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Shear-induced band texture of side group liquid crystalline polymers

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The shear-induced band texture of conventional end-on fixed side group liquid crystalline polymers (LCPs) has been investigated by using polarizing optical microscopy (POM), small angle light scattering (SALS) and infra-red dichroism techniques. The band spacing is about 1 μm, which increases very slightly on increasing the temperature of shearing and is independent of shearing rate within the range studied. The band texture is not seen to exhibit an interchange of dark and bright bands on rotation of the sample with respect to the polarizer/analyser, but a typical periodical structure is reflected by the SALS patterns of the band texture. The relaxation behaviour of the bands indicates that the band texture formed here is the result of the orderly aligning of domains exhibiting the focal-conic texture, and this is totally different from the case of main chain LCPs where the band texture is substantially an optical effect of the periodic zigzag or sinusoidal structure of parallel aligned microfibrils. Infra-red dichroism and rotating parallel-plate shearing measurements show that the axes of the backbone of the polymer tend to orient in the shearing direction and the end-on fixed mesogenic side groups tend to align perpendicular to the shearing direction.

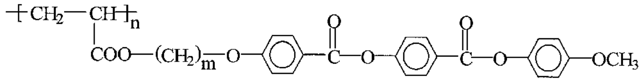
1. Introduction

The orientational behaviour of the polymeric liquid crystalline state in an external field is of theoretical and practical importance. A peculiar orientation effect of nematic main chain liquid crystalline polymers (LCPs) in the melt or in solution is the band texture formation during relaxation of the oriented nematic state after cessation of shearing [1]. The formation of the external field-induced band texture was first observed in aromatic polyamide fibres and films [2–4]. The alternating bright and dark band texture is an optical effect of the periodic zigzag or sinusoidal structure of microfibrils aligned parallel with each other, but normal to the bands observed using polarizing optical microscopy [5–10]. Although the band texture formation is very common in main chain LCPs, the molecular mechanism leading to the formation of the band texture remains to be understood. As to side group LCPs, they usually have a flexible backbone with mesogenic units longitudinally attached to it (end-on fixed). It is generally considered that the band texture could not be formed by conventional end-on fixed side group LCPs. Recently, a new class of side group LCPs has been found in which the mesogenic units are laterally attached to the backbone with or without flexible spacers (side-on fixed) [11–14]. Xu *et al.* [15] studied the morphology of oriented films obtained from this kind of side group LCP and reported the first example of a side group LCP exhibiting a band texture. The authors speculated that in such a case, the rigid side-on fixed mesogenic groups on the backbone may significantly affect the conformation of the backbone, making the polymer molecule as a whole rather rigid; as a result it may exhibit a behaviour similar to that of a main chain LCP. Zhou *et al.* [16] reported similar results for a side-on fixed poly-2,5-di(benzoyloxy)styrene, and Song *et al.* [17] reported that the band texture was formed in the smectic phase of a chiral side group LCP.

In this work, the shear-induced band texture of end-on fixed side group liquid crystalline polymers has been investigated in detail by using POM, small angle light scattering and IR dichroism techniques.

2. Experimental

The polymers used were three end-on fixed side group LCPs denoted SCP-*m* where $m = 2$, 6 and 11. They have the following repeating units:



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Their synthesis and preliminary characterization have been described elsewhere [18]. The apparent number average molar masses—in polystyrene (PS) equivalents—of these polymers were measured by GPC using tetrahydrofuran as solvent and PS as standard samples for calibration. All these polymers exhibit phase transition temperatures from smectic to nematic and then to the isotropic phase on being heated, as observed using an Olympus polarizing microscope (BH-2) equipped with a Mettler FP-52 hot stage at a heating rate of 10°C min^{-1}. The results are listed in table 1. Figure 1 shows the polarizing micrographs of the smectic focal-conic and nematic schlieren textures of the sample SCP-2.

Table 1. The values of M_n and the phase transition temperatures for the SCP samples.

Sample	M_n	$T_{\mathrm{Cr}\to\mathrm{Sm}}$/°C	$T_{\mathrm{Sm}\to\mathrm{N}}$/°C	$T_{\mathrm{N}\to\mathrm{I}}$/°C
SCP-2	4.3×10^3	73	185	223
SCP-6	4.1×10^3	75	181	221
SCP-11	3.9×10^3	68	165	176

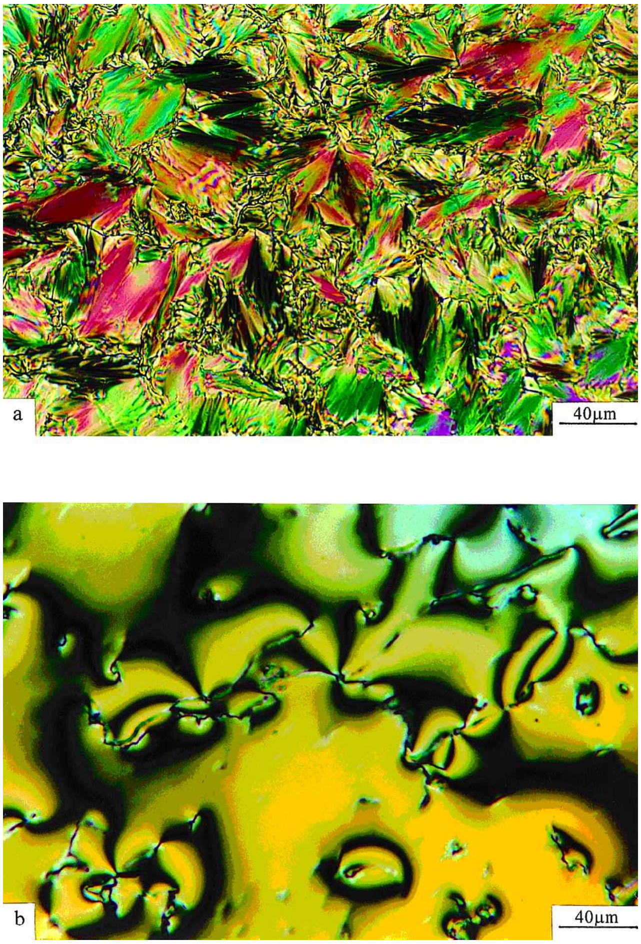

Figure 1. Polarizing optical micrographs of the smectic focal-conic texture and the nematic schlieren texture of sample SCP-2 at (*a*) 176°C and (*b*) 185°C.

The polymer melt mounted between two glass slides was sheared at 95 and 200°C and then quenched to room temperature to obtain a shear-oriented film. Specimen films for IR measurements were separated and peeled from the slide using dilute hydrofluoric acid and subsequently washed and dried.

The critical shear rate of band texture formation of these side group liquid crystalline polymers was studied by using a rotating parallel plate shearing apparatus which has been described previously [19]. The range of shear rates $\dot{\gamma}$ used was between 0 and 700 s^{-1}, varying with the distance from the centre of rotation as given by the following equation, which assumes a uniform velocity gradient across the thickness of the thin layer: $\dot{\gamma} = 2\pi Rn/h$ where R is the radial distance of the point of observation from the rotation centre, n is the rotation speed in s^{-1} and h is the thickness of polymer melt layer. The shearing temperatures were 90, 100, 150 and 170°C. The thickness of the melt layer was about 30 μm. After shearing, the specimens were quenched to room temperature and then observed by POM to determine the critical shear rate $\dot{\gamma}_c$.

The phase transition temperatures of the shear-oriented specimen and a powder sample of SCP-2 were measured by using a TA Instrument DSC-2910 at a heating rate of 10°C min^{-1} after calibration with pure indium. The band texture and the relaxation behaviour of bands were observed using a Model BH-2 Olympus polarizing microscope with a Mettler FP-52 hot stage. Small angle laser light scattering experiments were conducted using a SALS instrument (Model SL-1 made in this institute) with a 632.9 nm wavelength He-Ne laser. The Hv scattering patterns of the oriented specimen were photographically recorded. IR dichroism measurements of the oriented specimens were made using a Bruker IFS-113V Fourier transform IR spectrometer with a Perkin-Elmer gold wire grid polarizer at a resolution of 2 cm^{-1}.

3. Results and discussion

Figures 2(*a*) and 3(*a*) show the polarizing optical micrographs of oriented specimens of samples SCP-2 and SCP-6, respectively, sheared at 95°C in their smectic phases and subsequently quenched to room temperature. In these micrographs, a typical band texture with the long dimension of the bands extended in a direction perpendicular to the shear direction can be observed; the spacing of these bands could be estimated to be about 1 μm. In the smectic phase of main chain poly(esterimide)s, Pardey *et al.* [20] also found that the band texture could be formed. Taking account the similar

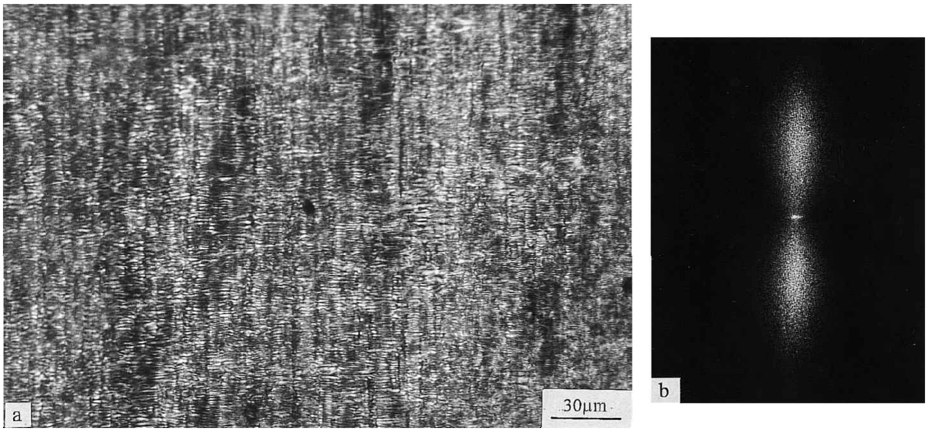

Figure 2. (*a*) Polarizing optical micrograph of an oriented specimen of SCP-2 sheared at 95°C and subsequently quenched to room temperature, and (*b*) the corresponding small angle laser light scattering Hv pattern (the shearing direction is vertical).

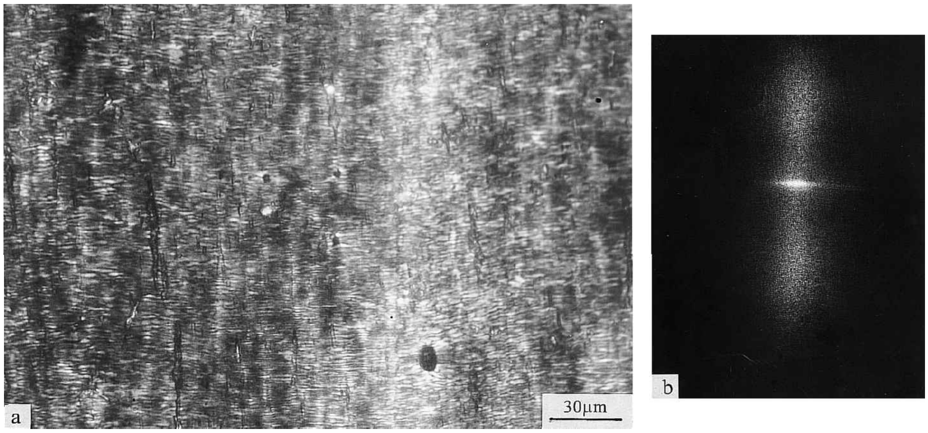

Figure 3. (*a*) Polarizing optical micrograph of an oriented specimen of SCP-6 sheared at 95°C and subsequently quenched to room temperature, and (*b*) the corresponding small angle laser light scattering Hv pattern (the shearing direction is vertical).

result of a band texture reported by Song *et al.* [17] for a chiral side group LCP, this indicates that end-on fixed side group LCPs can really form a band texture similar to that formed in main chain or side-on fixed side group LCPs by shearing. When the oriented sample with the band texture under observation was rotated with respect to the directions of the polarizer and analyser, the bright and dark bands did not interchange as they do for the main chain liquid crystalline polymers. However, as shown in figures 2(*b*) and 3(*b*), the small angle laser light scattering Hv patterns for the corresponding samples give a typical grating diffraction pattern with two scattering lobes normal to the bands. Therefore, it is safe to conclude that a periodic structure aligning along the shearing direction must have been formed in these oriented films after the cessation of shearing. Moreover, we found that sample SCP-11 did not exhibit a band texture after cessation of shearing, and in this way differs from a chiral side group liquid crystalline polymer having the same spacer length [17]. This indicates that chirality of the mesogen can play an important role.

After SCP-2 and SCP-6 were sheared using the rotating parallel plate shearing apparatus and then immediately quenched to room temperature, all the sheared specimens exhibited a radially outward growing band texture and a clear Maltese cross pattern between crossed polarizers, resembling a typical spherulite morphology. Figure 4 shows the band texture of SCP-2 sheared by the rotating parallel plate shearing apparatus

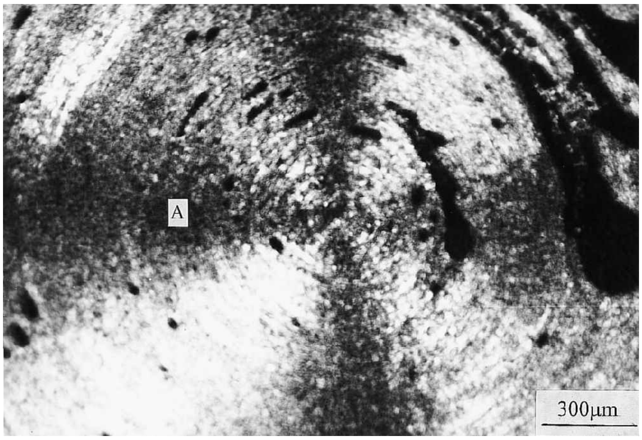

Figure 4. Polarizing optical micrograph of the band texture of SCP-2 sheared by the rotating parallel plate shearing apparatus at 90°C.

at 90°C. It was found from the interference colours on inserting a compensator ($\lambda = 530\,\mathrm{nm}$) that it showed a negative birefringence; that is, the molecular backbones were oriented along the shearing direction, perpendicular to the long axes of the bands. Figure 5 shows a POM micrograph of a magnified local area of figure 4 corresponding to shear rates from 410 to 416 s^{-1}. The band width does not change along the radial direction and remains about 1 μm, i.e. it is almost independent of the shear rate to which the melt has been subjected, in accord with the findings of Chen *et al.* [19] for main chain liquid crystalline polymers. From the radial distance of the demarcation circle between the banded and non-banded regions in the vicinity of the rotation centre, we found the critical shear rate $\dot{\gamma}_c$ for the formation of the band texture for sample SCP-2 at 90°C was about 7 s^{-1}.

The band texture variation of sample SCP-2 was studied at different shearing temperatures between $T_{\mathrm{Cr\text{-}Sm}}$ and $T_{\mathrm{Sm\text{-}N}}$. It was found that the influence of shearing temperature on the band spacing, around 1 μm, was very slight in this temperature range from 90 to 170°C. However, when the sample was sheared at a temperature above $T_{\mathrm{Sm\text{-}N}}$ and then quenched, for example at 200°C, as shown in figure 6, the band texture formed showed a large spacing of about 10 μm, which is different from that formed after shearing between $T_{\mathrm{Cr\text{-}Sm}}$ and $T_{\mathrm{Sm\text{-}N}}$. When the sample was rotated between the crossed polarizer, the dark and bright bands interchanged. It was found that the edge of some cracks formed along the shearing direction showed a zigzag form with a period in agreement with the band spacing, which is similar to the case for main chain LCPs. Further research is certainly needed to reveal the mechanism of the band formation at different temperatures.

The relaxation behaviour of the band texture in the oriented specimens of these side group LCPs sheared between $T_{\mathrm{Cr\text{-}Sm}}$ and $T_{\mathrm{Sm\text{-}N}}$ was found to be different from that of main chain thermotropic LCPs. In the latter case, the band texture relaxes gradually above the melting temperature and disappears into a threaded texture at temperatures very close to the clearing point. However, in the case of the side group LCP, as shown in figure 7 for sample SCP-2 sheared at 95°C, the band texture became more distinct and more straight and extended in the direction perpendicular to the shearing direction; but the band width showed almost no visible change when the oriented film was heated to 45°C, which is just higher than the melting temperature of 42.7° measured by DSC for this film. Figure 8 shows the DSC heating curves of an SCP-2 powder sample and the shear-oriented SCP-2 film. The smectic–nematic and nematic–isotropic phase transitions are found to be the same, at 184.3 and 232.3°C, respectively, on curves (*a*) and (*b*), which indicates that the thermal history undergone by the SCP-2 film does not influence the above phase transitions. The multiple peaks at 51.7, 67 and 79°C on curve (*a*) are the melting temperatures of the SCP-2 powder, while for the shear-oriented SCP-2 film the melting temperature moves to 42.7°C, where only one sharp endothermal peak is shown on the curve (*b*). The shift in the melting peak of the SCP-2 film is thought to result from the thermal history of the preparation. The crystals totally melted when the SCP-2 powder sample was heated to 95°C; it was then sheared at this temperature, but the crystals reformed on quenching to room temperature are far from perfect and consequently melt at a lower temperature of 42.7°C. When the above sample was further heated above the melting temperature, the band spacing remained almost unchanged and the focal-conic texture gradually emerged and became juxtaposed along the shearing direction. During this process, some thin parallel threads appeared along

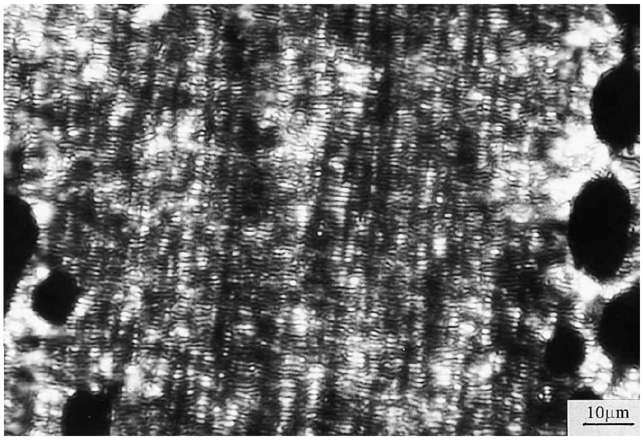

Figure 5. Polarizing optical micrograph of the band texture of the magnified local area (A) of figure 3 (the shearing direction is vertical).

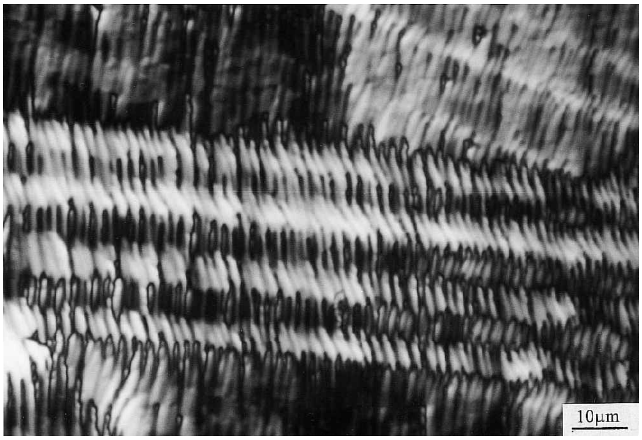

Figure 6. Polarizing optical micrograph of the band texture of SCP-2 sheared at 200°C and then quenched (the shearing direction is vertical).

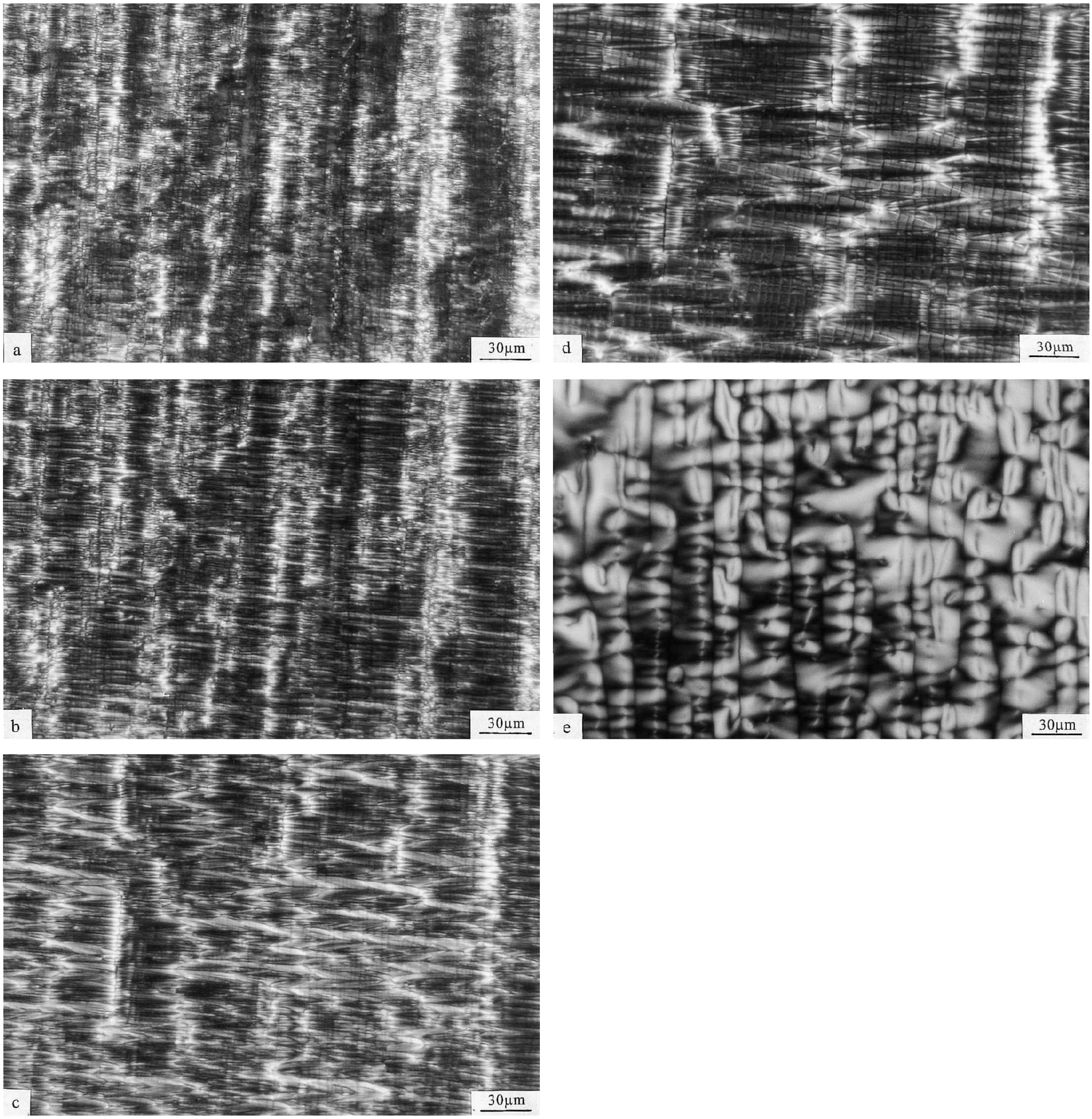

Figure 7. Polarizing optical micrographs of oriented specimens of SCP-2 sheared at 95°C during the process of heating at (*a*) room temperature, (*b*) 45°C, (*c*) 180°C, (*d*) 182.5°C and (*e*) 184.5°C (the shearing direction is vertical).

the shearing direction, as if they were segmenting the bands. This narrow ordered focal-conic texture was so stable that it was maintained until 180°C which is close to $T_{\mathrm{Sm\text{-}N}}$. Once the temperature reached 180°C, the band spacing increased dramatically and segmentation of the bands became more widespread. When further heated, the narrow ordered focal-conic texture gradually disappeared and eventually turned into a typical nematic schlieren texture at $T_{\mathrm{Sm\text{-}N}}$, but some degree of orientation remained until the temperature was above $T_{\mathrm{Sm\text{-}N}}$. These observations may suggest that the fundamental units involved in the molecular motion in such a side group LCP are domains with a focal-conic texture and that the band texture formed here is the result of a periodic alignment of those domains.

More detailed information about molecular orientation in an oriented film can be obtained from IR dichroism measurements. The polarized IR spectra of oriented

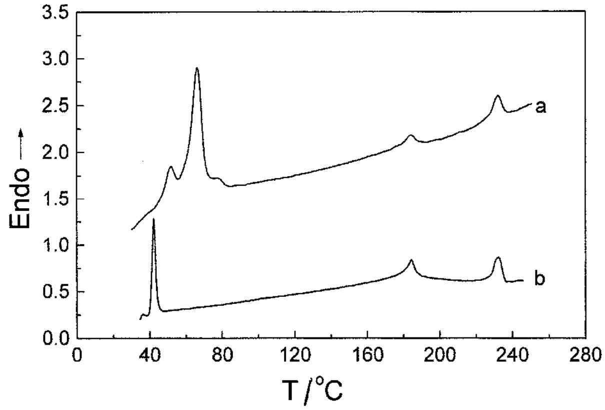

Figure 8. DSC heating curves at a heating rate of 10°C min^{-1} of (*a*) SCP-2 powder sample, and (*b*) shear-oriented SCP-2 film.

films of SCP-2 and SCP-6 all showed IR dichroism. Figure 9 shows the spectra of an oriented film of SCP-2 sheared at 95°C and then quenched to room temperature, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for radiations polarized in the shearing direction and perpendicular to the shearing direction, respectively. The main characteristic absorption bands are listed in table 2: five $\nu_{\mathrm{C-O-C}}$ bands at 1018, 1061, 1161, 1194 and $1269\,\mathrm{cm}^{-1}$ and two $\nu_{\mathrm{C=C}}$ bands of the phenylene ring at 1509 and $1606\,\mathrm{cm}^{-1}$ exhibit strong perpendicular dichroism. Since the C–O–C moiety and the phenylene ring are in the side group, their absorption bands can be used to characterize the orientation behaviour of the mesogenic side groups. The transition moments of these bands are directed along the axes of the mesogenic units and the ratio $A_{\parallel}/A_{\perp}$ is always less than 1 for these bands; therefore the ordering directions of the mesogenic units tend to be normal to the shearing direction. Taking into account the results from rotating parallel-plate shearing, the backbone tends to align in the shearing direction. These results indicate that the molecular orientation of these side group LCPs in the band texture is different from that of main chain LCPs.

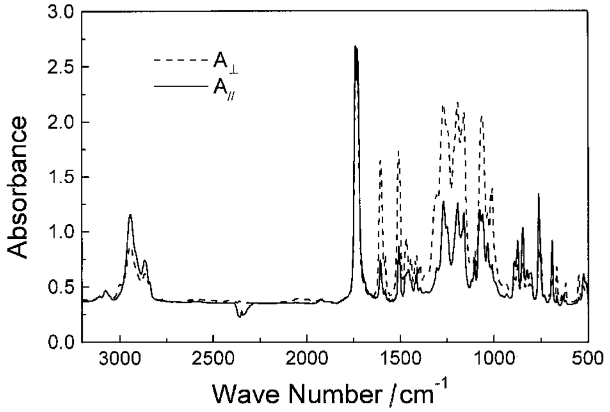

Figure 9. Polarized IR spectra of an oriented specimen of SCP-2 with the band texture formed after being sheared at 95°C.

Table 2. Some IR absorption band assignments and values of their dichroic ratios for the side group liquid crystalline polymer ($m = 2$) with band texture sheared at 95°C.

Band/cm^{-1}	Tentative assignment	$R = A_{\parallel}/A_{\perp}$
1018	C–O–C stretching	< 1
1061	C–O–C stretching	< 1
1161	C–O–C stretching	< 1
1194	C–O–C stretching	< 1
1269	C–O–C stretching	< 1
1509	phenylene ring stretching	< 1
1606	phenylene ring stretching	< 1

4. Conclusion

Conventional end-on fixed side group LCPs can form a shear-induced band texture. The increase in band spacing is almost undetectable with change in shearing temperature between $T_{\mathrm{Cr\text{-}Sm}}$ and $T_{\mathrm{Sm\text{-}N}}$ and is independent of shearing rate within the range studied. Different from the case of main chain LCPs, the band texture formed in these side group LCPs is an optical effect arising from periodically aligned domains in the form of focal-conics, and not from a periodic zigzag or sinusoidal structure of microfibrils. The main chains of the polymer tend to orient in the shearing direction, while the mesogenic side groups tend to align perpendicular to the shearing direction.

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