0.26 Å^{-1}, q_v= 0 Å^{-1}) is higher than the intensity of the peak in (q_z= 0.26 Å^{-1}, q_v= −0.03 Å^{-1}) (Figure 3), shows that the population of cylinders with their main axis approximately parallel to $\vec{v}$ remains higher. A similar observation was carried out on the low molecular liquid crystal 8CB in a couette cell geometry.[4] Indeed, 8CB shows also a splitting of the 001 reflection into two peaks very close on the $(\vec{\nabla} v, \vec{z})$ plane for the perpendicular orientation in the high shear regime,[4] suggesting the presence of two main orientations of $\vec{n}$ with respect to $\vec{z}$. This might be associated to a same driving force which produces two distinct orientations of cylinders within

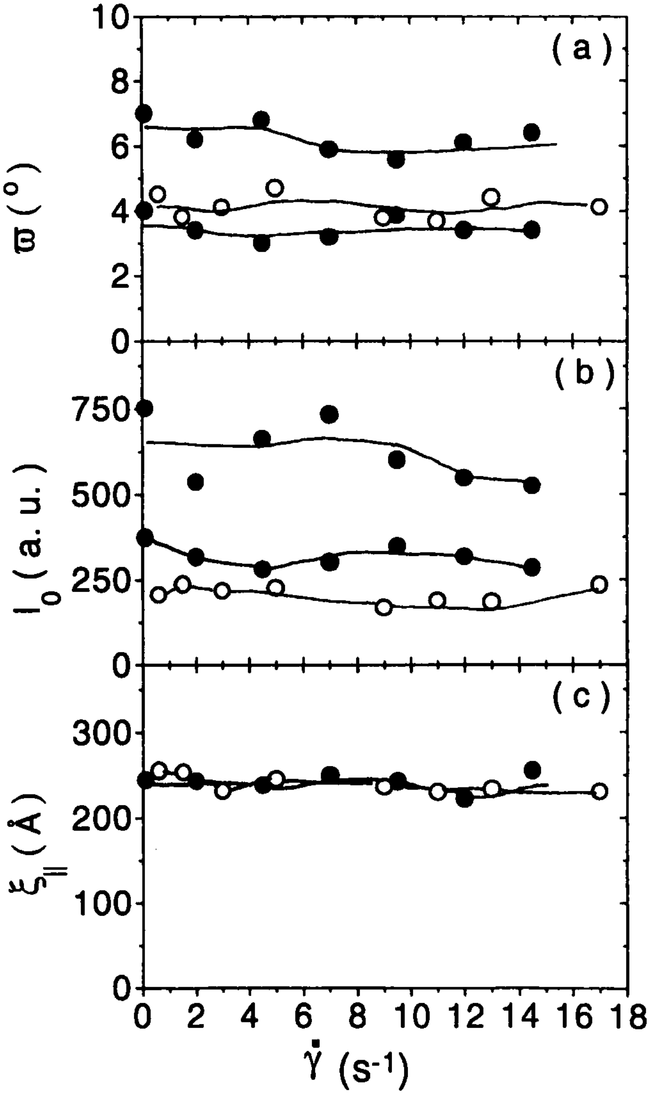


FIGURE 2 Dependence of the smectic 001 reflection versus shear rate $\dot{\gamma}$, for 84.5°C (•) $(\vec{z},\vec{v})$ plane and (o) $(\vec{\nabla}v,\vec{v})$ plane. (a) Mosaicity ϖ. (b) Intensity maximum I_0. (c) Length of correlation $\xi_\|$. 001 reflection is splitted in a pair of peaks on the $(\vec{v},\vec{z})$ plane: each of the two datasets for the $(\vec{v},\vec{z})$ plane on (a) and (b), corresponds to each of these two peaks; data with higher ϖ and I_0 correspond to the peak centred in (q_z= 0.26 Å^{-1}, q_v= 0 Å^{-1}) (*see text*). The errors in I_0, $\xi_\|$ and ϖ are estimated to be 5%, ± 20 Å and ± 1° respectively. Full lines are a guide for the eyes

the S_A phase of PA-OCH$_3$ under shear flow. We suggest an alternated distribution of these two orientations (as in a "zig-zag" structure) since it could fit with a stretched-relaxed mechanism of the layers oriented in the perpendicular direction.

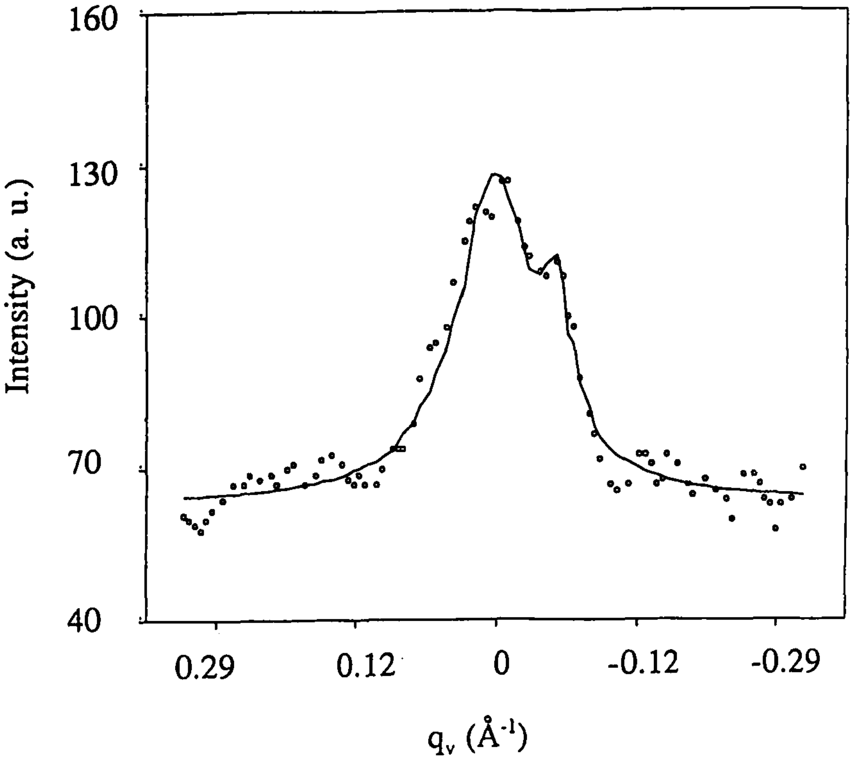


FIGURE 3 Neutron diffraction pattern (λ= 4 Å, sample-detector distance= 1.5 m) displayed on the $(\vec{v}, \vec{z})$ plane for $\dot{\gamma} = 2\ s^{-1}$ and 84.5 °C, obtained with the cone-plate shear cell. (a) (o) Projection of the 001 reflection along the $\vec{v}$ axis; (-) modelling with a pair of Lorentzian functions

The formation of multilamellar smectic cylinders under shear flow, with their principal axis parallel to the flow direction, was already theoretically predicted and experimentally observed for low molecular thermotropic systems.[1,3-4] The dynamics of thermotropics under shear flow has been theoretically studied close to the $N - S_A$ phase transition, where smectic fluctuations are still large, and in the well-aligned smectic regime.[1,3] The study in the S_A phase predicted that as a consequence of the thermal fluctuations of the smectic layers, there is a regime of viscosity within which $\vec{n}$ simultaneously takes the orientation parallel to $\vec{v}$

and $\vec{\nabla} v$.[3] The same kind of mixed orientation has been theoretically achieved, for low $\dot{\gamma}$, following the same procedure mentioned before, to predict the pure perpendicular orientation in the immediate vicinity of the $N - S_A$ phase transition of thermotropic liquid crystals.[1] In the last case it was also shown that the theoretical study exactly reproduced experimental results for 8CB.[4]

IV. CONCLUSIONS

We described the rheological behaviour of PA-OCH_3 under shear flow in the S_A phase. Our results put in evidence that the sequence of morphology adopted by the smectic layers of PA-OCH_3 is similar to that presented by thermotropic LCs and might be described in terms of the theories developed for these materials.[1,3]

The multilayer cylinder geometry seems to be thus a stable state for this polymeric system. From the comparison of both $(\vec{v}, \vec{z})$ and $(\vec{\nabla} v, \vec{v})$ planes, it appears nevertheless that the cylinders are not homogeneous since a larger number of layers contribute in the neutral direction $\vec{z}$, i.e., the perpendicular direction is reinforced.

We have also evidenced the shear induced apparition of the smectic phase at 90°C by observing an abrupt increase of the correlation length along the director. The orientation of the layers in the shear induced smectic is nearly of perpendicular type. At higher shear rates, a shear induced nematic reentrance occurs at the same temperature. In the last case, for $\dot{\gamma} > 10\ s^{-1}$ shear flow directly affects short range microdomain properties. The shear constraint acts, through the vorticity, on the interfacial tension force which is here stabilized by the polymeric interface, which tends to rigidify the lamellae and opposes to the bending imposed by the vorticity. The apparent lack of similarity with previous results obtained from shear flow experiments on other SCLCPs, which smectic layers simply adopt a parallel orientation under shear flow,[6] does not allows to reflect of the polymeric chain influence on the rheological behaviour of PA-OCH_3, which contributes to the remove table stability of the cylindrical-geometry.

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