

Investigation on the formation behaviour of banded texture in thermotropic main-chain liquid crystalline polymers with linear rod-like and two-dimensional mesogenic units

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The mechanism and the formation behaviour of banded texture in non-isothermal processes have been studied for two aromatic main-chain liquid crystalline polyesters designated as P(2,8) and PTDT-Br which contain the X-shaped and linear rod-like mesogens along the polymer backbones, respectively. For P(2,8) regular and perfect banded textures were observed within its oriented films which were prepared by shearing in mesomorphic state and subsequent cooling down to room temperature under various conditions. Bandwidth was dependent sensitively on the cooling conditions, about 8 μm for rapid and 2 μm for slow coolings. During the cooling of an oriented film the bands were first generated around 170°C, and their regularity was improved with lowering temperature. The bandwidth as well as the extinction angle of the bands were changed drastically. In such a cooling process the birefringence Δn , the difference between the refractive indices along the shear and lateral directions, of the oriented film was decreased gradually from about 0.06 to 0.03. In the case of PTDT-Br, clear and perfect banded texture could be observed only for the rapid cooling case. The banded formation behaviour was discussed on the basis of a contraction mechanism and it could be explained as the result of zigzag rearrangement of straightforward oriented fibrils under certain contraction effects. The origins of these effects were considered to be the elastic energy stored in the specimens during shearing and the thermal contraction during cooling. The latter was more evident in the rapid cooling case. The orientational relaxation of fibrils or the formation of banded texture occurs during cooling in a small temperature range after an 'induction stage', while the relaxation due to free thermal motion of individual molecules may proceed in the whole temperature region before the solidification of specimens. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Banded texture is one of the characteristics of oriented specimens of both lyotropic and thermotropic liquid crystalline polymers (LCPs)¹⁻¹⁵. Parallel bands of alternate brightness and thousand Ångströms to several microns in width can be observed in these specimens under a crossed polarizing microscope. The banded texture seems very common for main-chain LCPs with rod-like mesogens along the polymer backbones. Recently it was reported that banded texture can also be formed in main-chain LCPs with two-dimensional (X-shaped) mesogens^{16,17} and even in side-chain LCPs^{18,19}. The morphological features of specimens with banded texture have been studied in detail on different size levels

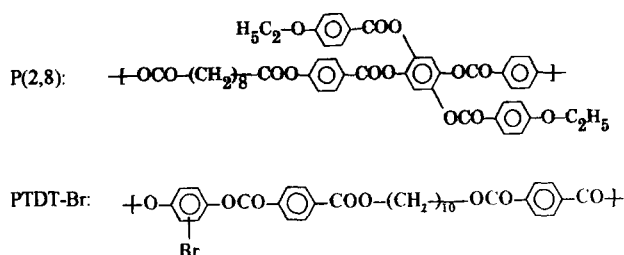
for some cases^{9,10,12}. Studies on the formation process of banded texture were reported only in a few cases. Kiss and Porter¹⁴ studied poly(γ -benzyl-L-glutamate) in *m*-cresol, reporting that the banded texture was observed during shear, when the solutions had a negative first normal-stress difference N_1 , while in the region of positive N_1 , banded texture developed only after cessation of shear. Marsano *et al.*¹⁵ observed banded texture in hydroxypropyl cellulose aqueous solutions after cessation of shear. They found that the time for band formation after shear was a decreasing function of shear rate and shear time. Optical texture for thermotropic copolyesters was observed under shear of oscillatory mode by Graziano and Mackley⁸, and banded texture was found for high molecular weight samples during the relaxation process after shear cessation. However the mechanism and the details of the formation

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process of banded texture are still not very clear. A contraction effect has been proposed by Nishio *et al.*²⁰ to explain the formation of banded texture in hydroxypropyl cellulose solutions after shear without discussion on its origin and relationship with molecular and technological parameters. In our previous studies^{10,13,17} the influence of molecular weight of main-chain polymers and shear rate, under which the oriented specimens were prepared, on the characteristics of banded texture was investigated. Clear and perfect banded texture was only observed for relatively higher molecular weight samples, and the band width decreases with increasing the molecular weight of polymers and the shear rate. These results could be understood on the basis of the contraction effect due to elastic energy stored in specimens during shearing and were considered as experimental evidence of this mechanism. However more experimental data are needed to check the versatility of the contraction mechanism of banded texture formation. In this work the mechanism and the formation behaviour of banded texture in non-isothermal processes were investigated for some main-chain polymers with rod-like and X-shaped mesogens.

EXPERIMENTAL

The following two aromatic polyesters were used in this study.



Polymer P(2,8) was obtained by synthesis of monomers 4,4'-(octamethylene dioxydioxo) dibenzoyl dichloride and 2,5-dihydroxy-1,4-phenylene di-*p*-ethoxybenzate, and polymer PTDT-Br was prepared from bromohydroquinone and 1,10-decanebisterephthaloyl chloride. The procedures of synthesis for these polymers have been reported elsewhere^{21,22}.

Thermal transition behaviour was determined with a Perkin-Elmer DSC-4 differential scanning calorimeter. The phase transition temperatures are listed in *Table 1*. Morphological observations were carried out with an Olympus BHSP polarizing microscope equipped with a hot stage. Small angle light scattering (SALS) Hv patterns were photographically recorded by using LS-1 type apparatus with a 632.8 nm wavelength He-Ne gas laser. The distance between the specimen and plate film was 6 cm, 10 cm or 12 cm in different experiments. Oriented specimens were prepared by shearing the mesomorphic polymer melt between two slides and subsequent quenching or slow cooling (about

2°C min⁻¹) to room temperature. Birefringence measurements for oriented specimens were carried out using an Olympus Berek Compensator under the polarizing microscope.

RESULTS AND DISCUSSION

It was found that the formation of banded texture and the band characteristics were dependent strongly on the cooling rate of specimens after shearing in their mesomorphic temperature range. Sample P(2,8) is a LCP with X-shaped mesogens in the backbone of molecules. *Figure 1* illustrates the polarizing micrographs and SALS Hv patterns of oriented P(2,8) film specimens obtained under relatively (a) high (quenching) and (b) low cooling rates respectively, where the shearing direction was horizontal. Very regular and perfect banded texture with clear boundaries between bands and long extensions of bands in a direction perpendicular to the shear direction can be observed for both cases. The band width is, however, quite different from these two specimens. They are about 8 and 2 μm, respectively, from direct estimation in the micrographs and are quite consistent with the calculated values from SALS measurements. Results of parallel experiments for sample PTDT-Br are given in *Figure 2*, the shear direction here is also horizontal. The morphological difference between specimens prepared by different cooling rates is even more significant for polymer PTDT-Br which has rod-like mesogens along the main-chain. Clear and perfect banded texture was only observed in rapid cooled specimens. This phenomenon has been noticed in studies of other main-chain polymers with rod-like mesogens.

According to our previous explanation of banded texture formation on the basis of a contraction mechanism the molecules are first oriented under shear and form fibrils with their axes tending to be parallel to the shear direction, and then the bands appear in a relaxation process after shear cessation. It is supposed that the zigzag rearrangement of fibrils during band formation is the result of a forced relaxation due to elastic energy stored in the sheared specimens. The elastic energy is dissipated mainly in the destruction of the ordered structure in different places along the fibrils. These places will then be the boundaries between the bands. Experimental results^{10,13,17} obtained in the studies of the influence of molecular weight of polymers and shearing rates on the characteristics of banded texture could reasonably support the contraction mechanism of banded texture formation.

There is no doubt that, in addition to the above-mentioned forced relaxation of fibrillar orientation, there should be another relaxation process of elastic energy dissipation in oriented specimens. It takes place due to thermal motion of individual molecules. This process will result in a quite random packing of molecules. So, the morphology of specimens after shearing depends on the competition of these two relaxation processes of different origins (*Figure 3*).

We may suppose that the energy dissipation process due to the forced relaxation of oriented fibrils can be characterized by a relaxation time τ_f , and the relaxation process due to thermal motion of individual molecules – a relaxation time τ_m . When the elastic energy is large

Table 1 Phase transition temperatures of the polyesters

Sample	T_g (°C)	T_{KN} (°C)	T_{NI} (°C)	T_{IN} (°C)	T_{NK} (°C)
PTDT-Br	—	142	189	184	98
P(2,8)	52	176	223	222	—

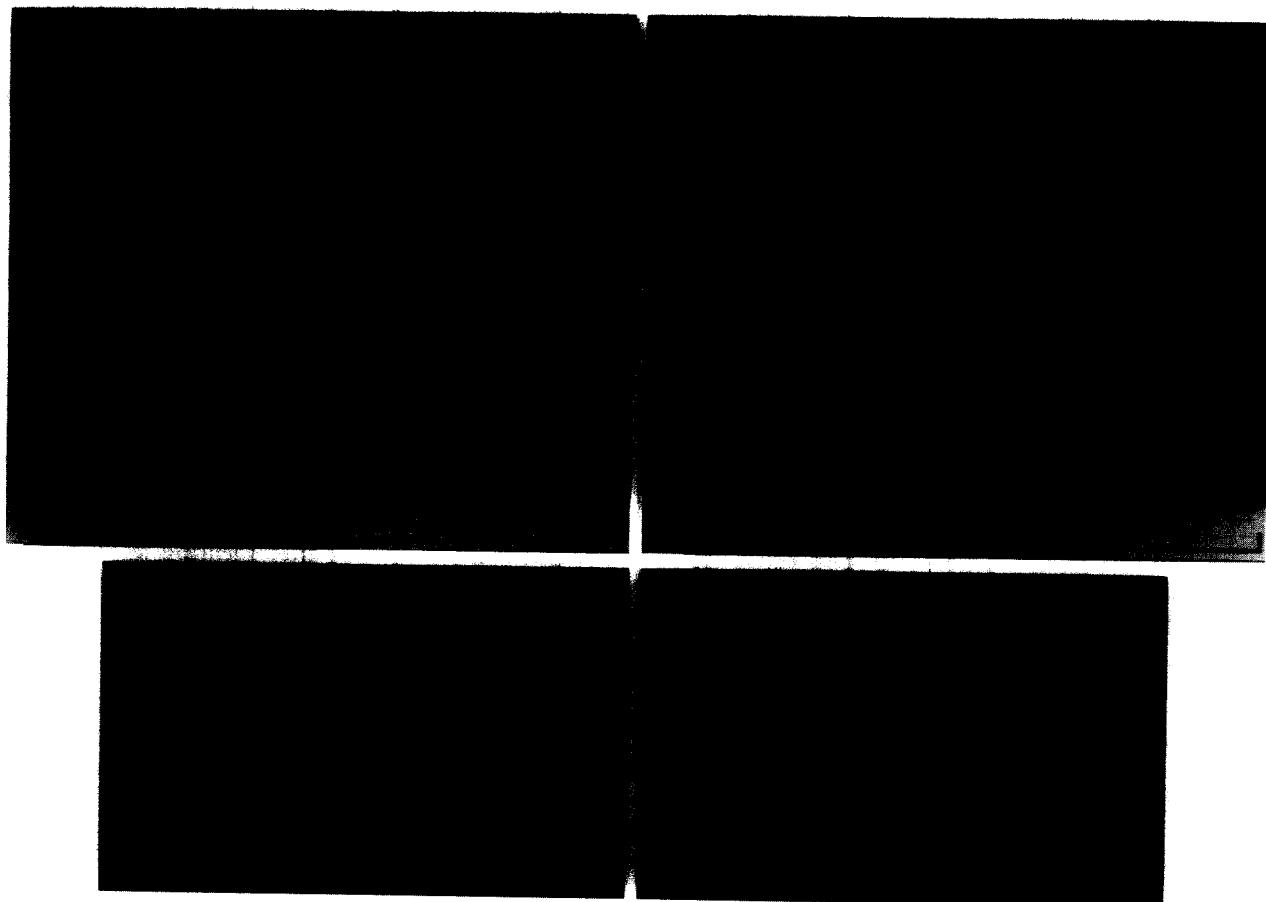


Figure 1 Polarizing micrographs and SALS Hv patterns of the P(2,8) oriented films obtained under relatively (a) high and (b) low cooling rates. The shearing direction is horizontal and the distances between the specimen and plate film are (a) 12 cm and (b) 6 cm, respectively

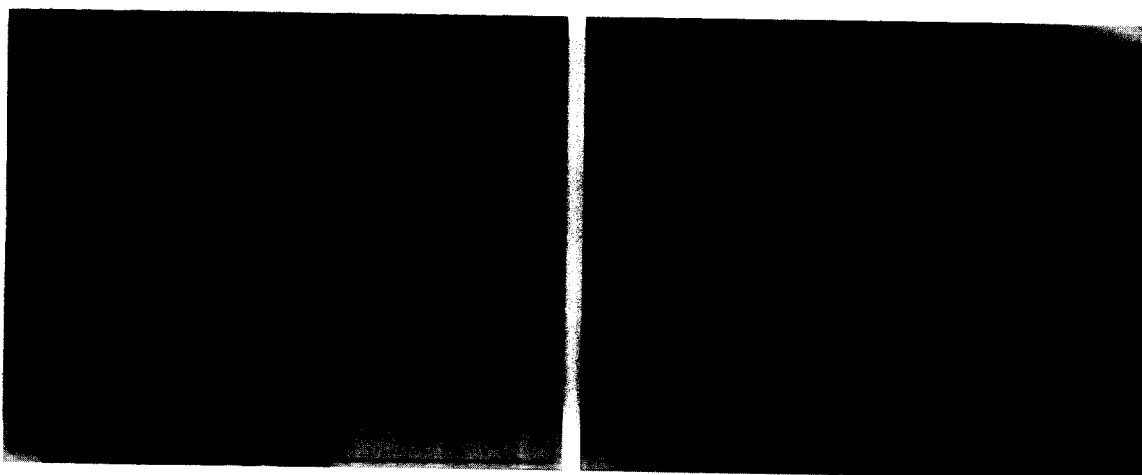


Figure 2 Polarizing micrographs of the PTDT-Br oriented films obtained under relatively (a) high and (b) low cooling rates

enough, then the necessary condition of banded texture formation can be expressed in terms of these relaxation times as

$$\tau_m \gg \tau_f \quad (1)$$

In this case the fibril relaxation is the predominant way of energy dissipation, and it may result in the formation of banded texture. In the opposite, if

$$\tau_m \ll \tau_f \quad (2)$$

then the molecular relaxation will predominate, and no banded texture should be observed.

The relaxation time τ_m is considered to increase with decreasing the mobility of polymer molecules. The molecular motion might be dependent on molecular structure and molecular interaction of polymer samples. In the case of flexible chain polymers, molecules may also assume the parallel orientation under shearing and form fibrils like liquid crystalline polymers. However, the orientation relaxation takes place easily as the result of thermal motion of individual molecules. The external

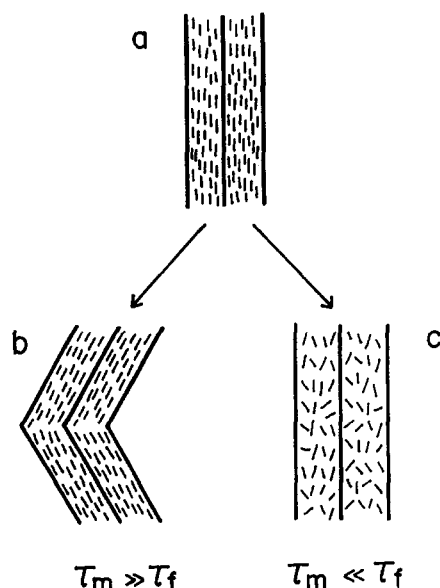


Figure 3 Schematic representations of orientational models of molecules and fibrils within an oriented LCP specimen: (a) during shearing and (b), (c) after shear cessation and dissipation of elastic energy stored within the sample

elastic force may even accelerate this process. So the relaxation time τ_m of flexible chain polymers may become very short, and no banded texture is formed after shear. On the other hand molecules of main-chain liquid crystalline polymers are rather rigid and take the extended conformations. It means the energy dissipation due to molecular motion of individual molecules might be a very slow process with long relaxation time τ_m . Although τ_f may also decrease due to less mobility of individual molecules, specimens with main-chain LCP molecules may fulfil the necessary condition of banded texture formation, because fibrils composed of these molecules are highly stable and rigid, and are more effective in bearing the external force as structural entities which play an important role in elastic energy dissipation. It means that the main change from flexible chain polymers to LCPs is the change in relative magnitude of the relaxation times τ_f and τ_m .

The relaxation times τ_f and τ_m both might be significantly temperature dependent. When the temperature is lower than some critical temperatures, for example the glass transition temperature or the crystallization temperature, the process of energy dissipation through fibril or molecular motions will be stopped or practically stopped. So the cooling rate or the cooling time t_c , in

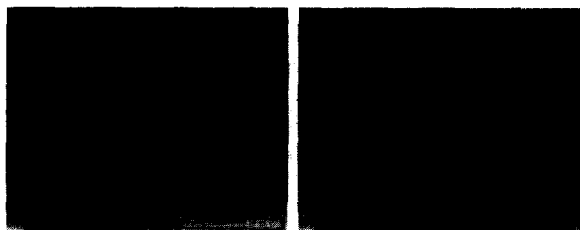


Figure 4 Polarizing micrographs of a P(2,8) oriented film which was (a) sheared in the mesomorphic state and subsequently quenched to room temperature, the same film was (b) reheated to mesophase and then slowly cooled down

which the temperature of the specimen reaches T_g or any other temperatures characteristic for stopping the forced relaxation process, may have their influence on the banded texture formation of LCPs in some cases. The observed cooling rate dependence shown in this work may then be explained and discussed as follows.

It was found that the results of sample P(2,8) (Figure 1) can be understood if we suppose that the relaxation time τ_f is comparable with t_c in this case. It means that in a slow cooling process the elastic energy stored in specimens after shearing is able to dissipate completely in the zigzag rearrangement of fibrils, and bands of small width are obtained. However, in a fast cooling process only part of the elastic energy could be dissipated in terms of orientation relaxation of fibrils before the temperature of the specimen becomes low enough to stop, or practically stop, the fibril relaxation process. Therefore, a large band width was obtained for fast cooled specimens. According to this idea an oriented specimen of P(2,8) prepared by quenching after shearing was retreated by heating to its mesomorphic temperature and subsequent slow cooling to room temperature. The band width decreases from $6\mu\text{m}$ to $3\mu\text{m}$ after this retreatment (Figure 4) and becomes quite close to that observed in Figure 1b. It implies that the elastic energy unexpended in a fast cooling process still can be dissipated for band formation in a reheating and slow cooling process, and the difference of specimens obtained by different cooling rates in banded texture morphology is really the result of the slow rate of fibril relaxation process which is comparable with the cooling rate in this particular case.

The results for sample PTDT-Br are rather complicated than those for P(2,8). Careful observations of the morphological changes in a slow cooling process indicates that some trace of unclear banded texture appears very soon after the shear cessation, and it remains almost unchanged with time at constant temperature or with temperature lowering as shown in Figure 5. According to the structure difference between molecules of samples PTDT-Br and P(2,8) it is reasonable to assume that t_c is obviously larger than τ_f for these PTDT-Br specimens, and the elastic energy stored during shearing is able to be dissipated completely in a slow cooling process. It implies that in the case of these PTDT-Br specimens the elastic energy due to shear is not large enough to form clear and perfect banded texture in oriented specimens. Then the difficulty here is how to explain the formation of banded texture in PTDT-Br specimens obtained by quenching after shearing. We suppose, in addition to the contraction effect due to shear induced elastic energy, these could be contraction effects of other origins, namely the thermal contraction due to cooling, which may also contribute the formation of banded texture. This effect becomes significant, when the cooling rate is high. Possibly, that might be the reason why banded texture is usually clearly observed in LCP specimens obtained by quenching after shearing.

Further evidence of the thermal contraction effect and its importance for banded texture formation were taken from the results of a PTDT-Br specimen obtained by slow cooling and subsequent quenching from a mesomorphic temperature range to room temperature. The polarizing micrographs of this specimen before and after quenching are given in Figure 6. Unclear and imperfect

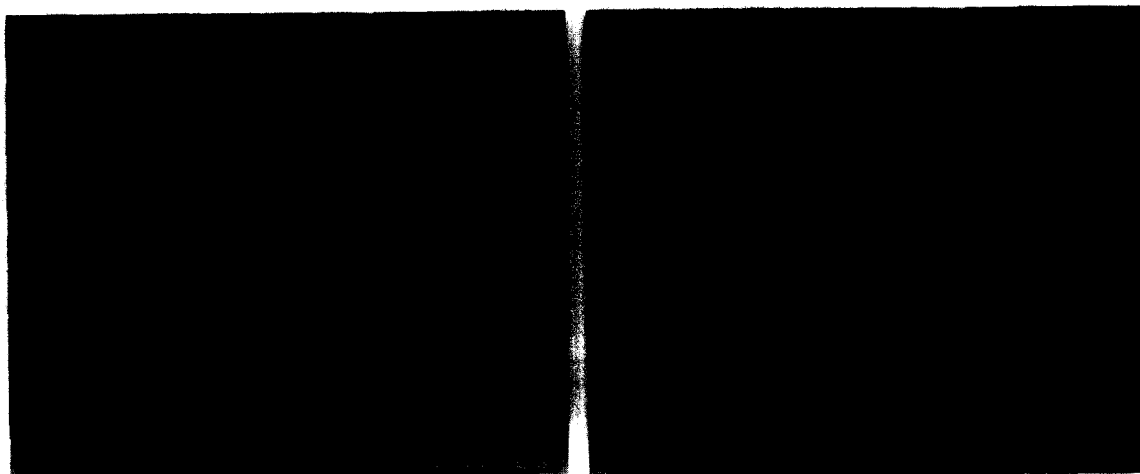


Figure 5 Polarizing micrographs of a PTDT-Br oriented film taken on cooling at (a) 136°C and (b) 120°C

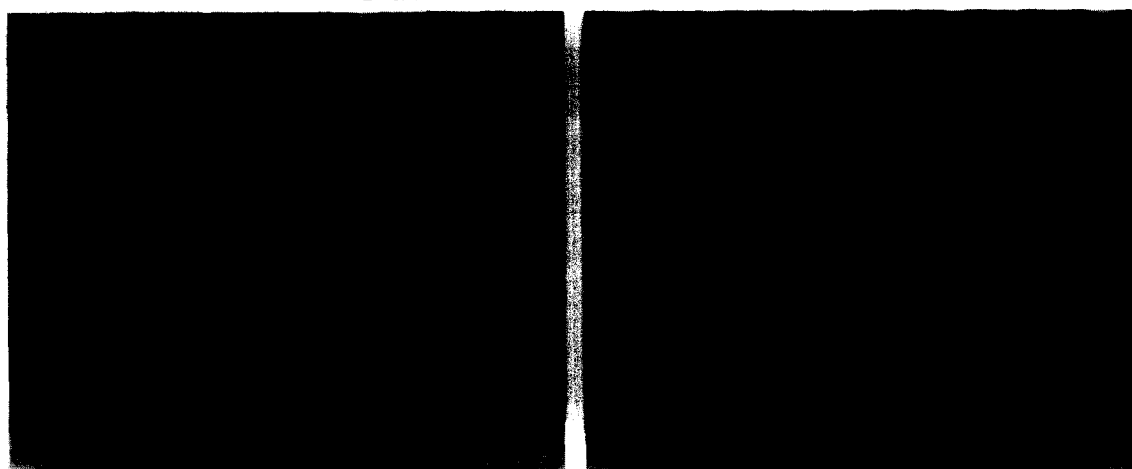


Figure 6 Polarizing micrographs of a PTDT-Br oriented film which was (a) slowly cooled to 120°C and (b) subsequently quenched from this state to room temperature

bands appeared in specimen after slow cooling to temperature around 120°C. The band width cannot be determined exactly, but it might be around 10 μm . The extinction direction in the bands was almost parallel to the shear direction having small deviations less than $\pm 5^\circ$. Clear banded texture was observed in the specimen after quenching. The band width is 8–10 μm , and the extinction angle becomes $\pm(15\text{--}18)^\circ$. This experiment has shown separately the two contraction effects in the formation of banded texture of this specimen.

The slow development of banded texture formation process for P(2,8) specimens makes it possible to follow and study this process experimentally by various techniques. So far it was difficult to do that for thermotropic liquid crystalline polymers usually having rod-like mesogens along their backbone of molecules.

The band formation process of P(2,8) specimens has been observed under a polarizing microscope, and typical micrographs of these specimens are presented in *Figure 7*. The specimen was first sheared along the horizontal direction at about 187°C, and at this stage no banded texture was observed as shown in *Figure 7a*. When the temperature of the specimen was down to about 173°C, the bands began to appear, but the picture was still very obscure (*Figure 7b*). Clear bands of large

areas were observed at about 166°C. The contrast between neighbouring bands increases with further cooling, but the band width keeps almost unchanged.

Figure 8 shows the SALS Hv patterns of a P(2,8) oriented film taken on cooling from its mesomorphic state. The sample was first sheared along the horizontal direction at about 185°C. At this time the Hv scattering pattern was essentially circular symmetric and slightly extended along the vertical direction, which is a typical scattering pattern of the nematic phase. With lowering temperature to about 170°C two weak scattering maxima of first-order with the reflection angle of about 1.0° are observable on the horizontal line parallel to the shearing direction, suggesting the beginning of band appearance at this stage. With further decreasing temperature the pattern becomes finer and the positions of scattering maxima extend gradually towards the larger angle side. This implies that the banded texture is developed with a decrease in the average band width at this stage. The bandwidth evaluated from the SALS measurement is plotted vs. temperature in *Figure 9a*. It can be seen that with lowering temperature the bandwidth was decreased drastically in the range of 150–165°C and then changed only slightly. Both the results from SALS and polarizing microscopy studies describe clearly the formation process of banded texture in P(2,8) specimens. Most of

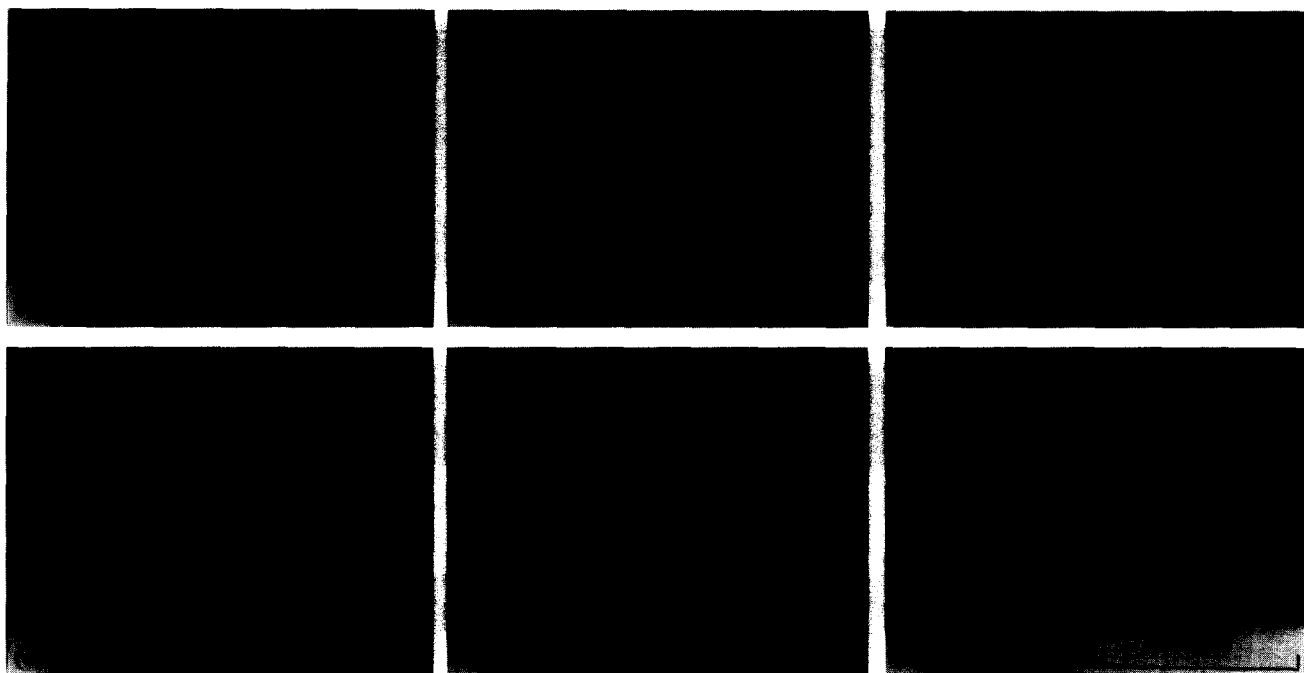


Figure 7 Polarizing micrographs of a P(2,8) oriented film taken at (a) 187°C, (b) 173°C, (c) 166°C, (d) 159°C, (e) 152°C and (f) 133°C, respectively

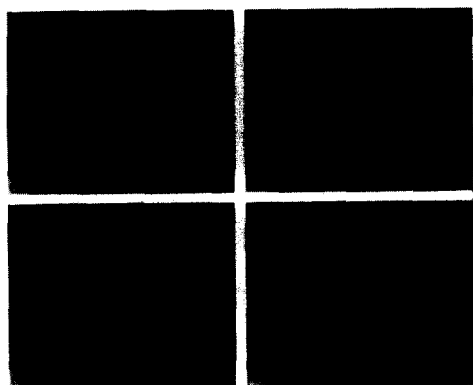


Figure 8 SALS Hv patterns of a P(2,8) oriented film taken at (a) 185°C, (b) 170°C, (c) 155°C and (d) 138°C, respectively. The distance between the specimen and plate film was 10 cm

the bands are formed in a relatively small temperature range after an 'induction stage'.

Figure 9b shows the change of birefringence, $\Delta n = n_s - n_l$, for an oriented P(2,8) specimen in a slow cooling process, where n_s and n_l are refractive indices for radiations polarized, respectively, in the shear direction and lateral direction within the film plane. The birefringence decreases gradually with cooling in a wide temperature range and becomes almost a constant value around 0.032 until 100°C, which is within the crystallization temperature range of this polymer on cooling. In a previous work we have studied the molecular alignment of sample P(2,8) in an oriented state¹⁷. It was found that in addition to the main chain axes of molecules the skeletal planes of the X-shaped mesogens are parallel to the film plane. Figure 10 shows the models of molecular alignment in (a) straight and (b) zigzag oriented fibrils respectively. The birefringence Δn may have high value for specimens with straight oriented molecules (Figure 10a), because the phenylene rings of the mesogens are not all parallel to the film plane. It may

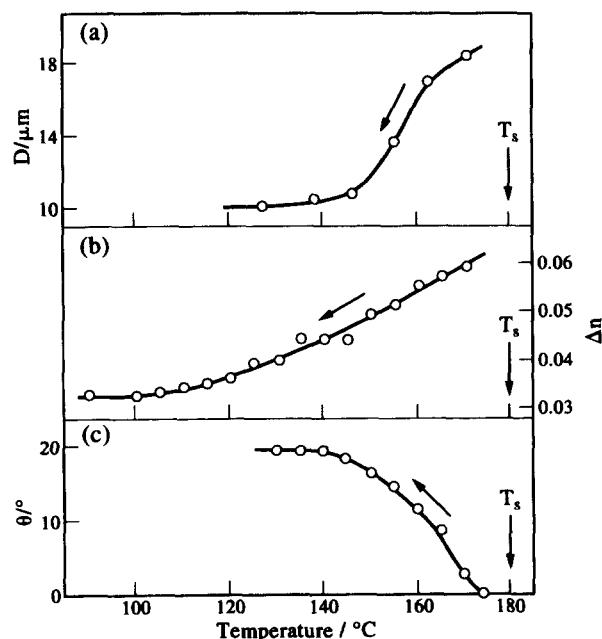


Figure 9 Temperature dependences of (a) bandwidth, (b) birefringence data and (c) distinction angle of bands measured during the band formation process in the P(2,8) oriented films

decrease after the zigzag rearrangement of the fibrils. Therefore the decrease of Δn observed in the process of banded texture formation (Figure 9b) might result from the inclination of fibrils from the shear direction. Figure 9c gives the extinction angle of bands in the band formation process of a P(2,8) specimen. In the first stage after shearing the extinction angle $\theta = 0$ implies the parallel alignment of fibrils and molecules with respect to the shear direction. θ increases in the temperature range from about 170°C to 145°C and then keeps almost unchanged with further cooling. It is clear that the change of birefringence (Figure 9B) cannot be completely attributed to the inclination of fibrils, because the decrease of Δn continues

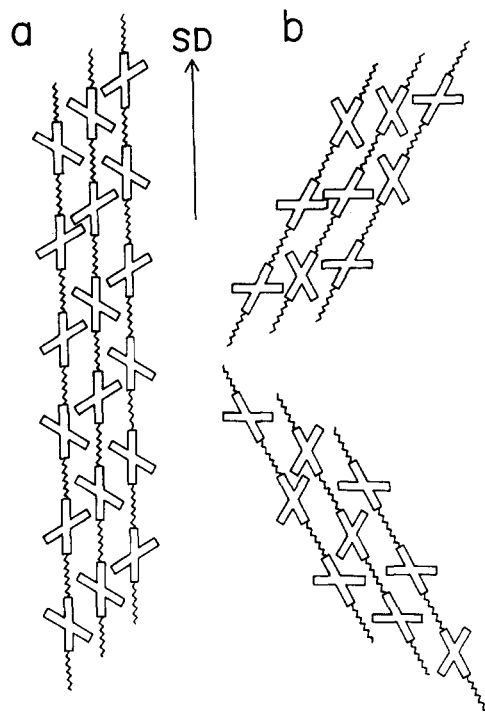


Figure 10 Schematic representations of polymer chain alignment model within the (a) straightforward and (b) zigzag-like oriented fibrils. The broken line indicates the shearing direction (SD)

during cooling below 140°C. It may indicate the existence of the orientational relaxation due to free thermal motion of individual molecules.

CONCLUSIONS

The formation of banded texture in main-chain LCPs with rod-like and X-shaped mesogens can be explained as the zigzag rearrangement of straight oriented fibrils under contraction effects. The origin of these effects could be the elastic energy stored in specimens during shearing and the thermal contraction during cooling. The latter is more evident in the case of rapid cooling. The orientational

relaxation of fibrils or the formation of banded texture occurs under cooling in a small temperature range after an 'induction stage', while the orientational relaxation due to free thermal motion of individual molecules may proceed in the whole temperature region before the solidification of the sample.

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