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Shear-induced layer alignment in the smectic phase of a side chain liquid crystal polymer

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Abstract

The effect of shear on the alignment of the smectic A phase formed by a polyacrylate side chain liquid crystal polymer (SCLCP) has been investigated using small-angle X-ray scattering (SAXS) with simultaneous rheology. Large amplitude oscillatory shear led to a highly oriented state with the layer normal parallel to the neutral direction. The sample mosaic width obtained after large amplitude shear (~10°, Gaussian HWHM) was comparable to that obtained by magnetic alignment of the mesogens. The smectic phase was found to exhibit shear thinning, with a sharp reduction in both dynamic shear moduli upon application of shear. Cessation of shear led to a rapid recovery in the moduli to their initial values, although the anisotropy of the SAXS peaks relaxed more slowly. Nevertheless, a high degree of alignment was retained even after the relaxation period. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Side chain liquid crystal polymer; Shear; Small-angle X-ray scattering

1. Introduction

There has been considerable technological interest recently in side chain liquid crystal polymers (SCLCPs) because they can exhibit both typical polymer properties, for example a glass transition temperature, as well as the electro-optical and non-linear optical properties characteristic of low molar mass materials [1,2].

Soft materials can be aligned by the application of fields. Whereas liquid crystals can be aligned by electromagnetic or shear fields, conventional polymers are usually oriented by flow fields, as experienced for example during extrusion under processing conditions. Liquid crystal polymers offer the possibility for orientation via electric/magnetic field alignment of the mesogens and/or shear-induced alignment of the polymer chain. In side chain liquid crystal polymers the mesogenic side groups are decoupled from the polymer backbone by flexible spacers, which can lead to interesting rheological effects. For example, Kornfield and coworkers have observed strain hardening in the nematic phase of an SCLCP, possibly due to realignment of mesogens from their preferred orientation normal to the polymer backbone into the direction of applied shear, along which the backbone orients [3,4]. This group has used rheo-optical experiments (using IR light to detect C-^{2}H stretching vibrations) to probe the effect of oscillatory shear on nematic SCLCPs, and have shown that large amplitude oscillatory shear can be used to orient the nematic phase, producing an increase in both birefringence and transparency [3–5]. In contrast, samples forming a smectic phase did not attain the clarity or high birefringence characteristic of the shear-aligned nematic polymers, although both dynamic shear moduli decreased significantly [4]. They thus suggested that macroscopic alignment of the sample could not be achieved by large amplitude shearing. In contrast, Noirez and Lapp [6] 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. Recently, rheology combined with infra-red dichroism was used to confirm a high degree of perpendicular orientation of a mesogen with respect to the layers in an SCLCP [7]. Furthermore, shear-induced orientation of mesogens was found to be retained after the cessation of shear [7].

In the work described in this paper, the effect of large amplitude oscillatory shear on the alignment of an SCLCP in a smectic phase was investigated using simultaneous small-angle X-ray scattering (SAXS) and rheology. This enabled the evolution of smectic structure during shear to

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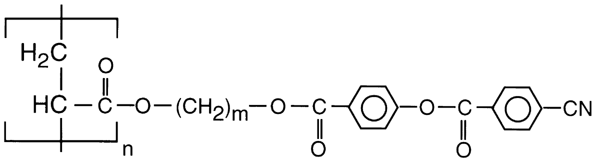
be probed in real time. Furthermore, SAXS provides information on structure at the layer lengthscale, averaged over the volume probed by the beam and so enables the macroscopic orientation of layers to be determined.

The SCLCP studied was a poly[4(4′-cyanobenzoyloxy)-benzoyloxy ω-n-alkylacrylate], with chemical formula



with $m = 12$ and is denoted P_{12}. This material (and others from the series with different values of m) has previously been characterized by methods including X-ray diffraction on magnetically oriented specimens and fibres [8]. The latter provided smectic layer spacings, and confirmed the perpendicular orientation of mesogenic groups with respect to the layers. Furthermore, comparison of the measured layer spacing with a molecular length estimated from a model enabled an interdigitated structure of mesogens to be deduced [8].

2. Experimental

2.1. Sample synthesis and characterization

The polymer P_{12} was synthesized by radical polymerization, as described elsewhere [8]. The sample was previously characterized using DSC, intrinsic viscosity measurements and X-ray diffraction as outlined earlier [8].

2.2. Simultaneous small angle X-ray scattering and rheology

SAXS experiments were conducted at the Synchrotron Radiation Source, Daresbury Laboratory, U.K., on beamline 16.1. This beamline is configured with an X-ray wavelength $\lambda = 1.5$ Å. Details of the storage ring, radiation, camera geometry and data collection electronics have been given elsewhere [9]. Scattered photons were collected on a multiwire gas-filled area detector. A scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used for callibration of the q scale ($q = 4\pi \sin \theta/\lambda$, where the scattering angle is defined as 2θ). Measurements of dynamic mechanical properties were performed, in tandem with the SAXS experiments, using a Rheometrics Solids Analyzer RSA II system with a shear sandwich geometry. The rheometer applies an oscillatory (sinusoidal) strain and the dynamic and loss shear moduli, respectively G' and G'', were measured as a function of the deformation conditions. Apertures were machined into the plates of the shear sandwich assembly to allow transmission of the X-ray beam, and were covered by Kapton windows of 6 μm thickness, as described previously [10]. The shear sandwich was contained in an insulated oven, with temperature control to ± 1°C. With the rheometer in situ at the X-ray beamline the shear direction **v** was vertical, and the X-ray beam was incident along the horizontal shear gradient direction ∇, the neutral direction $\mathbf{e} = \nabla\mathbf{v} \times \mathbf{v}$ also being horizontal. The aquisition of SAXS and rheology was synchronized using an electric trigger.

3. Results and discussion

Measurements of the temperature dependence of the isochronal dynamic shear moduli prove to be very sensitive to phase transitions in the SCLCP P_{12}. Fig. 1 shows the storage (G') and loss (G'') moduli during a heating ramp from 25°C to 115°C at 2°C min^{-1}. All measurements were made above the glass transition temperature for the polymer, 15°C, as previously determined by DSC [8]. Prior DSC measurements also indicated a transition assigned as crystal 1-crystal 2 at 60°C, and this is apparent in Fig. 1 from discontinuities in both G' and G''. Also evident is the crystal-smectic phase transition at 80°C, in excellent agreement with the value obtained by DSC [8]. Finally, DSC indicated that the polymer melts at 112°C, which is also apparent in the rheology data, especially in the discontinuous decrease in G'' at this temperature. SAXS patterns obtained for P_{12} mounted in the rheometer are shown in Fig. 2. The sample was heated into the smectic phase at 90°C, without shear, to produce the SAXS pattern shown in Fig. 2a. The mounting procedure (which involves compression) induces some ordering of lamellae, as shown by a diffraction pattern which is not completely isotropic, there being some concentration of intensity into off-equatorial arcs. The first order reflection from the smectic structure occurs at $q^* = (0.017 \pm 0.003)$ Å^{-1}, corresponding to a domain spacing $d = (54 \pm 1)$ Å, in reasonable agreement with the value obtained previously [8] $d = 57$Å. In the present experiment, it was only possible to detect the first order lamellar reflection, the highest order reflections observed previously [8] falling

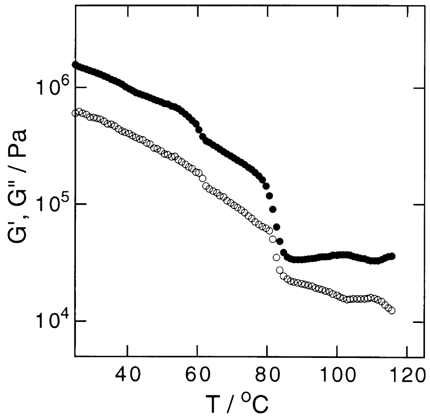


Fig. 1. The temperature dependence of the dynamic shear moduli of P_{12} at a frequency $\omega = 10$ rad s^{-1} and a strain amplitude $A = 1\%$ (● G'; ○ G''). The heating rate was 2°C min^{-1}.

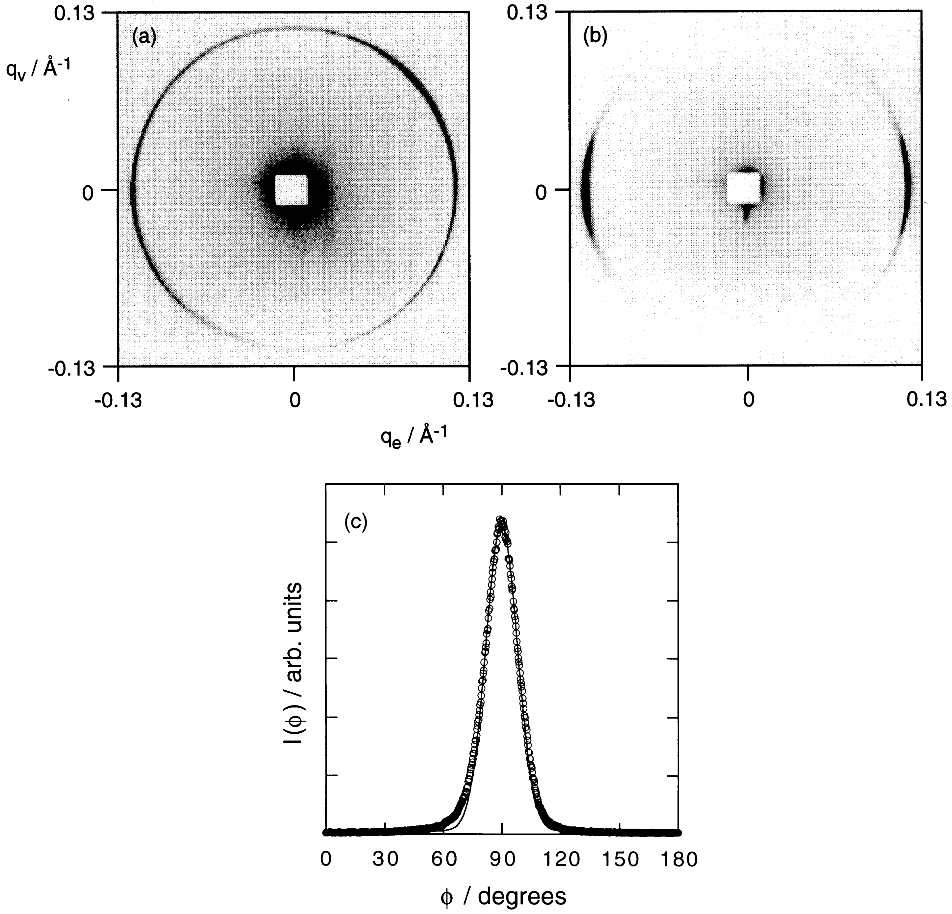


Fig. 2. The SAXS patterns obtained at 90°C: (a) prior to shearing, (b) under shearing at $\omega = 100$ rad s^{-1}, $A = 100\%$, after 15 minutes of shearing, (c) Gaussian fit to the intensity profile as a function of azimuthal angle, ϕ, defined with respect to **v** (vertical). The grey scale levels are lower for (a) so that forward scattering is more visible.

outside the area of the detector. That the polymer could be oriented using large amplitude shear is confirmed by Fig. 2b, which shows the SAXS pattern obtained during shear, after 12 minutes of shearing at $\omega = 100$ rad s^{-1}, and a large strain amplitude $A = 50\%$. Shearing led to the concentration of the first order reflection into arcs centred on the equator, i.e. a decrease in mosaic width associated with layer alignment. Fig. 2b shows that the layers aligned normal to the shear plates, i.e. in the (**v**,∇**v**) plane. Gaussian fitting of the azimuthal intensity (integrated in a narrow band centred on q^*) profiles after shearing under these conditions (see Fig. 2c) indicated an angular spread characterized by a Gaussian HWHM = 9.5°. In contrast to our results indicating orientation in the (**v**,∇**v**) plane, a different layer orientation has been reported for a smectic SCLCP subjected to steady shear, i.e. layers in the (**v**,**e**) plane [6]. In terms of the notation introduced by Safinya and coworkers [11] for the three possible orientations of layers formed in smectic A liquid crystals under shear, we observe the *a* orientation whereas Noirez and Lapp [6] reported the *c* orientation.

The dynamics of the process of alignment were monitored during large amplitude oscillatory shear at different strain amplitudes. Fig. 3 shows data from simultaneous SAXS/rheology experiments on P_{12} at 100°C during shear at $\omega = 100$ rad s^{-1}, with $A = 80\%$. Under these conditions G' is less than G''. The height and HWHM from Gaussian fitting to azimuthal intensity profiles similar to those shown in Fig. 2b are shown in Fig. 3a. During shear, the height of the Gaussian increases and its width decreases, consistent with an increase in anisotropy of the first order reflections. A steady state is reached after about 7 minutes, the HWHM then being 6.2°, a value which compares favourably to the mosaic widths obtained for the same polymer by magnetic alignment of mesogens or by drawing fibres [8], the Gaussian HWHM in that case being at best (10 ± 1)°. Shearing was stopped after 15 minutes, as shown in Fig. 3b; the dynamic shear moduli then recovered to their pre-shear values within 2 minutes. The relaxation associated with the reorientation of smectic layers, as probed through the anisotropy of SAXS reflections, started immediately after the shearing was stopped. However, the associated relaxation timescale was longer than that for the recovery of the shear moduli, as illustrated by Fig. 3a. This may be because measurements of the dynamic elastic moduli reflect the local defect structure in the smectic phase, whereas SAXS probes the global alignment of the smectic layers, the

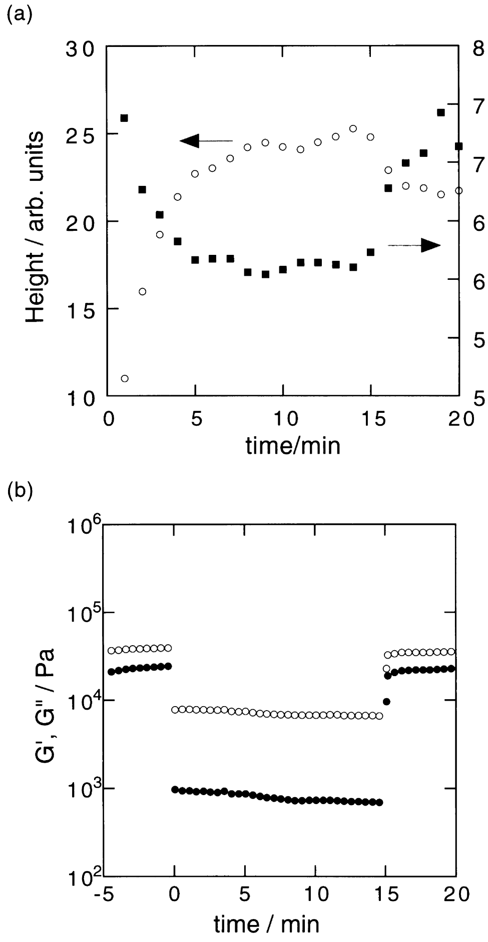


Fig. 3. Data obtained during a shearing experiment at $T = 100°C$, $\omega = 100\ \mathrm{rad\ s^{-1}}$, $A = 80\%$ for 15 min, then $A = 1\%$ for 5 min. (a) The parameters are from fitting of a Gaussian to the variation of intensity with azimuthal angle of the first order SAXS reflections (○) peak height, (■) HWHM of peak, (b) Dynamic shear moduli, measured concurrently (●) G', (○) G'' (also includes data obtained for 5 min prior to shearing).

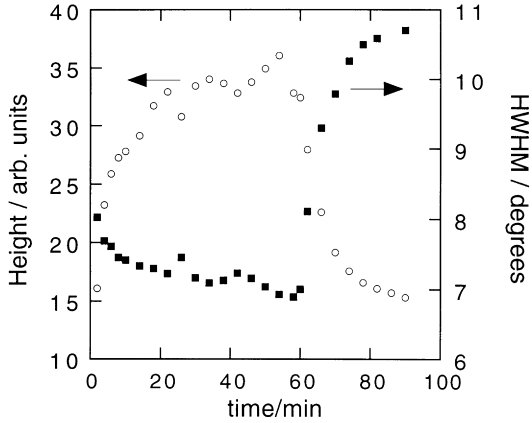


Fig. 4. Data obtained during a shearing experiment (after the sample was homogenized in the isotropic phase) at $T = 100°C$, $\omega = 100\ \mathrm{rad\ s^{-1}}$, $A = 80\%$ for 60 min, then $A = 1\%$ for 30 min. The quantities are obtained from fitting of a Gaussian to the variation of intensity of the first order SAXS reflections with azimuthal angle. (○) Peak height, (■) peak HWHM.

dynamics of the former occuring on a shorter timescale than the latter. Also noteworthy is the observation that a high degree of alignment of the sample was retained (Gaussian HWHM = 7.2°, see Fig. 3a), although relaxation experiments in this case were not pursued to long times.

Experiments were also performed at a fixed frequency, $\omega = 100\ \mathrm{rad\ s^{-1}}$ and different A, to probe the dependence of sample alignment on strain amplitude. No alignment was observed following shear at $A = 10\%$ for 15 min, although it was observed after shear at $A = 50\%$, the corresponding Gaussian arc having a HWHM = 9.3° (data not shown). It is noteworthy that although $A = 10\%$ is well outside the linear viscoelastic regime (which extended to $A \approx 1\%$ in P_{12}), shearing with this strain amplitude did not produce macroscopic alignment of the sample. Similar observations have been made for ordered mesophases formed by block copolymers in solution [10,12]. Whereas increasing strain amplitude at a high frequency leads to a high degree of alignment, experiments at lower frequencies (eg. $\omega = 0.1\ \mathrm{rad\ s^{-1}}$) indicated essentially no shear-induced orientation. The effect of steady shear was not explored because the rheometer does not operate in a steady shear mode. However, steady shear experiment using a Couette cell with in situ synchrotron SAXS are planned for future work.

To investigate the effect of shear history on the kinetics of shear-induced orientation and the relaxation process, experiments were conducted after the sample was heated into the isotropic phase. This ‘erased’ the memory of the sample of its prior shear treatment, as confirmed by the development of a ring of scattering when P_{12} was cooled back into the smectic phase. This ring was characterized by almost no anisotropy (Gaussian fitting to the azimuthal intensity variation produced a HWHM = 54° for peaks centred off the equator). Large amplitude shearing at $\omega = 100\ \mathrm{rad\ s^{-1}}$, $A = 80\%$ again led to a development of pronounced anisotropy, with the equatorial arcs continuing to sharpen for about 20 minutes, as illustrated by Fig. 4. A steady state was then achieved, with a corresponding azimuthal intensity HWHM = 7°. The dynamic shear moduli obtained concurrently with the SAXS patterns behaved in a similar manner as illustrated in Fig. 4, i.e. shearing produced strong and rapid shear thinning. Furthermore, cessation of shear led to recovery of the initial values of G' and G''. Fig. 4 shows that the relaxation of orientation occured over a timescale of about 20 min, however alignment of the sample was retained, with an ultimate mosaicity defined by a Gaussian HWHM = 10.7°. This is somewhat higher than the value obtained after the first shearing experiment, however it is similar to that obtained for the same polymer by magnetic alignment of the mesogens or drawing of fibres [8]. However, it should be noted that a higher degree of magnetic alignment can often be achieved in SCLCPs where there is a high temperature nematic phase, because its fluid nature enables easier orientation of the mesogens. The absence of a nematic phase in P_{12} prevents this alignment procedure.

4. Summary

In summary, SAXS combined with rheology yields a wealth of insight into the shear-induced alignment of a smectic SCLCP. Shearing at high frequency and large strain amplitudes led to macroscopic alignment of the polymer P_{12} with layers oriented in the $(\mathbf{v},\nabla\mathbf{v})$ plane. The dynamic shear moduli decreased markedly on application of large amplitude shear. A high degree of anisotropy of arcs corresponding to first order layer reflections was observed, and quantified by Gaussian fits to the azimuthal intensity variation, corresponding HWHM being as low as 6°–7° under shear at $\omega = 100$ rad s^{-1}, $A = 80\%$. This compares favourably to mosaic widths obtained by magnetic alignment. The timescale for saturation of alignment depended on shear history, ranging from 5 to 20 min, the relaxation time varying similarly. Although some orientation was lost following cessation of shear, a high degree of anisotropy was retained. It is thus apparent that shear provides a good method for permanent alignment of SCLCPs.

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