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Structure and shear orientation of a side chain liquid crystal polymer studied by small angle X-ray scattering

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We have studied the structure and shear flow behaviour of a side chain liquid crystal polymer, namely P_{12} , in the smectic (SmA_d) phase. Simultaneous oscillatory shear and small angle X-ray scattering experiments showed that, as expected, the shearing of P_{12} at high frequency and large strain amplitudes leads to the alignment of the smectic layer normals parallel to the neutral direction. It was also found that, on erasing the memory of the prior shear alignment through melting, P_{12} can unexpectedly orient with the smectic layers perpendicular to the shear flow direction (b -configuration). We speculate that the b -configuration is adopted due to a counterbalance between the rather long spacer in P_{12} which decouples mesogens from the backbone, and the oscillatory character of the shear applied to P_{12} .

1. Introduction

The study of layered materials under shear has been the subject of numerous theoretical and experimental works over recent years [1–11]. Thermotropic smectic phases formed by side chain liquid crystal polymers (SCLCPs) are among the layered systems studied under shear flow [5–8, 12–14]. SCLCPs contain a main chain, which can be a flexible polymer chain, and mesogens laterally attached to the main chain. In the smectic phase, in the absence of external constraints, the mesogens are aligned in smectic layers and the polymer main chain preferentially occupies the space available between the layers.

Interesting shear alignment effects can be observed in SCLCPs, because the mesogenic groups are decoupled from the polymer backbone by flexible spacers. The smectic phase in SCLCPs offers the possibility of orientation via shear-induced alignment of the polymer chain. For example, Kornfield and co-workers have used rheo-optical experiments (using IR light to detect $C-H$ stretching vibrations) to probe the effect of oscillatory shear on smectic SCLCPs. They have suggested that large amplitude oscillatory shear (LAOS) can be used to orient the smectic phase partially, producing a significant decrease in both

dynamic shear moduli [12]. Noirez and Lapp [5] have used steady shear to orient the smectic phase of an SCLCP, the conformation of which was investigated in detail by small angle neutron scattering [5]. In addition, it has also been shown that the formation of multilayer cylinders oriented along the velocity direction is a stable geometry which can be observed at different temperatures and shear rates in the smectic phase of another SCLCP [6, 8].

Recently, infrared dichroism was used to confirm a high degree of perpendicular orientation of mesogens with respect to the layers in an SCLCP subjected to shear [15]. Furthermore, the shear-induced orientation of mesogens was found to be retained after the cessation of shear. Simultaneous small angle X-ray scattering (SAXS) and LAOS experiments also provided evidence for the orientation of the mesogens in the direction perpendicular to the flow, in the smectic phase of an SCLCP [16].

Three main directions are defined for shear experiments: the velocity axis, \mathbf{v} , the velocity gradient axis, $\nabla\mathbf{v}$, and the vorticity axis, \mathbf{e} . Under shear, the layers in the smectic phase of SCLCPs typically align with their normal either along $\nabla\mathbf{v}$, in the so-called parallel orientation [5], or with their normal along \mathbf{e} , in the so-called perpendicular orientation [6, 8]. The parallel state is termed c and the perpendicular state a in the notation of Safinya *et al.* [2]. The transverse orientation

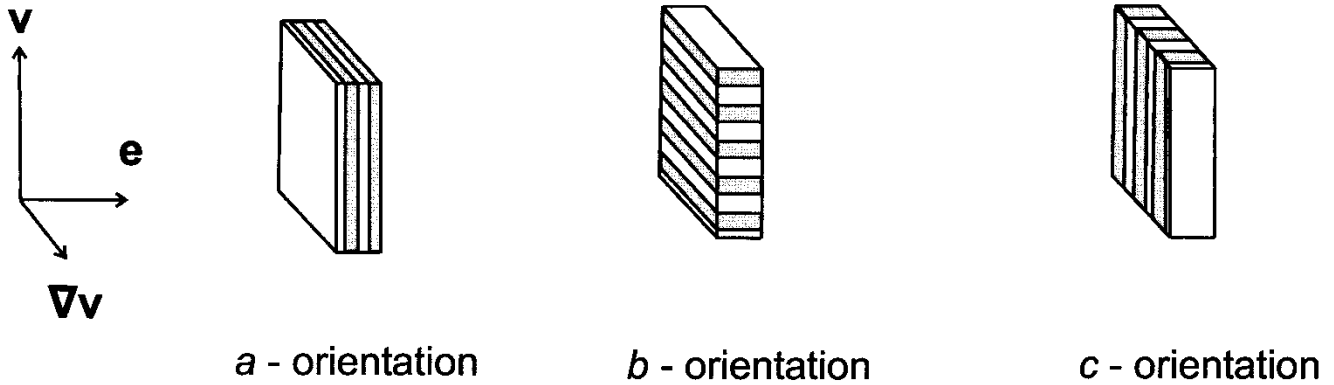
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b (layer normal along \mathbf{v}) is an unfavourable configuration in which the smectic layers align perpendicular to the velocity, and has never been observed in an SCLCP. Figure 1(a) shows the orientations adopted by the smectic layers in the a -, b - and c -configurations.

Here we compare the behaviour at rest and under shear flow of an SCLCP, denoted P_{12} , at several

temperatures and various shear conditions in the smectic phase. An initial study of shear-induced orientation via small angle X-ray scattering (SAXS) has been undertaken for P_{12} [7]. The study showed that large amplitude oscillatory shear led to a highly oriented state with the layer normal along the neutral direction (a -orientation). The smectic phase was found

(a)



(b)

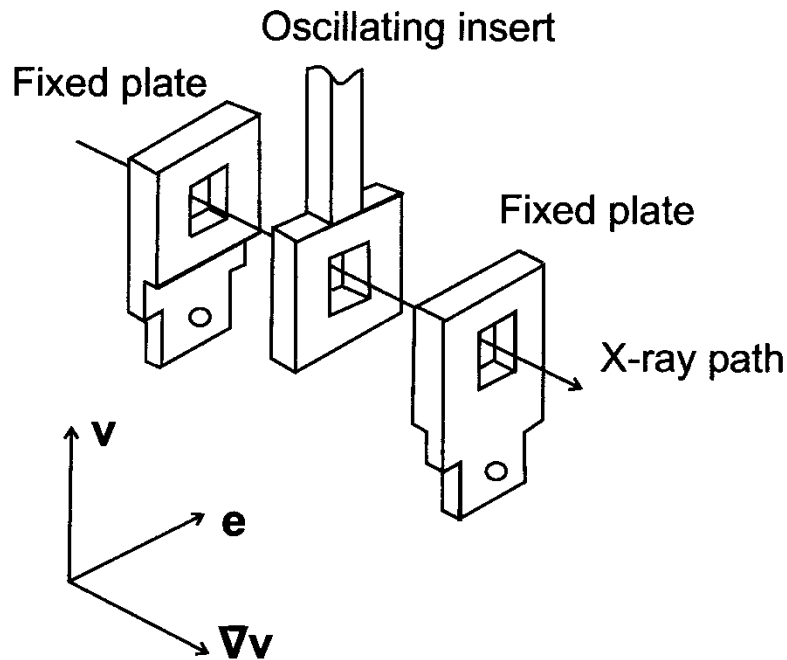


Figure 1. (a) Scheme of the orientation adopted by the smectic layers in the a -, b - and c -configurations. (b) Scheme of the shear sandwich geometry and its orientation with respect to the incident radiation.

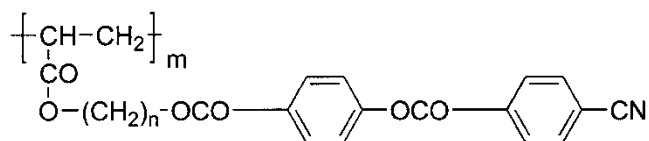
to exhibit shear thinning with a sharp reduction in both dynamic shear moduli upon application of shear.

The present paper provides further insight into shear-induced changes in alignment and layer structure (conformation) of P₁₂, exploring the existence of transient states of alignment of the smectic phase.

2. Experimental

2.1. Materials

The side chain polyacrylates are identical to those used earlier [7, 17, 18]. They were synthesized by radical polymerization, according to a procedure described elsewhere [17]. Their chemical structure is:



where the subscript $n=12$ is the number of methylene groups in the spacer. The polymer is denoted by P₁₂. The polymorphism and transition temperatures have been previously identified using polarizing optical microscopy (POM) and confirmed by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) [17]. XRD studies show that at high temperature this polymer possesses a partially bilayer smectic phase where the mesogenic groups align perpendicular to the layers and are partially interdigitated (SmA_d phase) [17]. In particular, P₁₂ exhibits the sequence of mesophases $T_g-15-\text{Cr}_1-60-\text{Cr}_2-80-\text{SmA}_d-112-\text{I}$ (°C). Cr₁ and Cr₂ are two unidentified crystalline phases and I is the isotropic liquid phase [17].

2.2. Small angle X-ray scattering

SAXS experiments were performed at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, Warrington, UK. Samples were studied on beamline 16.1 (X-ray wavelength $\lambda=1.41 \text{ \AA}$). Samples were subjected to oscillatory strain using a Rheometrics solid analyser RSA II system with shear sandwich geometry. A detailed description of the rheometer is provided elsewhere [19, 20]. It enables the collection of simultaneous rheology data. The shear sandwich cell comprises three rectangular polycarbonate plates; the two external plates are fixed, while the central piece oscillates vertically. Figure 1(b) shows the orientation of the shear tools and shear directions with respect to the incident radiation. The sample is loaded on both sides symmetrically about the insert piece. Oscillatory shear was applied at a fixed temperature in the range 90–130°C.

The shear sandwich plates are perpendicular to the

X-ray beam which is incident along $\nabla \mathbf{v}$, while \mathbf{v} and \mathbf{e} correspond to the vertical shear and horizontal neutral directions, respectively (figure 1(b)). The $(\mathbf{q}_v, \mathbf{q}_e)$ plane is accessed in SAXS experiments ($|q|=4\pi \sin \theta/\lambda$, where the scattering angle is 2θ), which were performed using a two-dimensional area detector. In particular, in this configuration, the b -orientation and the a -orientation are identified by reflections centred at $\phi=90^\circ, 270^\circ$ and $\phi=0, 180^\circ$, respectively, where ϕ is the azimuthal angle measured with respect to the horizontal.

Scattering patterns from wet collagen (rat-tail tendon) were used for calibration of the q scale. The SAXS data were corrected to allow for sample transmission and background scattering (using the empty polycarbonate shear tools as reference). The data from the two-dimensional area detector were finally converted into one-dimensional intensity profiles by integration in a triangular sector. The resulting corrected intensity curves are denoted $I_c(q)$.

2.3. Determination of the electron density profile

The electron density profile in the SmA_d phase of P₁₂ has already been determined, using static XRD patterns obtained for samples aligned in an external magnetic field [17]. In this work we apply the same procedure but for samples aligned under shear flow.

Briefly, the projection of the electron density along the normal z to the layers, $\rho(z)$, is expanded in a Fourier series according to [17]:

$$\rho(z) = \sum_n a_n \cos\left(\frac{n2\pi z}{d}\right) \quad (1)$$

where d is the smectic layer spacing. By measuring the intensities of the Bragg reflections and correcting these values for the Lorentz factor, it is possible to obtain $|a_n|$. However, the sign of these coefficients remains undetermined. Therefore, all the possible combinations of signs must be tried and the set of signs which leads to a physically acceptable $\rho(z)$ is finally selected.

It is worth mentioning that SAXS profiles studied in this work have two or three orders of reflection, leading to four or eight possible sign combinations for the coefficients in equation (1). In keeping with the procedure reported in the literature [17], the resulting $\rho(z)$ must have a central maximum, and its intensity should ideally be higher than the intensity of any other maximum within a distance equal to the smectic layer spacing. Briefly, these criteria, which dramatically reduce the number of possible solutions for $\rho(z)$, favour a configuration in which the mesogenic groups are aligned perpendicular to the smectic layers, with a small overlap at the centre of the interlayer spacing [17].

3. Results and discussion

3.1. P_{12} at rest

The as-mounted sample at 90°C (SmA_d phase) in the rheometer showed a nearly spherically averaged powder diffraction pattern (results not shown), consisting of three diffraction rings in the positional ratio 1:2:3, corresponding to the first three reflections of a smectic phase (first-order peak centred at $q^* = 0.1173 \text{ \AA}^{-1}$) [21]. It is possible to calculate the smectic layer spacing $d = (53.6 \pm 0.1) \text{ \AA}$, which is in good agreement with values 57 and 54 \AA previously reported [7, 17].

3.2. P_{12} shear flow behaviour: oscillatory shear

Using the shear sandwich tool in the rheometer (total sample thickness 0.1 mm), the sample was sheared in the SmA_d phase, at 90°C with a frequency $\omega = 100 \text{ rad s}^{-1}$ and a strain amplitude $A = 100\%$ (corresponding to a displacement of 0.05 mm). The SAXS pattern showed three equally spaced reflections with $q^* = 0.1186 \text{ \AA}^{-1}$. However, it was not possible to obtain a high level of orientation under these conditions. The temperature was then increased to 100°C , and the amplitude to $A = 200\%$, with the frequency fixed at

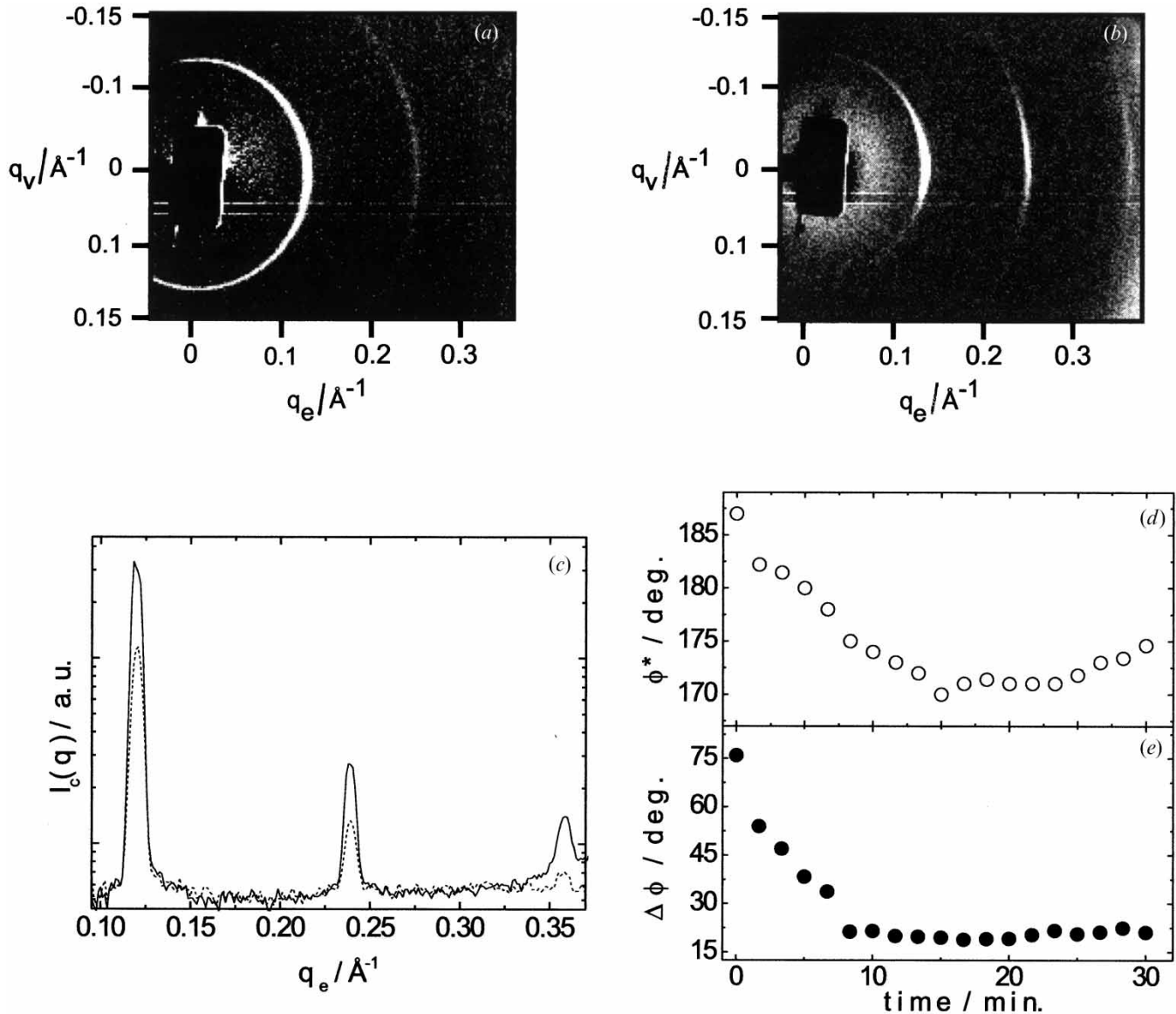


Figure 2. Data obtained during shear of P_{12} at 100°C , using a frequency $\omega = 100 \text{ s}^{-1}$, and associated strain amplitude $A = 200\%$. SAXS pattern in the (q_v, q_e) plane (a) at the beginning of the shear and (b) when the sample has been sheared for 30 min (a -orientation). (c) SAXS pattern plotted against q_e corresponding to data in (a) (---) and (b) (—). (d) Azimuthal angular position of q^* (defined with respect to the horizontal); (e) HWHM, extracted from fitting the first-order scattering peak to a Gaussian function.

$\omega = 100 \text{ rad s}^{-1}$. These conditions led to a high degree of orientation of the smectic layers in the *a*-configuration, as indicated by arcs observed in the SAXS pattern, oriented along the (horizontal) neutral direction (figures 2(a) and 2(b)). The position of q^* remained approximately fixed under shear (figure 2(c)); but the intensity of all three peaks increased with time due to the progressive orientation of the layers. Simultaneously, the azimuthal angular position of the first-order scattering peak, ϕ^* , changed from 187° to 175° , indicating a tilt of 5° of the layer normal with respect to the vorticity direction (figure 2(d)). This misorientation has previously been observed for the smectic phase of a flow-aligning side chain liquid crystal polymer [8], as well as in the nematic phase of liquid crystal polymers [8], and results from the balance of hydrodynamic torques on the liquid crystal director, which selects a particular angle termed the Leslie angle [22–24].

Gaussian fitting of the azimuthal intensity of the first-order scattering peak also indicated an angular spread characterized by a Gaussian with HWHM, $\Delta\phi$, which is reduced from 76° to 21° after the sample has been sheared for 30 min (figure 2(e)), showing that the orientation of the smectic phase is indeed improved under these shear conditions.

The electron density profile was determined using $I_c(q)$ in figure 2(c) for the sample sheared for 30 min. The relative intensity of the three orders of reflections were 1, 0.12 and 0.1 for the first, second and third order, respectively, from which the corresponding relative amplitudes $|a_1|=1$, $|a_2|=0.69$ and $|a_3|=0.92$ were determined. The presence of three diffraction peaks in the SAXS pattern leads to eight possible combinations of one sign of the coefficients in equation (1). Using the criteria to select $\rho_{-+-}(z)$ already discussed, we are left with the solution $\rho_{-+-}(z)$ (figure 3). The electron density profile for the sample following shear at 100°C is similar to that obtained for P_{12} oriented in a magnetic field, at 90°C (figure 3, data taken from reference [17]). It has been shown that in terms of the molecular features, the central maximum (1, figure 3) corresponds to the region of the overlap of the mesogenic cores arranged between the layers [17]. The first minimum (2, figure 3), corresponds to the region of the mesogenic cores adjacent to the region of the overlap. The secondary maximum (3, figure 3) is attributed to the region of compressed spacers, while the secondary minimum (4, figure 3) is attributed to the region of the polymeric backbones.

The temperature of the sample was then decreased from 100 to 50°C and then increased to 120°C , at a rate of 3°C min^{-1} . The dynamic moduli were recorded during the cooling heating cycle in the linear viscoelastic regime, $A=1\%$, $\omega=1 \text{ rad s}^{-1}$ (figure 4). A sharp

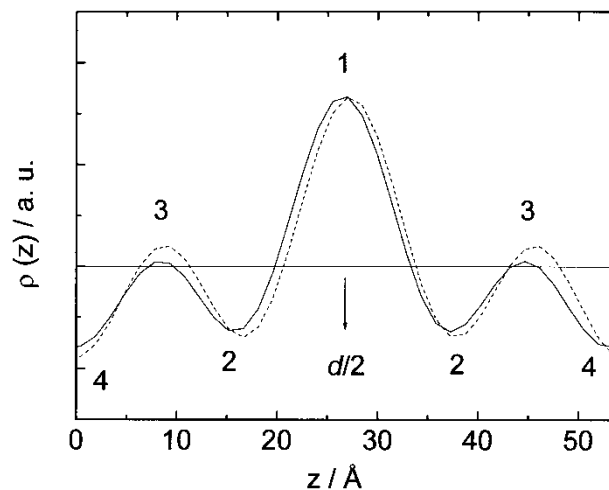


Figure 3. Projection of the electron density profile, $\rho_{-+-}(z)$ solution, for (—) sample oriented in a magnetic field, at 90°C (data taken from reference [17]), and (---) after shearing the sample for 30 min at 100°C with $A=200\%$ and $\omega=100 \text{ rad s}^{-1}$ (*a*-orientation).

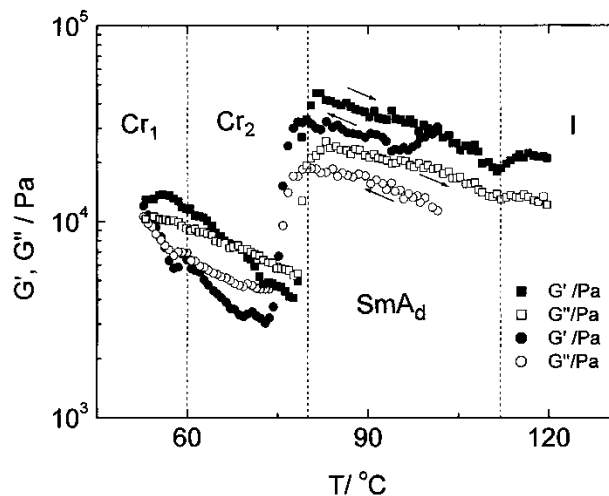


Figure 4. Temperature dependence of the elastic moduli for P_{12} with $\omega=1 \text{ rad s}^{-1}$ and $A=1\%$: increasing temperature ramp for storage modulus G' (■) and loss modulus G'' (□), and decreasing temperature ramp for G' (●) and G'' (○). The arrows indicate the direction of the temperature ramp.

transition from the crystal phase to the smectic phase is located via a large increase in both moduli between 73 and 82°C . The clearing point is apparent from dips in the temperature dependence of both moduli at 112°C , in excellent agreement with the smectic–isotropic transition measured by DSC. Three orders of reflection in the SAXS pattern, with a positional relation 1:2:3, showed that the sample retains smectic order up to 112°C at which point melting of the lamellar structure was observed [17]. The value of $d=2\pi/q^*$ increases

continuously upon reducing temperature (figure 5(a)). This parameter decreases again, when the temperature is increased, recovering its initial value within the experimental error (figure 5(a)).

According to previous DSC data [17], P_{12} is in Cr_1 , Cr_2 and SmA_d phases within the intervals of temperatures 50–60°C, 60–80°C and 80–112°C, respectively. Our SAXS data show no direct evidence allowing us to differentiate between Cr_1 and Cr_2 phases, i.e. both were identified as smectic phases. However these phases can be distinguished from the SmA_d phase, since the third-order peak is more intense for Cr_1 and Cr_2 . In addition, the dynamic elastic moduli in the Cr_1 and Cr_2 phases are much lower than in the SmA_d phase. In order to relate the change of intensity of the third-order scattering peak to the structural organization of the smectic layers, the electron density profile was

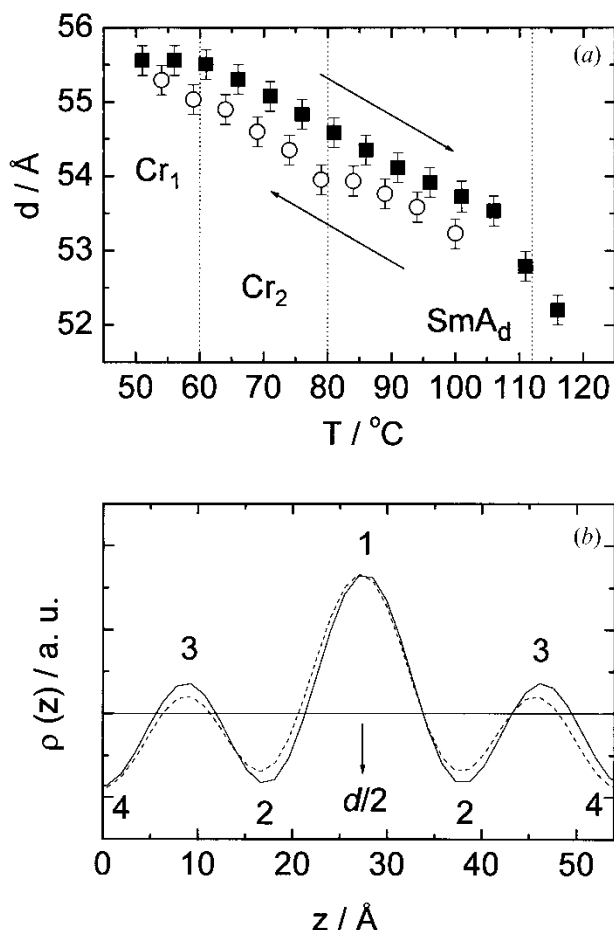


Figure 5. (a) Dependence of the smectic phase parameter, d , with temperature for (○) increasing and (■) decreasing temperature ramps; (b) projection of the electron density ($\rho_{-+-}(z)$ solution) obtained at 50°C (—), and on orienting the sample in a magnetic field at 90°C (---) (data taken from reference [17]).

determined at 50°C (Cr_1 phase). The relative intensity of the three orders of reflections were 1, 0.18 and 0.32 for the first, second and third order, respectively, while the corresponding amplitudes were $|a_1|=0.595$, $|a_2|=0.505$ and $|a_3|=1$. We are again left in this case with the solution $\rho_{-+-}(z)$, after applying the selection criteria already discussed (figure 5(b)). The shape of $\rho_{-+-}(z)$ as a whole is similar to that previously obtained for the sample at 90°C (figure 5(b)). But there is a redistribution of the spacers between the layers, as indicated by the relative decrease of minima (2) and increase of maxima (3) (figure 5(b)).

In order to erase the memory of the sample orientation, the temperature was then increased to 130°C, in the isotropic phase, with $\omega=100\text{ rad s}^{-1}$ and $A=400\%$ for 1 min. SAXS confirmed the loss of reflections from the smectic phase. The sample was then quenched to 90°C, after stopping the large amplitude shear. After 2 min, three orders of reflection in a 1:2:3 positional relationship ($q^*=0.1198\text{ Å}^{-1}$) were observed in the direction perpendicular to the equator. This result indicates orientation of the smectic layers with their normal parallel to the shear direction (b -orientation) and the smectic layer spacing $d=(52.6\pm 0.2)\text{ Å}$.

The b -orientation is improved when the polymer is sheared at $\omega=100\text{ rad s}^{-1}$ and $A=200\%$ (same temperature). The SAXS pattern shows the first two orders of reflection consisting of arcs oriented perpendicularly to the shear direction (figure 6(a)). These arcs are reinforced along diffuse scattering rings corresponding to some proportion of completely unaligned layers with interlayer distances equal to the smectic layer spacing. Figure 6(b) shows $I_c(q)$ as a function of the scattering vector q_v . The position q^* remained approximately equal to 0.1196 Å^{-1} but the intensity of the first-order scattering peak increases with time due to the progressive orientation of the layers in the b -orientation (figure 6(c)). The position ϕ^* also remained constant, approximately equal to 87° during shear, which corresponds to a tilt angle of 3° within the experimental error. Simultaneously, the azimuthal width $\Delta\phi$ was reduced from 108° to 46° after the sample had been sheared for 15 min (figure 6(d)), showing that the b -orientation is indeed improved under these shear conditions.

The temperature of the sample was then increased to 100°C, where the sample is softer (same frequency and strain). An SAXS pattern in the b -orientation, characterized by two orders of reflection ($q^*=0.1207\text{ Å}^{-1}$), was obtained during shear (9 min). The HWHM monotonically grows with time from 76° to 123° with a simultaneous decrease of the peak height showing that the higher temperature (i.e. softer sample) leads to

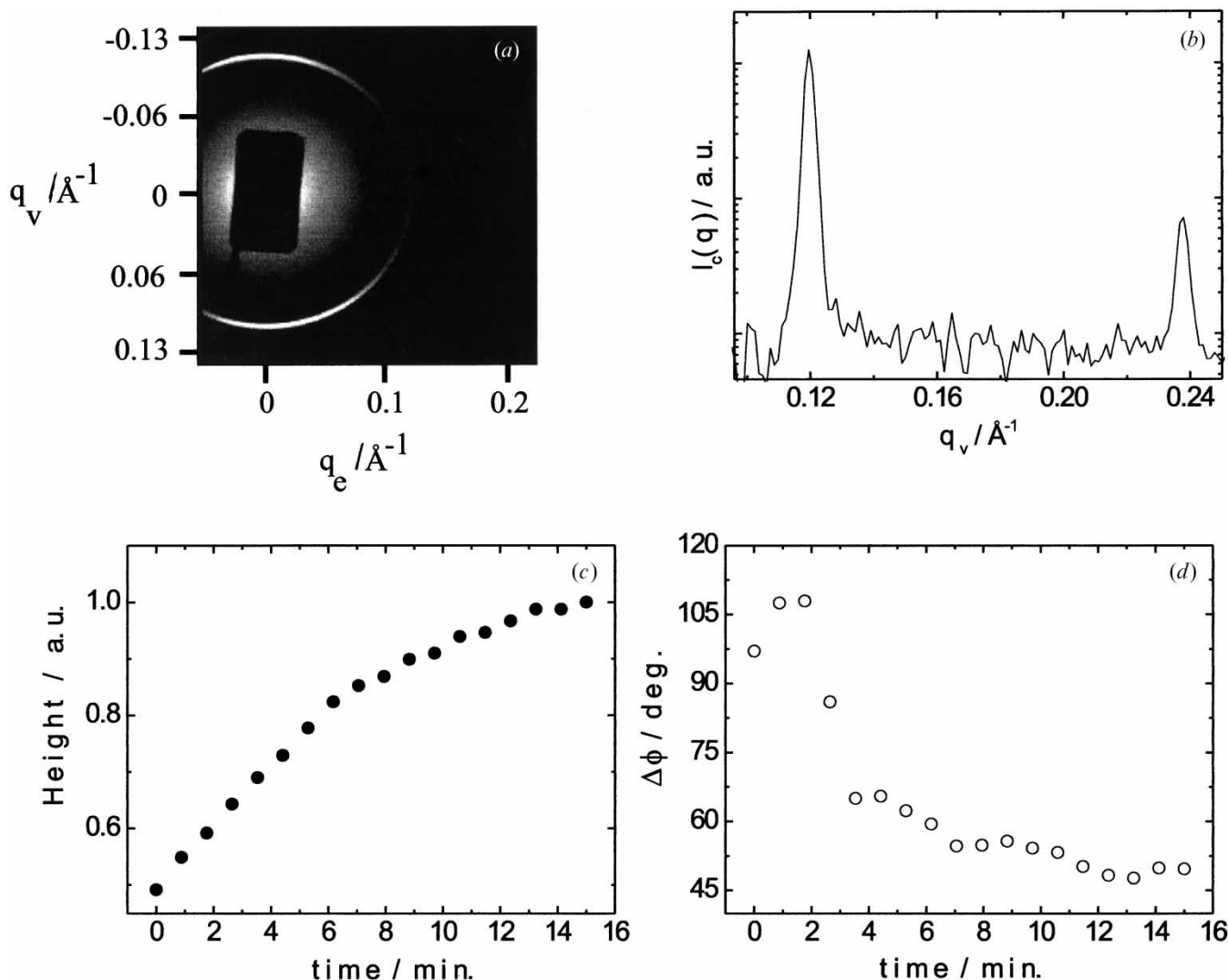


Figure 6. Data obtained during shear of P_{12} at 90°C , at a frequency $\omega=100\text{ s}^{-1}$, and associated strain amplitude $A=200\%$, 15 min after quenching from 130°C . (a) SAXS pattern in the (q_v, q_e) plane when the sample has been sheared for 15 min (b -orientation). The second-order peak is not shown because the contrast scale used does not allow the first- and second-order reflections to be seen simultaneously with the b -orientation. (b) SAXS pattern plotted against q_v corresponding to data in (a). (c) Height and (d) HWHM as a function of time, extracted from the fitting of the first-order scattering peak with a Gaussian function.

a reduction in alignment in the b -orientation with time. In addition, ϕ^* grows from 88° to 105° , proving that the system loses b -orientation and tends increasingly to adopt the a -configuration. Therefore our results show that, as expected, the b -orientation is less stable at high temperature than at low temperature, because increasing temperature softens the smectic layers, enabling them to re-orient.

4. Summary

New results are presented concerning the alignment of SCLCP P_{12} under shear flow in the SmA_d phase. We

observed that, in good agreement with previous reports [7], shearing P_{12} at high frequency and large strain amplitudes leads to macroscopic alignment of the polymer in the a -configuration. It was also found that following melting (which erases the memory of the prior shear alignment) P_{12} can unexpectedly orient in the b -configuration. In this configuration, the mesogens orient along the shear direction. We speculate that this can occur due to the lengthy spacer in P_{12} , which decouples mesogens from the backbone. It is also possible that the b -orientation is associated with the oscillatory character of the shear applied to P_{12} in this

work. We have already mentioned that this orientation has not been observed before for SCLCPs, but it should be noted that only experiments using continuous shear have been previously reported.

It appears that the b -configuration, which should indeed correspond to a transient non-equilibrium state, is relatively stable in the low temperature SmA_d phase (90°C). However, this configuration is weakened and the system tends to adopt the a -orientation at the higher temperature SmA_d phase (100°C). For smectic layers with their normal directed along \mathbf{v} , in the b -configuration, shear flow tends to tilt the layers, giving rise to a restoring force [2]. This process might induce flow instabilities which could lead to a change from b - to a -orientation at the higher temperature SmA_d phase of P_{12} . However, this is indeed a preliminary explanation, and further simultaneous LAOS/SAXS experiments should be undertaken to evaluate the reproducibility of the b -orientation in P_{12} .

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