

# Influences of substrate surfaces on the band formation behaviour in an oriented thermotropic liquid crystalline polyester

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The influences of substrate surfaces on the formation behaviour of banded texture and its thermal stabilities have been studied for an aromatic X-shaped main-chain liquid crystalline polyester. The oriented polymer films prepared by shear on a glass substrate were found to exhibit a strong bounding effect, which was very effective in stabilizing or keeping the structural orders of oriented polymer chains, even for a long time in the mesomorphic state and also in stimulating the band formation process during cooling. Such an influence is considered to arise from strong interfacial interactions between the solid substrate and the mesomorphic polymer molecules deposited on it. Similar phenomena were also observed in the case of PET film adopted as substrate. However, they were quite different when the glass substrate was replaced by a Teflon sheet: the uniformity of polymer chain alignments on it was difficult to maintain even in a rapid cooling process after shear cessation, resulting in a formation of irregular banded texture. The melting-induced re-orientation behaviour of polymer chains was also examined for a drawn fibre. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Banded texture, as one of the characteristics of oriented specimens, has been investigated for many lyotropic and thermotropic liquid crystalline polymers (LCPs)<sup>1–14</sup>. Parallel bands of alternate brightness, hundreds of nanometres to several microns in width can be observed in these specimens after shear cessation. Such a texture seems quite common in main-chain LCPs, with rigid rod-like mesogens along the polymer backbone. Recently, we have found that banded texture has also possibly formed in some main-chain LCPs with non-linear (X-shaped) mesogens<sup>15</sup> and even in some special side-chain polymers<sup>16–18</sup>. The morphological and structural features of banded texture have been studied in detail on different size levels for some cases<sup>7,8,10,12,15</sup>.

Although the mechanisms of band formation have been proposed through some experimental and theoretical analyses for lyotropic LCPs<sup>13,14,19</sup>, the details are still not very clear and the suggested models seem not suitable for explaining some phenomena in the thermotropic case. In previous studies<sup>8,11,12,15</sup>, the influences of molecular weight and shear rate, under which the

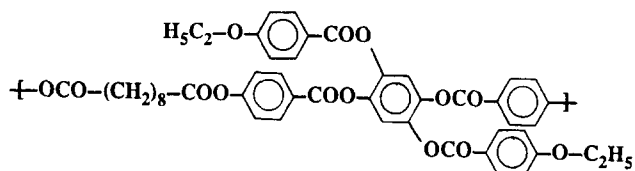
oriented films were prepared, on the properties of banded texture were investigated for some thermotropic main-chain LCPs. In addition to these influences, the cooling condition after shear cessation was also found to affect sensitively the formation behaviour of banded texture and its properties in some thermotropic LCPs<sup>20</sup>. Banded texture was readily generated on rapid cooling for all the compounds under investigation. The whole orientational orders of specimens, however, may become quite disturbed when the cooling rate was lowered, and, therefore, no banded texture could be formed. The only exception was found in a polymer with so-called X-shaped mesogens along its backbone. Banded texture could be observed clearly even in its slowly cooled specimens, and the bandwidth was much smaller than by rapid cooling. These results could be understood on the basis of a proposed contraction mechanism due to the elastic force or energy stored in the specimens during shear. However, there are likely to be other factors which affect the band formation behaviour, for example anchoring effect arising from substrate surface, on which the oriented specimens are prepared, was found particularly important. In this work, we have further investigated the formation behaviour of banded texture and its thermal properties for the same compound used

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in the previous studies<sup>15,20</sup>, by taking into consideration the influences of different substrate surfaces.

## EXPERIMENTAL

The LCP compound used in this work has the so-called X-shaped mesogens along its main chain, and was designated as P(2,8)<sup>15,20</sup>. It was prepared by solution polycondensation of the monomers 4,4'-(octamethylene dioxydioxo) dibenzoyl dichloride and 2,5-dihydroxyl-1,4-phenylene di-*p*-ethoxybenzoate at low temperature and has the following chemical constitution. The procedures of synthesis have been described elsewhere<sup>21</sup>.



Thermal transition behaviour was determined with a Perkin-Elmer DSC-4 differential scanning calorimeter (d.s.c.). The transition temperatures from crystalline to nematic and from nematic to isotropic phases in the heating process are 176°C and 223°C, respectively. Morphological observations were carried out with an Olympus BH-2 polarizing microscope equipped with a hot stage.

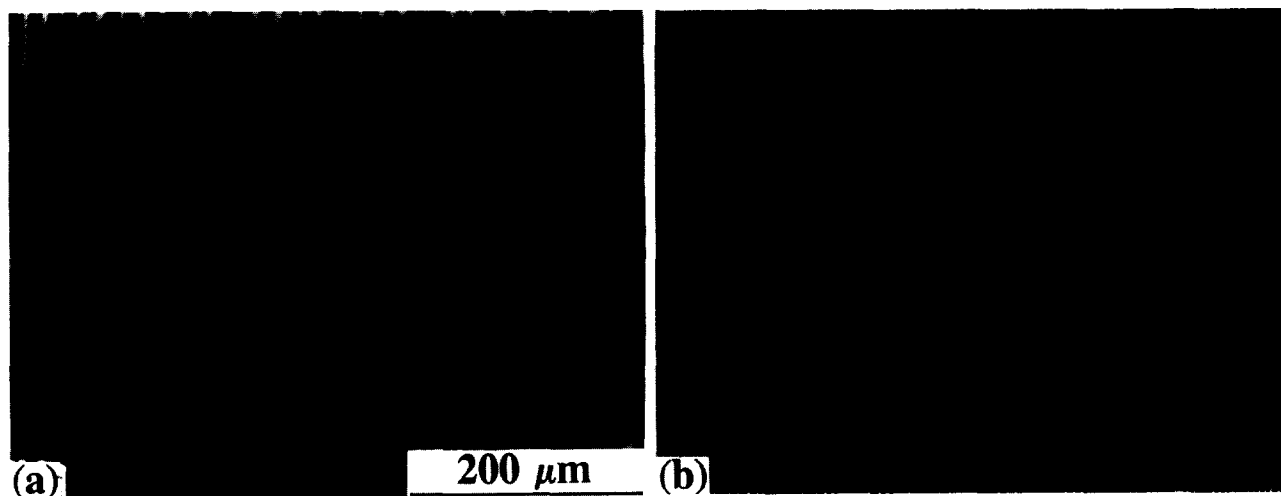
Oriented film specimens were prepared by shearing the polymer sample inserted between two glass slides on a hot plate at the temperature of the nematic phase. The samples submitted to shear had never been heated to the isotropic state, to avoid thermal decomposition of the polymer. The shear was carried out by pushing the glass plate on the upper side of the sample at a rate of about 2–3 cm s<sup>-1</sup> by hand. The after-sheared films were subsequently taken away from the hot plate and cooled in air rapidly to room temperature within about 30 s. To obtain a slowly cooled sample, the film was left on the hot plate, which was switched off after shear, and cooled

to room temperature in about 1 h. The shear of nematic polymer melt was also executed by pushing a glass plate on poly(ethylene terephthalate) (PET) and Teflon sheets as described. Oriented fibre specimens were obtained by drawing with tweezers the mesomorphic polymer melt in air and subsequently cooling rapidly to room temperature.

## RESULTS AND DISCUSSION

For ordinary thermotropic main-chain LCPs, it was found that the banded texture is usually not formed during slow cooling after shearing the polymer compounds in their mesomorphic state. In those specimens the shear-induced orientational orders may become heavily disturbed as a whole. That is because, during slow cooling, the easy thermal motions of individual polymer chains will become the predominant way of relaxation of molecular orientations, which prevents formation of ordered structure. In such a situation, rapid cooling after shear cessation is generally required to minimize the random molecular thermal motions and hence cause the formation of banded texture. As mentioned above, the P(2,8) is a special thermotropic compound, in which it is easy to generate very regular and uniform banded texture even in the slow cooling process after shear cessation. Such a slow development of banded texture made it possible to investigate the band formation behaviour in more detail with various techniques<sup>20</sup>.

It was also found that the orientational order of P(2,8) specimens were sometimes quite stable in a reheating process. *Figure 1a* illustrates the polarizing micrograph of an oriented film which was prepared by rapid cooling after shearing the mesomorphic melt on a glass plate. The banded texture obtained is quite regular and has an average bandwidth of about 10 μm. This specimen was rapidly heated and transformed into the mesophase again. Although the outlines of banded texture may become quite obscure or completely disappear in some regions, the whole orientational properties of the specimen are not destroyed and the optical extinction due to molecular orientations becomes even more apparent. Also, the ordered structures could be maintained even



**Figure 1** Polarizing micrographs of an oriented film prepared by shear in the mesomorphic state on a glass plate and subsequently fast cooling to room temperature (a). This film was then melted again and held in the mesophase for ca. 5 min and then cooled down to room temperature (b)

for a very long time at the same temperature region, or with further heating of the specimen to temperatures much higher than the d.s.c.-determined clearing point. The polymer chain orientations are kept so regularly in the melting state that during cooling they are still able to organize very clear banded texture (*Figure 1b*). These phenomena are quite different from those observed in some linear main-chain LCPs, where both the banded texture and macroscopic orientational order may become considerably perturbed when the specimens are melted.

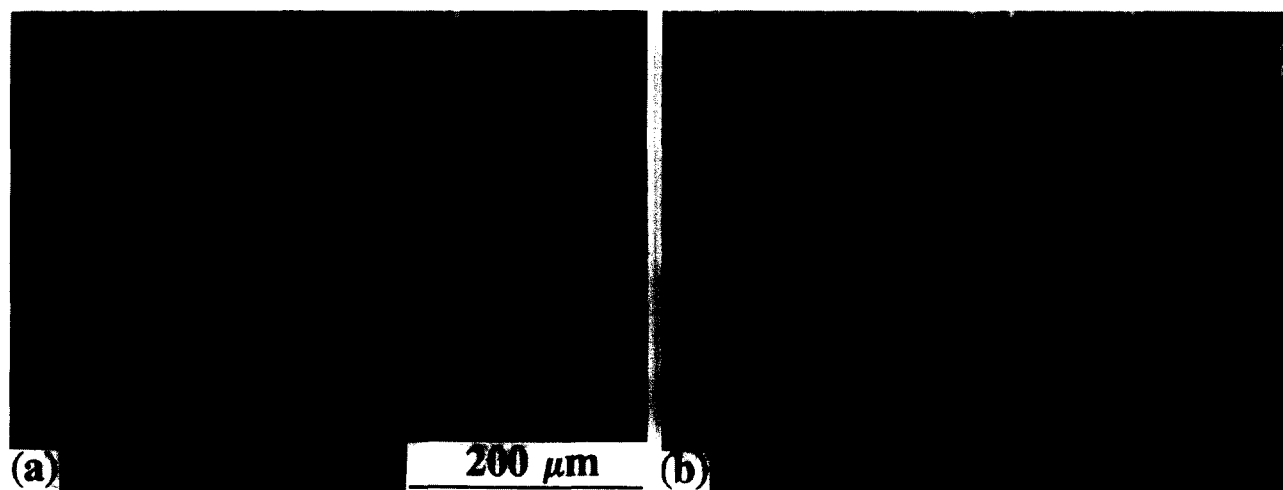
The above-mentioned orientational stabilities are considered to originate from some strong interactions between the surface of the glass plate and polymer chains deposited on it. The freedom of molecular thermal motions and hence the macroscopic fluidity of the specimen may be severely restrained even at a high temperature range. Such a bounding effect on molecular orientations has been studied mainly for the small molecular systems of liquid crystal, it is also named 'anchoring effect'. This effect seems more significant in some LCP systems, where the polymer chains are of relatively strong intermolecular interactions or less freedom of thermal motions in the mesomorphic state. The strong bounding effect, sometimes, is even able to stabilize the polymer chain orientations in all the parts of the specimen of several micrometres in thickness.

The importance of the bounding effect can also be verified through a comparison of structural changes in two oriented specimens which are strongly bound and very weakly influenced by the substrate surface. These two specimens were prepared by shear on glass plates and subsequently cooled to room temperature. Then one of them was taken away from the glass plate and laid on the top of the other. Both of them were exhibiting regular banded textures as shown in *Figure 2a*, where the optical focus was brought on the film at the upper side. These overlapped films were then heated and melted to the mesophase. After about 5 min, they were rapidly cooled back to room temperature. The morphological changes are shown in *Figure 2b*. As described above, no significant orientational perturbations can be seen in the lower side of the film deposited directly on the glass surface. On the other hand, the structural orders of the upper side of the film are considerably destroyed after

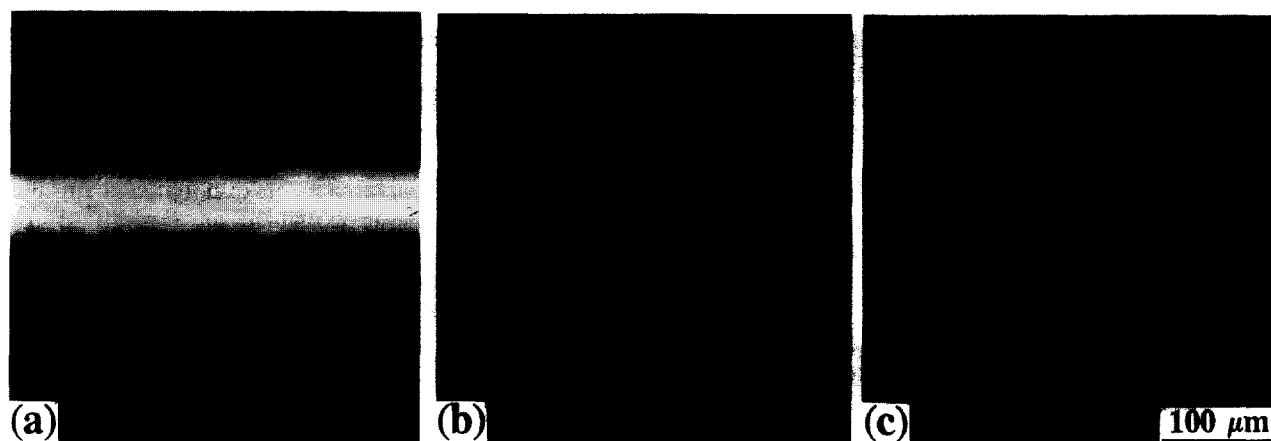
melting. That is to say, the maintenance of regular structural orders cannot be realized only by the weak intermolecular interactions in the melting state.

The bandwidth in oriented P(2,8) specimens is dependent sensitively on the cooling condition after shear: it decreases strongly with lowering cooling rate<sup>20</sup>. The zigzag-like rearrangements of polymer chains during band formation was explained as a result of forced orientational relaxations due to the dissipation of elastic force stored in the specimen by shear. It is thought that a complete dissipation may take place in a relatively long time for the P(2,8) compound, due to its low molecular mobilities. The quick decrease of temperature on rapid cooling will suppress the molecular thermal motions rapidly and hence only a small part of the elastic force is able to dissipate from the polymer chains, resulting in the formation of large bandwidth texture. According to this consideration, an oriented specimen prepared by rapid cooling was treated again by reheating to the mesomorphic state and subsequently slowly cooled to low temperature. After this treatment the bandwidth was found to decrease significantly<sup>20</sup>. That phenomenon is quite similar to the results obtained in this work, as illustrated in *Figure 1*. It was found that the formation of banded texture was also possible in other cases, where, after shear cessation, the melting state of the specimen was preserved for a long time before the following cooling. The resultant banded texture was always of small width, regardless of changing the cooling condition from the melting state.

It is reasonable that the elastic force stored in the polymer chains may dissipate more easily by keeping the oriented specimen at high temperatures than by immediate cooling from the mesophase after shear cessation. During the dissipation process at high temperatures, only indistinct traces of bands could be observed. The further development of banded texture during the successive cooling may probably result from the self-rearrangements of polymer chains, partially stimulated by the thermal contraction effect. In this case, the bounding influence from substrate surface may also play an important role for preventing the polymer chains from orientational perturbations, which is required as an indispensable condition for the band formation.



**Figure 2** Polarizing micrographs of two overlapped oriented films, (a) before and (b) after heat-treatment on glass plate

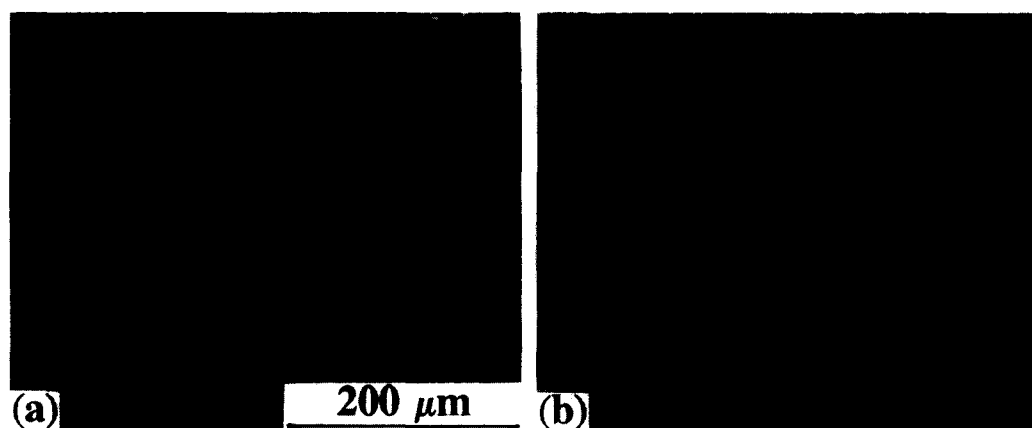


**Figure 3** Polarizing micrographs of a drawn fibre heated on glass plate at (a) 155°C; (b) 165°C; (c) 175°C

For thermotropic main-chain LCs, banded texture has been mainly observed in oriented thin films prepared by shear. The fibres drawn in the mesophase followed by fast cooling, in general only exhibit a straightforward manner of polymer chain orientations which are parallel to the drawing direction. In this work, relaxation behaviour of polymer chain orientations was also examined for a drawn P(2,8) fibre. The prepared fibre, shown in *Figure 3a*, was treated by heating on a glass plate. It was partially melted around 165°C. At this stage, the outline of the fibre was slightly disturbed and many thin whiskers appeared near the edges (*Figure 3b*). With further melting of the specimen, these whiskers were able to flow and extend along the lateral directions of the fibre (*Figure 3c*). The structural orders had been significantly destroyed in the middle part of the specimen. After the extensive growth of whiskers, a stripe pattern was formed with its outlines being slightly diffuse at the end parts of the stripes. The morphology of this specimen was quite similar to the case of an oriented thin film, in which banded texture was formed during the relaxation of polymer chain orientations after shear. It was also found that the relaxation behaviour during melting may be greatly different when the fibre was melted on some other types of substrate. For example, with using a Teflon sheet as substrate, the fibre structure will become considerably disordered after melting. The melt almost does not flow and extend on the substrate

surface. As substrate material, Teflon is not desirable for the shear-induced band formation, as described later. From this comparison, we conclude that the generation of ordered stripe pattern is also a result of boundary-induced molecular rearrangements during the orientational relaxation process in this case.

Studies concerning the band formation have so far been mostly performed with the glass slides as substrate. To further show the importance of bounding effect, some other types of substrate, such as the ordinary PET and Teflon films, were also adopted in this work in order to compare their influences on the band formation behaviour. For PET, the situation is quite similar to that on glass plate. Regular banded textures both in large and small widths were formed, depending on the shear and cooling conditions as described for *Figure 1*. Besides, a distinct stripe pattern was also observed in the melting state of an oriented fibre. On the other hand, the Teflon substrate does not favour the generation of banded texture on its surface, as depicted in *Figure 4*. Although after shear cessation the specimen was cooled as quickly as possible to minimize the influence of structural order perturbations, the banded texture obtained is still less regular (*Figure 4a*). It was also found that, if the after-sheared specimen was first held in the melting state only for 1–2 min, then the resultant orientational orders of the specimen will become considerably diffuse as a whole (*Figure 4b*). This phenomenon is probably due to



**Figure 4** Polarizing micrographs of an oriented film prepared by shear in the mesomorphic state on a Teflon sheet and subsequent fast cooling (a). The after-sheared film was first held in the mesophase for ca. 1–2 min and then cooled down (b)

the very weak influence of the Teflon substrate restraining the free thermal motions of polymer chains.

The bounding effect is considered to arise from some interfacial interactions between the solid substrate and the liquid crystalline molecules deposited on it, and such interactions are quite complicated, because of the molecular mobilities as well as the variable morphologies of the substrate surface. In such a situation, it is also necessary to carry out in detail some dynamic molecular simulations to clarify the mechanisms of these interactions and their influences on the band formation behaviour.

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