Morphological study of oriented films obtained from side-chain liquid crystalline polymers

Guozhong Xu, Wei Wu, Deyan Shen, Jianan Hou, Shufen Zhang and Mao Xu*

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, China

and Qifeng Zhou

Department of Chemistry, Peking University, Beijing 100871, China

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The morphological features of side-on fixed liquid crystalline polymers in an oriented state are investigated using polarizing microscopy, small angle light scattering (SALS) and infra-red dichroism techniques. A conventional side-chain polymer with mesogenic units attached longitudinally to the backbone is also studied for comparison. Banded texture usually only reported for main-chain liquid crystalline polymers is observed for these side-on fixed polymers under the crossed polarizing microscope, and SALS measurements also show typical grating diffraction patterns. This implies that side-on fixed rigid mesogens may significantly affect the conformation of the main chain of molecules, and the molecule as a whole may become rather rigid, exhibiting behaviour similar to that of the main chain. Infra-red dichroism measurements indicate that the main-chain axes of the molecules tend to orient in directions close to the shear direction. The side-on fixed mesogens are packed around the backbone, but their axes are not parallel to the latter.

(Keywords: morphology; liquid crystalline polymer; polarization)

INTRODUCTION

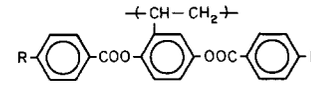
High performance materials can be prepared by processing liquid crystalline polymers in their mesomorphic state. It is believed that the mesomorphic order may help to retain higher molecular orientation in the materials after processing. One of the characteristic morphological features for these oriented samples is their banded texture. Parallel bands of alternate brightness can be observed in these samples under a crossed polarizing microscope. These bands are usually thousands of Angstroms to several microns in width, and are extended in a direction perpendicular to the direction of shear under which the samples were prepared.

The banded texture was first observed for aromatic polyamide fibres and film specimens[1-3], and has been reported for both lyotropic and thermotropic liquid crystalline polymers, including aromatic polyamides[1-5], polyisocyanates[6], polypeptides[7], cellulosic derivatives[8-12], aromatic polyester or co-polyesters[13-19], and polyazomethineether[20]. In our detailed studies with oriented films of aromatic polyesters, a general picture was given to describe their morphological features on different size levels, and a forced relaxation mechanism for banded texture formation was discussed[16-19]. The banded texture seems very common for main-chain liquid crystalline polymers.

Molecules of side-chain liquid crystalline polymers usually have a flexible main chain with mesogenic units longitudinally attached to it (end-on fixed). The behaviour of side-chain and main-chain liquid crystalline polymers is quite different, and no banded texture has been reported for side-chain polymers. Recently, a new class of mesomorphic side-chain polymers has been synthesized. In the molecules of these polymers the mesogenic units are laterally attached (side-on fixed) to the backbone through or without a flexible spacer[21-24]. The two types of connection between the rigid mesogenic units and the flexible main chain may have different influences on the molecular conformation, and also on their properties. In this work, the morphological features of side-on fixed liquid crystalline polymers were studied, and banded texture was observed in their oriented specimens.

EXPERIMENTAL

Two side-chain liquid crystalline polymers having the following structure were used in this work, and are designated as S(MO) for R=OCH_3 and S(H) for R=H respectively:



*To whom correspondence should be addressed

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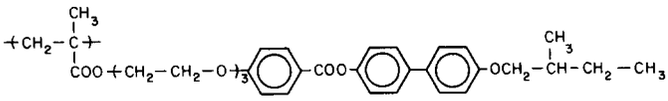
Table 1 Side-chain liquid crystalline polymers

Sample	M_n (10^4)	T_g (°C)	T_m (°C)	T_i (°C)
S(MO)	4.2	156	–	–
S(H)	5.4	159–195	–	–
E	3.8	46	63.6	171

An end-on fixed side-chain polymer, sample E, with the following structure was also used in this work for comparison:



The apparent number average molecular weight of the samples was determined by the g.p.c. technique using tetrahydrofuran as the solvent. The results are given in *Table 1*. Also listed are the transition temperatures of the samples obtained from d.s.c. measurements by using a Perkin–Elmer DSC-4 differential scanning calorimeter.

Oriented film specimens with a thickness of about 10 μm were prepared by shearing the mesomorphic polymer melt (at about 275–285°C for S samples, and at about 130°C for sample E) between two glass slides at shear rates of magnitude of order $10^2\,s^{-1}$, and subsequently quenching to room temperature. To prepare oriented specimens for i.r. measurements, NaCl single crystal slides were used instead of glass slides, and the thickness of the specimens was around 10 μm.

The morphology of the oriented specimens was studied using an Olympus polarizing microscope (type BHS-753P) equipped with a hot stage. Light scattering experiments were conducted with a 632.8 nm wavelength He–Ne gas laser. The H_v scattering patterns for specimens were recorded photographically. Infra-red spectra and dichroism measurements of the specimens were studied using a Bruker IFS–113V Fourier transform i.r.-spectrometer at a resolution of $2\,cm^{-1}$; 256 scans were signal-averaged and stored on a magnetic disc system.

RESULTS AND DISCUSSION

The melt cast specimens of S samples were not crystalline. Their glass transition temperatures were determined by d.s.c. measurements, and the data are given in *Table 1*. Above T_g the specimens exhibit a threaded optical texture of the mesomorphic state (*Figure 1*). No transition from the liquid crystalline state to isotropic melt was observed in d.s.c. studies up to about 370–380°C, the temperature at which 5% weight loss was detected for both S samples in nitrogen during thermogravimetric measurements.

Figure 2 gives the polarizing micrographs of oriented specimens for samples S(MO) and S(H). A typical banded texture with parallel bands extended in a direction perpendicular to the shear direction can be observed in these micrographs. The width of the bands was estimated to be about 1–1.5 μm.

The small angle light scattering (SALS) technique has been proved to be very useful in studies of banded texture[3,16,19]. The SALS H_v patterns for sample S(MO) are shown in *Figure 3*. The unoriented specimen gives a circular symmetric H_v pattern (*Figure 3a*), which is usually observed for nematic mesophase. A typical grating diffraction pattern was obtained for the oriented specimen (*Figure 3b*). Scattering intensity distributed along a line parallel to the direction of shearing, which is vertical in this case, can be observed. As explained in previous studies, the average band width can be determined from the angular position of the intensity maxima of the grating diffraction. The estimated value of band width from SALS measurements of these specimens is reasonably consistent with that from direct microscopic observations. The bright spot at small scattering angles is believed to be due to the non-uniformity of these manually prepared specimens. They were not uniformly oriented, and banded texture was only observed in some areas of the specimens. The intensity along the horizontal line in *Figure 3b* is

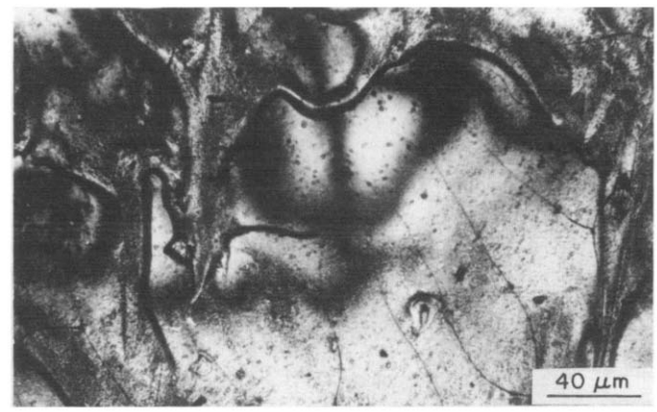


Figure 1 Polarizing micrograph of sample S(MO) in the mesomorphic state

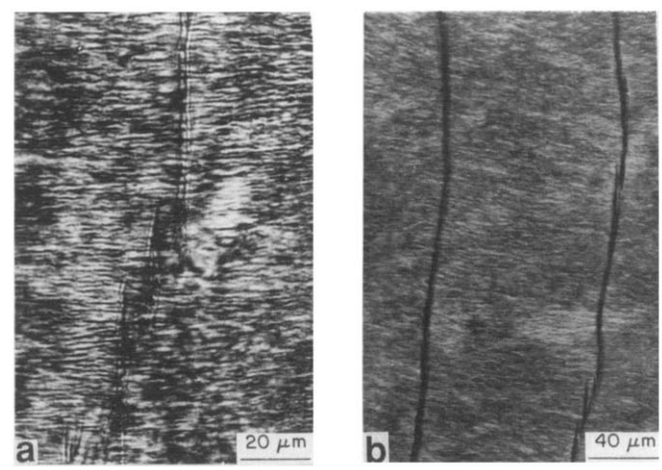


Figure 2 Polarizing micrographs of oriented specimens of (a) sample S(MO); and (b) sample S(H). The shear direction is vertical

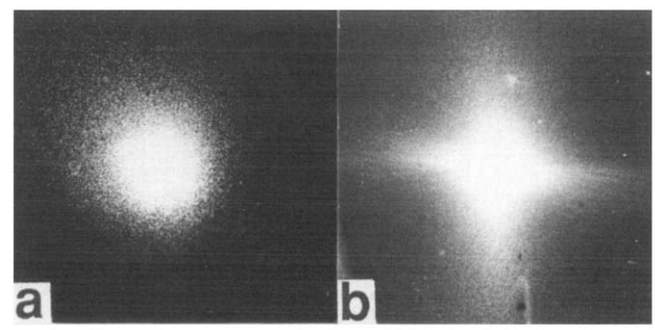


Figure 3 SALS H_v patterns of sample S(MO): (a) unoriented specimen, (b) oriented specimen with banded texture (shear direction is vertical)

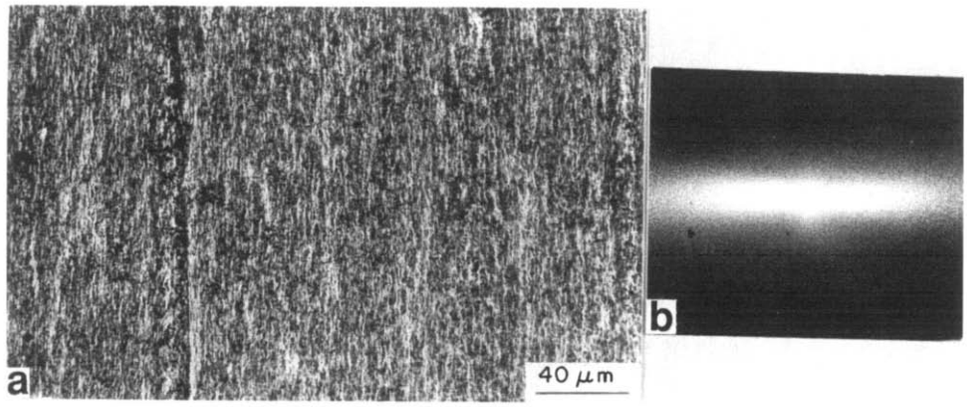


Figure 4 (a) Polarizing micrograph and (b) SALS hv pattern of oriented specimen of sample E. The shear direction is vertical

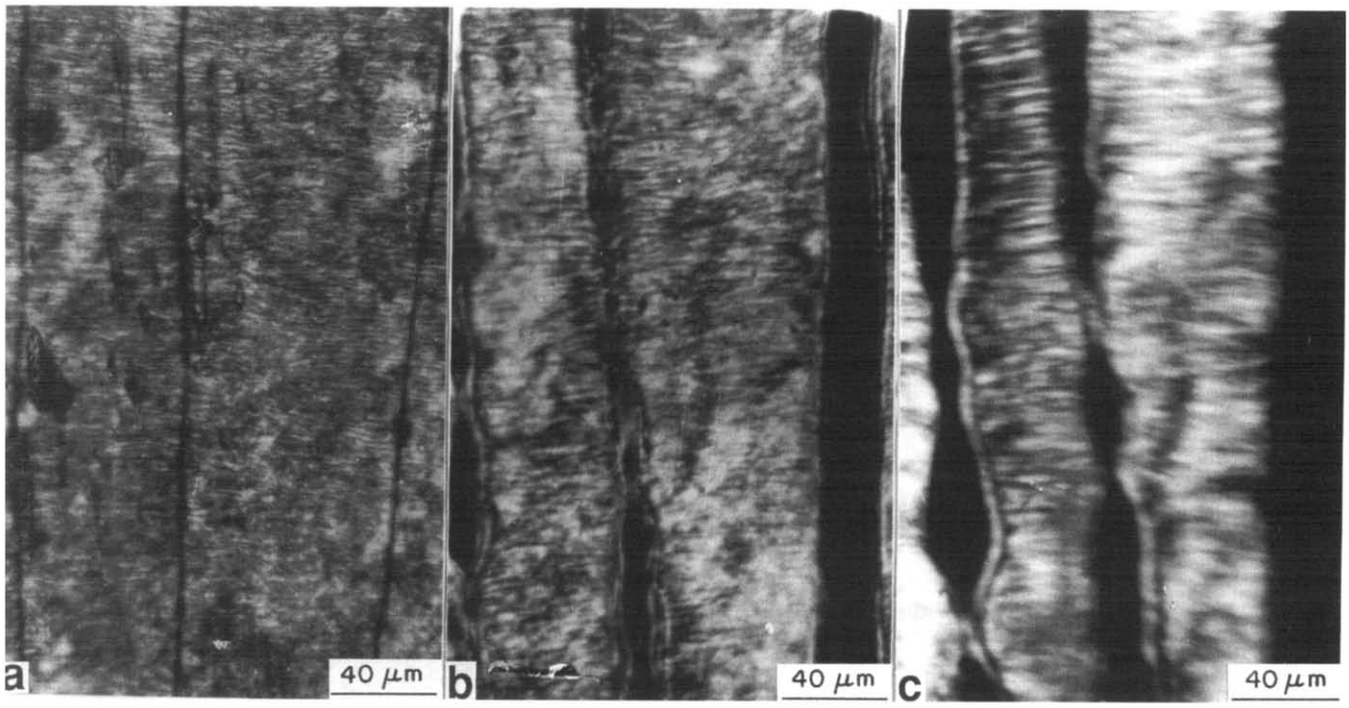


Figure 5 Polarizing micrographs of an oriented specimen of S(MO) at different temperatures. (a) 132°C; (b) 275°C; and (c) 285°C. The heating rate is about 10°C min^{-1}

the scattering due to cracks or thickness fluctuation, and is very common for polymer samples after shearing or stretching.

Figure 4 gives the results for sample E, an end-on fixed side-chain liquid crystalline polymer. No banded texture was observed for oriented specimens of this sample. The polarizing micrograph (*Figure 4a*) only shows the trace of shear direction which results in strong light scattering along a direction perpendicular to the shear direction, as shown in *Figure 4b*.

Comparison of the results of samples S and E is very impressive. It indicates how significantly the morphological features of side-chain polymers in an oriented state may change when their mesogens are attached differently to the main chain. It is also clear from these results that a banded texture, usually observed only for main-chain liquid crystalline polymers, was really formed in these side-on fixed polymers. To our knowledge, this might be the first example for side-chain liquid crystalline polymers exhibiting the banded texture.

We have studied the thermal stability of the banded texture in oriented specimens of main-chain liquid crystalline polymers. The banded texture was found to be thermally very stable in the heating process, and usually disappeared only at temperatures very close to the clearing point. Similar results were observed for the banded texture in side-on fixed liquid crystalline polymers. *Figure 5* shows the polarizing micrographs of oriented specimens of sample S(MO) at different temperatures. The banded texture remains almost unchanged in a wide temperature range. At higher temperatures (*Figures 5b* and *5c*) an increase in band width can be detected. Also observed at these temperatures is the development of dark regions along the cracks within the film specimens. It was not supposed to be the results of orientational relaxation, but the decomposition of the polymer molecules at these temperatures. The polymer may lose its mesophase behaviour due to decomposition, and it should first take place at the surface area in the form of cracks, as in the specimens. There is some evidence

for this idea from the fact that these dark regions remain isotropic after cooling down to room temperature.

In our previous studies on the banded texture of main-chain polymers, a contraction effect was proposed to explain the formation mechanism[19]. The semi-rigid molecules of main-chain liquid crystalline polymers are rather rigid, and take the extended conformation due to the introduction of mesogens into their backbone. They are packed in parallel in the form of fibrils under shear along the shearing direction. Formation of the banded texture after shear cessation is not the result of a free thermal relaxation of individual molecules, but the result of a zigzag rearrangement of the fibril as a whole under crushing along the orientation direction. It means that the elastic energy stored during shearing may give the driving force, and the high stability of the ordering of parallel alignment of neighbouring molecules due to the very limited molecular motion of these polymers is a necessary condition for band formation. In the case of flexible chain polymers, molecules may also assume parallel orientation under shearing; however, the orientational relaxation takes place easily as the result of random thermal motions of individual molecules. The external elastic force may even accelerate this process. So, no regular banded texture should be expected. For conventional side-chain liquid crystalline polymers, the longitudinally attached mesogenic units do not significantly affect the molecular conformation, and the molecules usually exhibit the behaviour similar to flexible chains. Therefore, no banded texture is formed after shearing.

According to the contraction mechanism described above, formation of the banded texture in sheared specimens of the side-on fixed polymers used in this work implies that molecules of side-chain liquid crystalline polymers may become rather rigid as a whole, and take the more extended rod-like conformation, when mesogenic units with three benzene rings are attached laterally to the backbone without a flexible spacer.

The optical anisotropy of the bands was studied on a polarizing microscope by using a tint plate (530 nm). When the shearing direction of the specimen is parallel to the fast speed direction of the tint plate, the bands exhibit the colour green. They become yellow when these two directions are perpendicular to each other. This means that the bands have a larger refractive index value for radiation polarized in the band extension direction. It may imply that the axes of mesogens which have three benzene rings connected in a series in the *para*-position are oriented more or less perpendicular to the shear direction.

More detailed information about molecular orientation in oriented film specimens can be obtained from i.r. dichroism measurements[16]. *Figure 6* gives the i.r. spectra for an oriented specimen of sample S(MO). The difference between the absorbances for radiations polarized in the shear direction A_S, and in the lateral direction A_L, can be detected from the figure. Two i.r. bands, 2905 cm^{-1} and 2939 cm^{-1}, were used to discuss the orientation of the main-chain axis of the polymer molecules. They can be assigned to the CH stretching of the main chain, and their transition moments are perpendicular to the axis of the main chain. The ratio of A_S/A_L is always less than unity for these two bands. It implies that in the oriented specimens the main chain of the molecules tends to orient in the shear direction. This phenomenon has always been

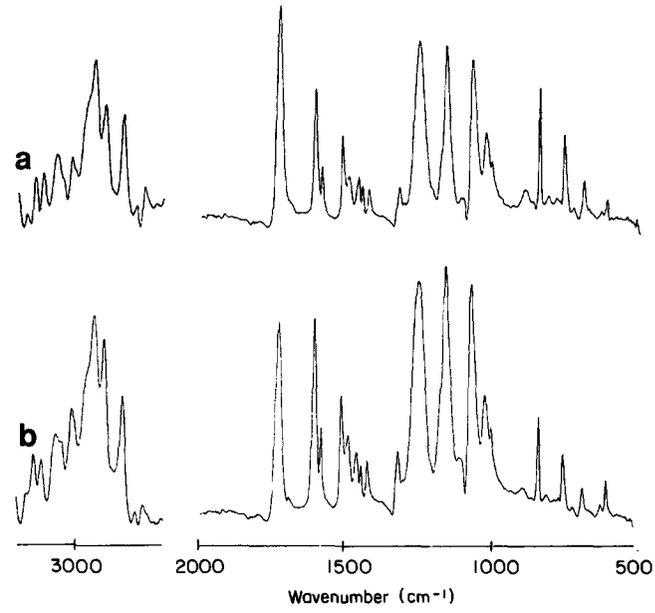


Figure 6 Infra-red spectra for oriented specimen of sample S(MO): (a) A_S, and (b) A_L

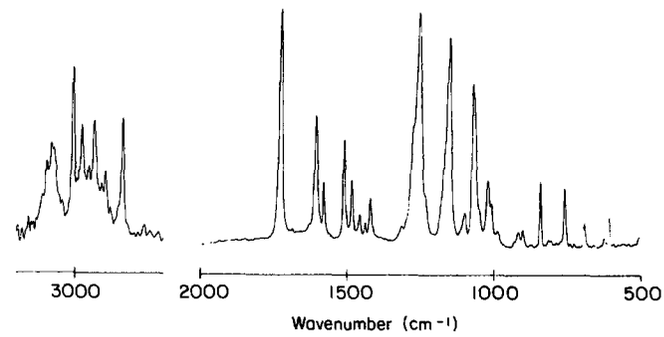
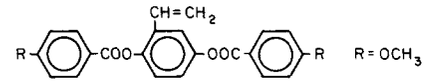


Figure 7 Infra-red spectrum of the model compound of the mesogens

observed for main-chain liquid crystalline polymers, but it was not expected for end-on fixed side-chain polymers.

It is interesting to learn how the laterally attached mesogens are packed around the main chain. *Figure 7* is an i.r. spectrum of a model compound for the mesogens used in S samples which has the following structure:



The assignment of the i.r. bands related to the mesogenic units in sample S(MO) was obtained according to the spectrum of the model compound, and is given in *Table 2*. The dichroism mode of these bands for S(MO) can be determined from *Figure 6* according to the value of the A_S/A_L ratio, and is designated as π bands for $A_S/A_L > 1$ and σ bands for $A_S/A_L < 1$. Results are given in the last column of *Table 2*. It should be noted that all the bands having a transition moment perpendicular to the axis of the mesogen exhibit π dichroism, and bands with a transition moment parallel or approximately parallel to the mesogen axis show σ mode of dichroism. Taking into account the orientation of the main-chain axis, it can be supposed that the mesogens tend to be packed perpendicularly around the main chain. This result is consistent with that from optical anisotropy measurements.

Table 2 Band assignments and dichroism mode of sample S(MO)

Band (cm^{-1})	Dichroism mode	Tentative assignment
611	σ	Phenyl ring in-plane deformation
694	π	Phenyl ring out-of-plane deformation
760	π	Phenyl ring CH out-of-plane bending
845	π	Phenyl ring CH out-of-plane bending
1026	σ	Phenyl ring CH in-plane bending
1074	σ	C–O stretching
1162	σ	C–O stretching
1256	σ	C–O stretching
1512	σ	Phenyl ring stretching
1602	σ	Phenyl ring stretching
1726	π	C=O stretching
2842	σ	CH_3 stretching
2905	σ	Main chain CH stretching
2939	σ	Main chain CH stretching

CONCLUSIONS

Banded texture which is common for oriented specimens of main-chain liquid crystalline polymers can also be observed in oriented specimens of side-chain polymers with mesogenic units attached laterally to the main chain. This implies that the rigid mesogens may significantly affect the conformation of the main chain of the molecules when they are side-on fixed. The molecule as a whole becomes rather rigid, and may exhibit behaviour similar to that of the main-chain ones.

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