Morphological studies of oriented specimens of thermotropic liquid-crystalline polyesters with two-dimensional mesogenic units

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Morphological studies have been carried out in detail by means of differential scanning calorimetry, polarizing and scanning electron microscopies, small-angle light scattering, X-ray diffraction, infra-red spectroscopy and refractive-index measurements for oriented specimens of thermotropic liquid-crystalline polyesters with so-called two-dimensional mesogenic units along the polymer chains, which were synthesized by solution polycondensation of the monomers 4,4′-(alkylene dioyldioxy)dibenzoyl dichloride and 2,5-dihydroxyl-1,4-phenylene di-*p*-alkyloxybenzoate at low temperatures. All the studied polyesters, designated respectively as P(2,6), P(2,8) and P(5,8), were found to exhibit nematic liquid-crystalline behaviour above their melting points. Mat-like or banded textures have been observed in oriented films of these specimens, which were prepared by shearing in the mesomorphic state and subsequent quenching to room temperature. More regular and perfect bands were exhibited in specimen P(2,8) than in P(5,8) and P(2,6), and their average bandwidths evaluated optically were around 6, 8 and 12 μm, respectively. These three specimens had different molecular weights, and such differences were found to influence strongly the features and ease of formation of the banded structure: the bandwidth was decreased and band quality was improved with increasing molecular weight. Furthermore, bandwidth could also be changed sensitively on varying the shearing rate during preparation of oriented specimens. In the case of P(2,8), the orientation direction of fibrils aggregated by polymer chains was found to deviate from the shearing direction alternately by a deviation angle of about $\pm 30°$, on going from band to band. Based on the scanning electron microscope observations and X-ray diffraction data, it was understood that the zigzag planes of oriented fibrils, which have average diameter ranging from 50 to 100 nm, are parallel or nearly parallel to the specimen surface, and they are stacked layer-like along the specimen thickness direction. Moreover, it was suggested from the three-dimensional infra-red spectra and refractive-index data that the planes including the intersected X-shaped mesogens may be oriented parallel or nearly parallel to the zigzag plane or film surface, and all the phenylene rings tend to orient their planes parallel to the zigzag plane as a whole. The banded texture and its interior structure were found to be quite thermally stable even at temperatures somewhat higher than the isotropization point of the unoriented polymer, suggesting that the thermal motions of individual polymer chains are severely limited and do not easily destroy the fibrillar structure and other supermolecular structures formed in the process of preparing oriented films.

(Keywords: thermotropic LC polyesters; morphology; two-dimensional mesogens)

INTRODUCTION

Banded texture is one of the characteristics of oriented specimens of liquid-crystalline polymers (LCPs). Parallel bands of alternate brightness can be observed in these specimens under a crossed polarizing microscope. The bands are usually thousands of angstroms to several micrometres in width and extended in the direction perpendicular to the direction of shear under which the specimens were prepared. The banded texture seems very common for main-chain LCPs with rod-like mesogens along polymer backbones. Observations of banded texture have been reported for both lyotropic and thermotropic LCPs[1–13]. The morphological features of these oriented specimens on different size levels and the influences of molecular weight and shear rate on the characteristics of bands have been studied in detail for some cases[10,13].

Recently it was found that banded texture can be formed also in specimens of main-chain LCPs with two-dimensional (X-shaped) mesogens[14] and even of side-chain LCPs[15]. It is of great interest to study the structural features of these specimens. In this work the banded texture behaviour of the main-chain aromatic polyesters with X-shaped mesogenic units was investigated.

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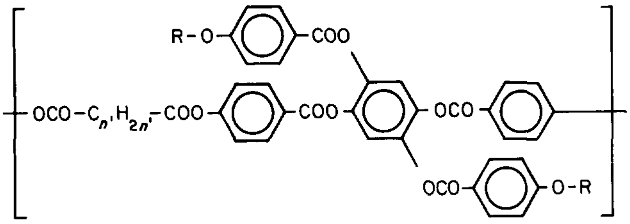
EXPERIMENTAL

A series of aromatic polyesters were synthesized by solution polycondensation of the monomers 4,4′-(alkylene dioyldioxy)dibenzoyl dichloride and 2,5-dihydroxyl-1,4-phenylene di-*p*-alkyloxybenzoate at low temperatures, and have the following structure:



The syntheses of these polymers have been reported elsewhere[16], and they were designated as P(n', n), where n' is the number of carbons in the alkyl substituent R ($-C_{n'}H_{2n'+1}$). The specimens used in this study are P(2,6), P(2,8) and P(5,8) having respectively hexa- ($n=6$) and octamethylene ($n=8$) flexible spacers along the main chains.

Thermal transition behaviour was determined with a Perkin–Elmer DSC-4 differential scanning calorimeter (d.s.c.). Oriented specimens were obtained by shearing the polymer melt inserted between two glass slides at temperatures of the mesomorphic state and subsequently quenching to room temperature. Morphological observation was carried out with an Olympus BHSP polarizing microscope equipped with a hot stage. Small-angle light scattering (SALS) H_v patterns were photographically recorded by using a LS-1 type apparatus with a 632.8 nm wavelength He–Ne gas laser. The distance between the specimen and flat film was 11.5 or 12 cm in different experiments. X-ray diffraction patterns of the oriented specimens were recorded onto flat films with Ni-filtered Cu K_α radiation (40 kV, 30 mA). The morphology of a section fractured along the shearing direction of an oriented specimen was observed with a Hitachi scanning electron microscope of type S-530. Three-dimensional refractive indices of oriented films along the shearing (n_s), lateral (n_l) and thickness (n_t) directions were measured with an Abbe refractometer of type 2W. Infra-red spectra of the specimens were obtained by using a Bruker IFS-113V Fourier-transform infra-red spectrometer with a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

The polymers with X-shaped mesogens used in this work all exhibit mesomorphic behaviour above their melting points. The data of molecular weights of these polymers and their transition temperatures obtained by d.s.c. measurements are given in *Table 1*. A thread texture typical of the nematic mesophase was observed for these specimens in their melt states. *Figure 1* shows the polarizing micrographs of the P(2,8) and P(5,8) specimens.

Oriented films were prepared by shearing the original samples in their mesomorphic states, which have never been heated to the isotropic phase, and subsequent quenching to room temperature. The polarizing micrographs for oriented films of these specimens prepared under similar conditions are shown in *Figure 2*, where the shearing direction is horizontal. Very regular and perfect banded texture was observed for the P(2,8) specimen. Bands with clear boundaries may have long distant extensions and cover almost the entire field of view (*Figure 2a*). Bandwidth for this specimen is around 6 μm. The banded texture in the P(2,8) specimen is so regular and uniform that even higher-order grating diffractions can be observed in the SALS H_v measurements (*Figure 3*). A similar phenomenon has been reported for a main-chain liquid-crystalline polyester with rod-like mesogens[9]. Specimens of P(2,6) and P(5,8), however, show imperfect banded textures. They are usually not regular and uniform in structure and have short extension for each band; besides, the banded texture can only be observed in part of the specimens. The observed bandwidths of the two specimens shown in *Figures 2b* and *2c* may have larger values, being around 12 and 8 μm respectively. The different behaviours between these specimens in the oriented state are supposed to result from the difference in their molecular

Table 1 Molecular weights and transition temperatures

Sample	M_w	T_m (°C)	T_i (°C)
P(2,6)	5430	142.3	203.9
P(5,8)	4760	128.6	169.9
P(2,8)	13 300	175.8	222.5

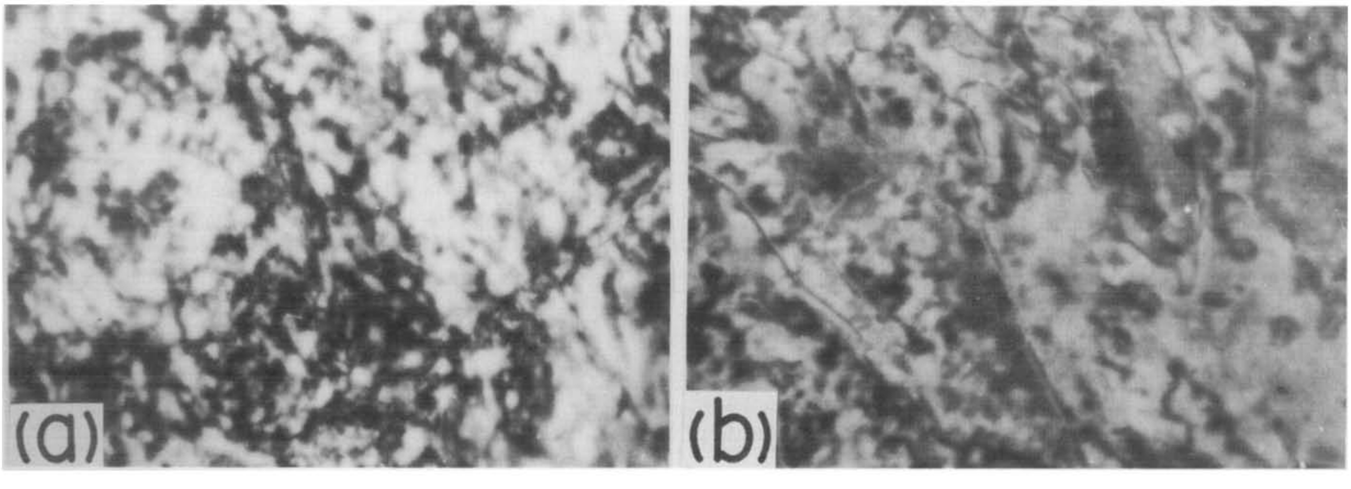


Figure 1 Polarizing micrographs of (a) P(2,8) and (b) P(5,8) specimens taken in their mesomorphic states

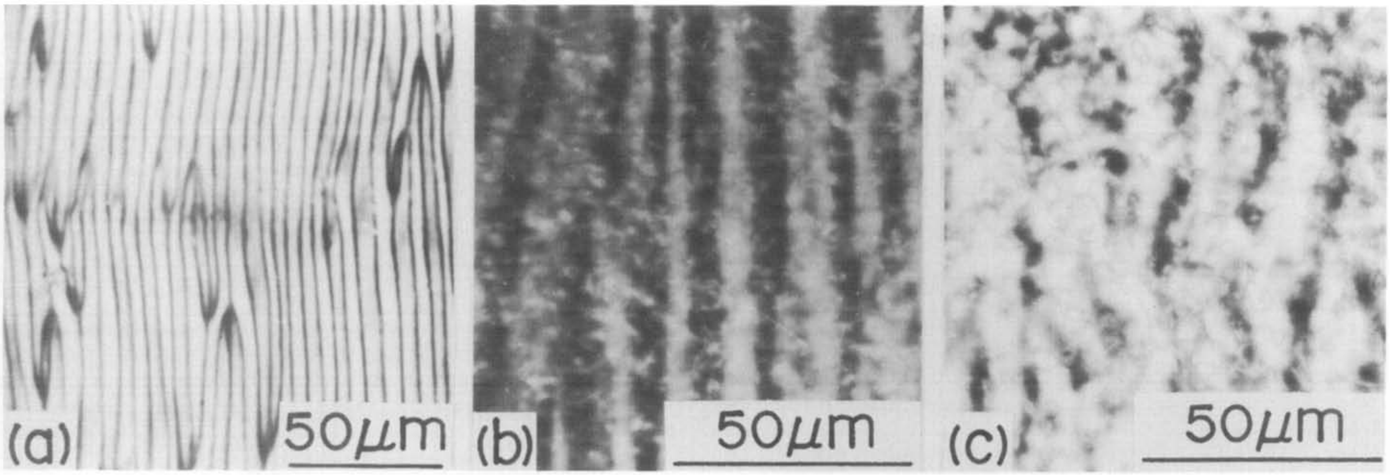


Figure 2 Polarizing micrographs taken for oriented films of (a) P(2,8), (b) P(5,8) and (c) P(2,6) specimens. The shearing direction is horizontal

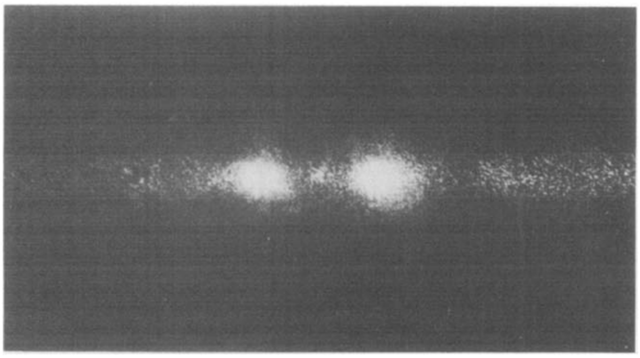


Figure 3 Small-angle light scattering H_v pattern of the P(2,8) oriented film

weights. It has been shown in one of our previous studies[13] that the ease of band formation for main-chain LCPs may depend strongly on the molecular weight. Regular and perfect bands can only be observed for specimens of sufficiently high molecular weight, and the bandwidth would decrease with increasing molecular weight. These phenomena were consistent with the fact that banded texture is not known to occur in low-molecular-weight liquid-crystalline systems.

The influence of molecular weight on the formation of banded texture and the band characteristics can be understood on the basis of the contraction mechanism. Besides the molecular-weight dependence, the band features are also expected to depend on the parameters for preparation of bands, e.g. the shear rate under which the oriented specimens are prepared, according to the contraction mechanism. *Figure 4* gives the polarizing micrographs of two P(2,8) specimens obtained under relatively high and low shear rates, respectively. It is obvious that the bandwidth increases significantly with decreasing shear rate. The SALS H_v patterns of these specimens are also shown in *Figure 4*, and typical grating diffraction patterns can be observed. The average values of bandwidth determined from the positions of the scattering intensity maxima are about 2.0 and 5.8 μm respectively, which are consistent with those estimated from the microscopic observations. The results shown above imply that the main-chain LCPs with X-shaped and rod-like mesogens may have the same mechanism of banded texture formation.

The morphological features have been studied in detail for the P(2,8) oriented specimens. It was found that the directions of optical axes of the bands may deviate from the shearing direction alternately by an angle of $+\theta$ or $-\theta$ from band to band, and these axial directions just coincide with the orientation directions of the fibrils of which the oriented specimens are composed. The fibrillar structure can be demonstrated clearly in the fractured areas of oriented specimens. *Figure 5* is the polarizing micrograph of an oriented specimen that has been stretched in the lateral direction. The fracture develops perpendicularly to the stretching direction, and the fracture surface is upwards in this micrograph. Many thin fibrils aligned in a zigzag manner can be observed near the fracture section, and they are packed parallel to each other within each band. Moreover, the orientations of these fibrils deviate from the shearing direction alternately by about ±30° from band to band. We have further observed the fine textures with a scanning electron microscope (SEM). A very regular zigzag-like structure of fibrils can be seen in *Figures 6a* and *6b*, which were viewed from the direction perpendicular to the specimen surface. The fibrils are packed layer-like along the thickness direction of the specimen. Some loose individual fibrils on the outside of the fracture edge can also be seen. The estimated diameter of these fibrils ranges from 50 to 100 nm. The fibrils are bent continuously but not very sharply in the boundary region between two adjacent bands. *Figure 6c* shows a texture viewed from the direction parallel to the film plane and perpendicular to the fracture surface. It is expected that only straight fibrils parallel with the film surface are observable in this case, and their average diameter is very close to the value estimated from *Figures 6a* and *6b*. Some loose thick fibrils as assembled by many thin ones are also observed on the fracture plane. According to the morphological difference between the textures shown in these pictures, it can be reasonably assumed that the zigzag planes of fibrils are parallel or nearly parallel to the film surface, and also they are stacked layer-like together along the film thickness direction.

In order to examine the propriety of the supposed arrangement model of zigzag-like fibrillar structure and the molecular orientation, we have also taken X-ray diffraction patterns for these oriented specimens. *Figure 7a* was obtained with the incident X-ray beam

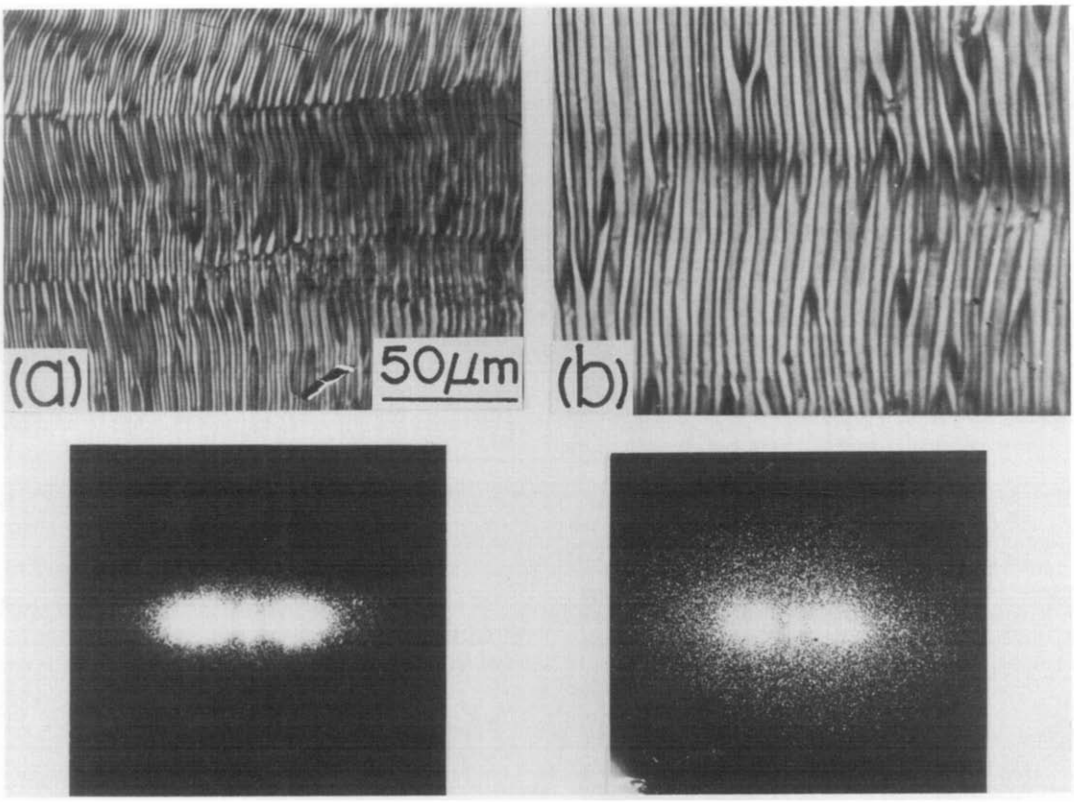


Figure 4 Polarizing micrographs of two P(2,8) oriented films obtained under relatively high (a) and low (b) shearing rates

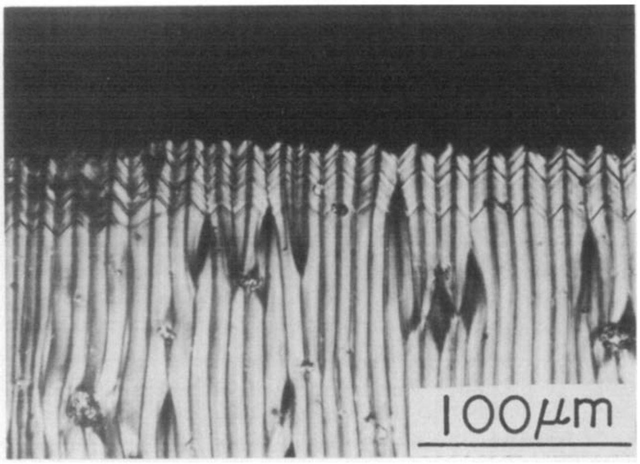


Figure 5 Polarizing micrograph of the P(2,8) oriented film that was fractured along the shearing direction

perpendicular to the film surface; here the shearing direction is vertical. In this pattern only four very broad diffraction spots can be observed at about $2\theta = 21°$ typical of liquid-crystalline nature, which are distributed symmetrically with respect to the equator and to the meridian. The broad diffraction halos around $2\theta = 20°$ of an LCP or amorphous polymer are in general considered to be caused by the diffraction related to the average lateral distance between neighbouring molecules, and for oriented specimens the halo is usually split into arcs or spots when the molecules are uniaxially oriented. Information about the molecular orientation can be obtained from the azimuthal angle distribution of the spots. For the present case the two pairs of spots, tilting by an azimuthal angle of about ±30° from the equatorial direction, can reasonably be considered to originate from such an orientational fashion in that the alignment direction of polymer chains may deviate from the elongational direction by just about ±30°. This feature corresponds well to the polymer fibrillar zigzag textures shown in *Figures 5* and *6*. *Figure 7b* is a diffraction pattern taken with the X-ray beam perpendicular to the shearing direction but parallel to the film surface. Different from the pattern in *Figure 7a*, the broad spots at the same 2θ angle are located on the equator but not split. That is to say, the projection of oriented molecules on the cross-sectional plane parallel to the shearing direction may be straight and vertical, but not with the zigzag manner as seen within the planes parallel to the film surface. Consequently, the X-ray diffraction data may suggest that the molecules within each fibril are packed together with their axes parallel to the fibril axis. The results on the molecular and fibrillar alignments in these oriented specimens are quite consistent with those observed in some other LCP systems with rod-like mesogens[9–13].

It can be seen that the present LCP molecules have two-dimensional X-shaped mesogens, which are quite different from the normal LCP systems having linear rod-like mesogens. Therefore, it is of great importance to determine the geometric relationship between the orientations of the molecules and the intersected X-shaped mesogens. The infra-red (i.r.) spectroscopic technique has frequently been utilized in the investigation of oriented LCP systems, since it can offer to some extent molecular-level structural and orientational information[9,13]. In this work we have also measured the i.r. spectra for some of the oriented specimens that exhibit the banded texture. Shown in

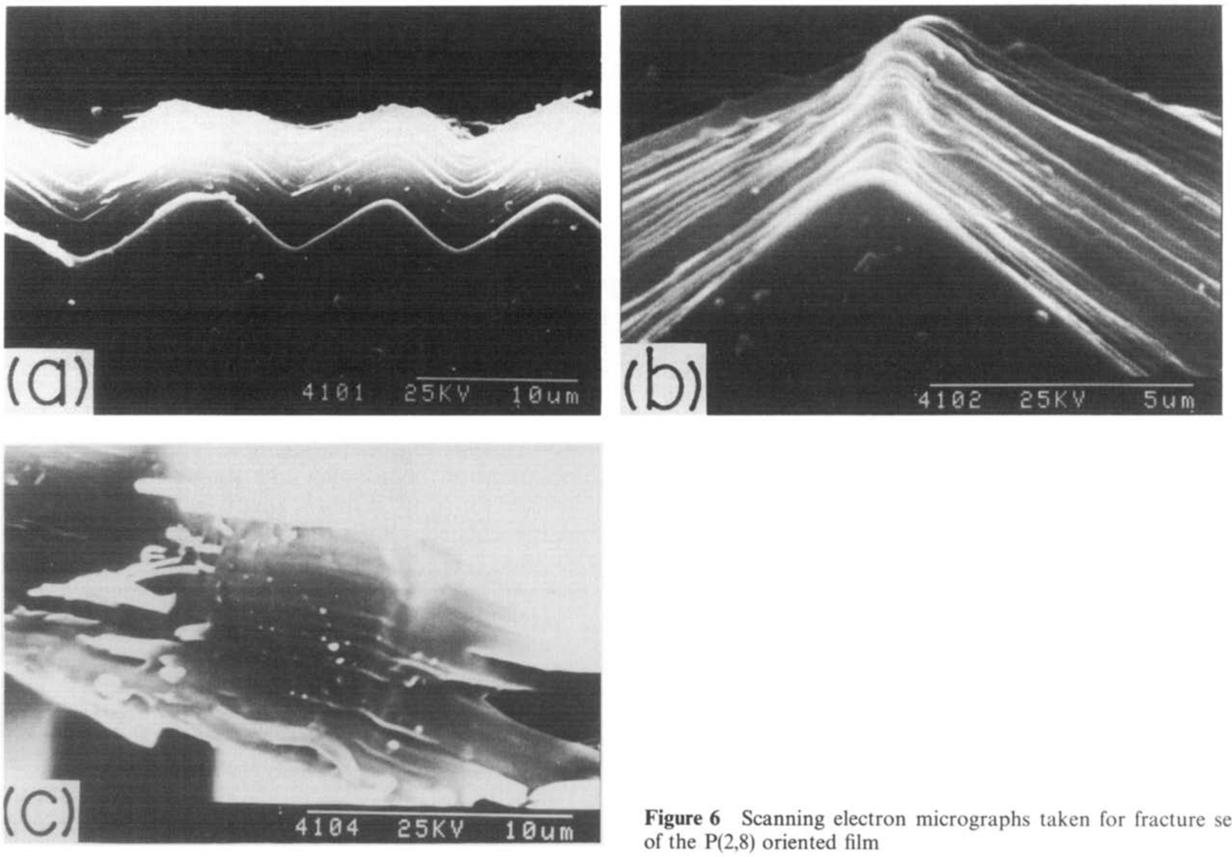


Figure 6 Scanning electron micrographs taken for fracture sections of the P(2,8) oriented film

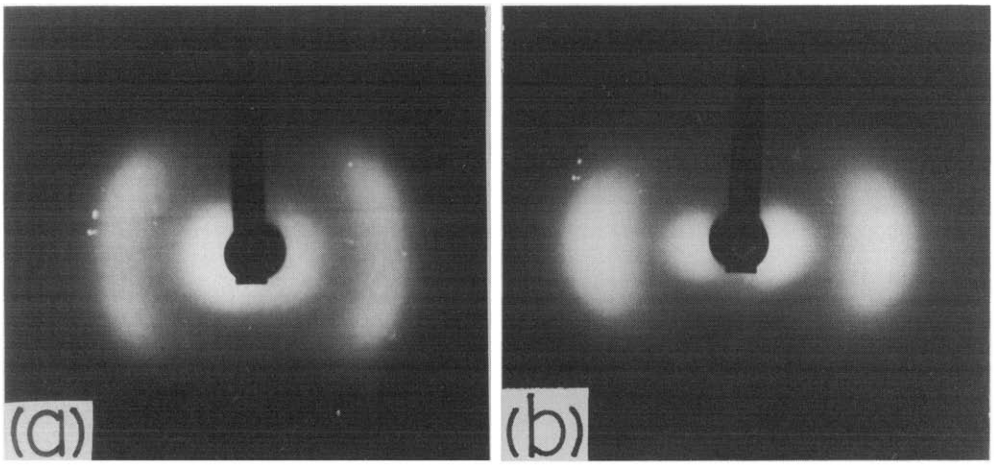


Figure 7 X-ray diffraction patterns of the P(2,8) oriented film taken with the incident beam (a) perpendicular both to the film surface and the shearing direction and (b) parallel to the surface but perpendicular to the shearing direction, which is vertical

Figures 8a and *8b* are the polarized i.r. absorbance spectra A_S and A_L measured with the electric vector of the perpendicularly incident beam parallel to the shearing and lateral directions, respectively. Most of the bands appearing in this frequency region originate from the intrinsic vibrations of the mesogenic units, including the skeletal and out-of-plane vibrational modes of phenylene rings (1600 and 750–850 cm^{-1}) and the symmetric and asymmetric C–O–C stretching modes of ester groups (1000–1350 cm^{-1})[9,12,13,17]. Although the specimen is well oriented, however unexpectedly, almost no difference can be detected between these two spectra. That is to say, the components of the transition moment of each band along the two directions are very close to each other in magnitude. Two well assigned bands were taken for discussion. The bands at 1601 and 1258 cm^{-1} have been assigned to the skeletal vibration of the phenylene rings and the asymmetric C–O–C stretching mode, respectively, in the analyses of LCPs with similar rod-like mesogens[9,12,13,17]. Their transition moments were considered to be along the axes of the rod-like mesogens. So hopefully, the dichroism data of these bands will give some information about the orientation of the planes including the X-shaped mesogens. It is clear from the X-ray diffraction and microscopic studies shown above that the branches of the X-shaped mesogens connected directly along the main chain are parallel to the specimen surface with their axes deviated from the

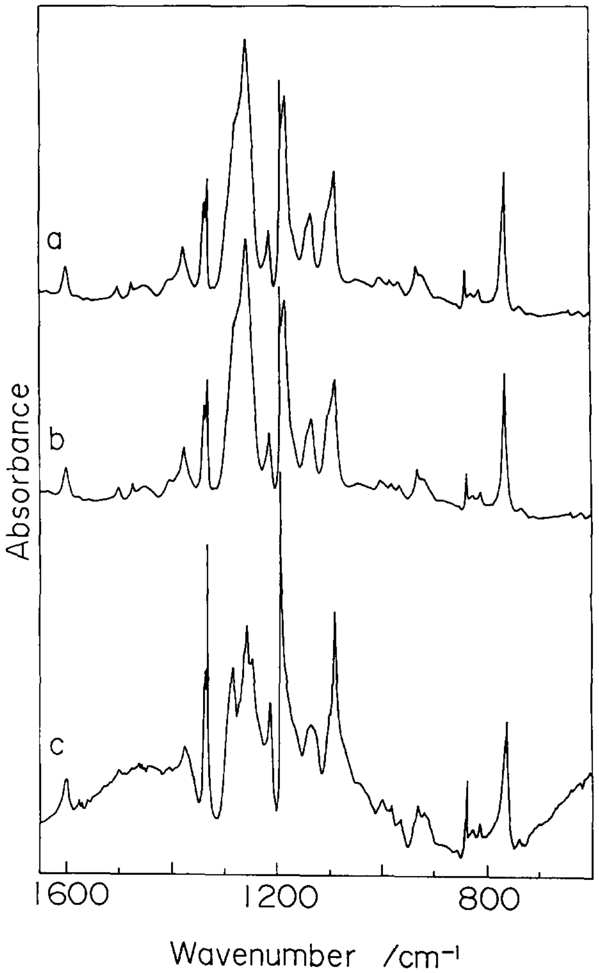


Figure 8 Polarized infra-red absorbance spectra measured for the P(2,8) oriented film: (a) A_S, (b) A_L, (c) A_T

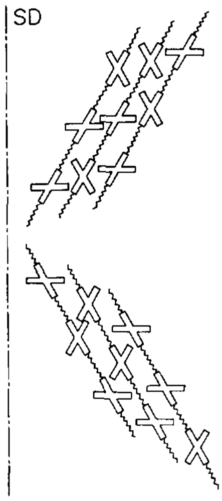


Figure 9 Schematic representation of the molecular alignment model within the zigzag-like oriented fibrils. The broken vertical line indicates the shearing direction (SD)

shearing direction by angle $+\theta$ or $-\theta$, which is usually around 30° in our cases. The other branches outward from the main chain make an angle of about 60° with the main-chain axis. The plane of the X-shaped mesogen may rotate around the main chain or deviate from the specimen surface. When the mesogens lie within the plane of the specimen, there will be two equally possible positions for the outward branches or the right and left ones, as shown in *Figure 9*. If the mesogen planes are all perpendicular to the specimen surface, then the dichroism ratio A_S/A_L for the π bands, like the 1601 and 1258 cm^{-1} bands, should be around 3, when $\theta = 30°$ is used in the calculation. The value of A_S/A_L may decrease and approximate to unity only when the mesogen planes tend to be parallel with the specimen surface. Therefore, the i.r. dichroism data shown above may imply the existence of a preferred parallelism between the planes of the X-shaped mesogens and the film surface in these oriented specimens.

In general, the refractive index is considered to be related closely with the polarization of molecules and has been measured carefully for many polymers to characterize their orientation features[18–22]. It is well known that the benzene ring is highly anisotropic in its polarization behaviour. The polarizability in directions within the ring plane is much larger than that in the perpendicular direction. It makes the refractive-index method very sensitive in detecting the orientation of benzene rings in specimens. In the present work we have measured the three-dimensional indices for the P(2,8) oriented specimens. The difference in the corresponding values between different specimens was less than the experimental error. Typical values of refractive indices obtained along the shearing and lateral directions within the specimen plane are $n_s = 1.6858$ and $n_l = 1.6861$ respectively, and that along the thickness direction is $n_t = 1.6263$. The values n_s and n_l are very close to each other, suggesting the same degree of polarization of molecular chains along the two directions. The relatively large value of birefringence, $\Delta_{(sl)t} = \frac{1}{2}(n_s + n_l) - n_t$, of about 0.06 does suggest strongly the existence of a planar orientation tendency of structural moieties, especially the phenylene rings, in the specimens. Generally, the phenylene rings of aromatic polyesters may not be coplanar[23]. The large value of birefringence shown above, however, indicates that the phenylene rings of the X-shaped mesogens may tend to be aligned with their planes parallel or nearly parallel to the mesogen plane or specimen surface in the oriented state. The planar orientation of the phenylene rings is supported also by evidences from the i.r. dichroism measurements. The band at 839 cm^{-1} is related with the CH out-of-plane vibration mode of the phenylene rings, and its transition moment is perpendicular to the ring plane. The absorbance of this band has low and almost equal values in the A_S and A_L spectra, but an obviously increased value in the A_T spectrum (*Figure 8c*), which is equivalent to a spectrum measured with the incident beam polarized in the direction parallel to the film thickness direction, obtained by a specimen tilting technique[24,25].

The thermal stability of the banded texture has also been examined with the microscope. *Figure 10* gives polarizing micrographs taken at different temperatures for one of the P(2,8) oriented specimens. The texture remains almost unchanged as seen in *Figure 10a*, which was taken at 165°C, a temperature just below the melting point. After getting into the mesomorphic state, the zigzag fracture edge in the upper part of the specimen becomes rather diffuse, but as a whole no significant changes or textural disturbances could be observed within the other regions (*Figure 10b*). This situation is kept even to temperatures much higher than the d.s.c.-determined clearing point, before thermal decomposition of the specimen (*Figure 10c*). *Figure 10d* is a micrograph

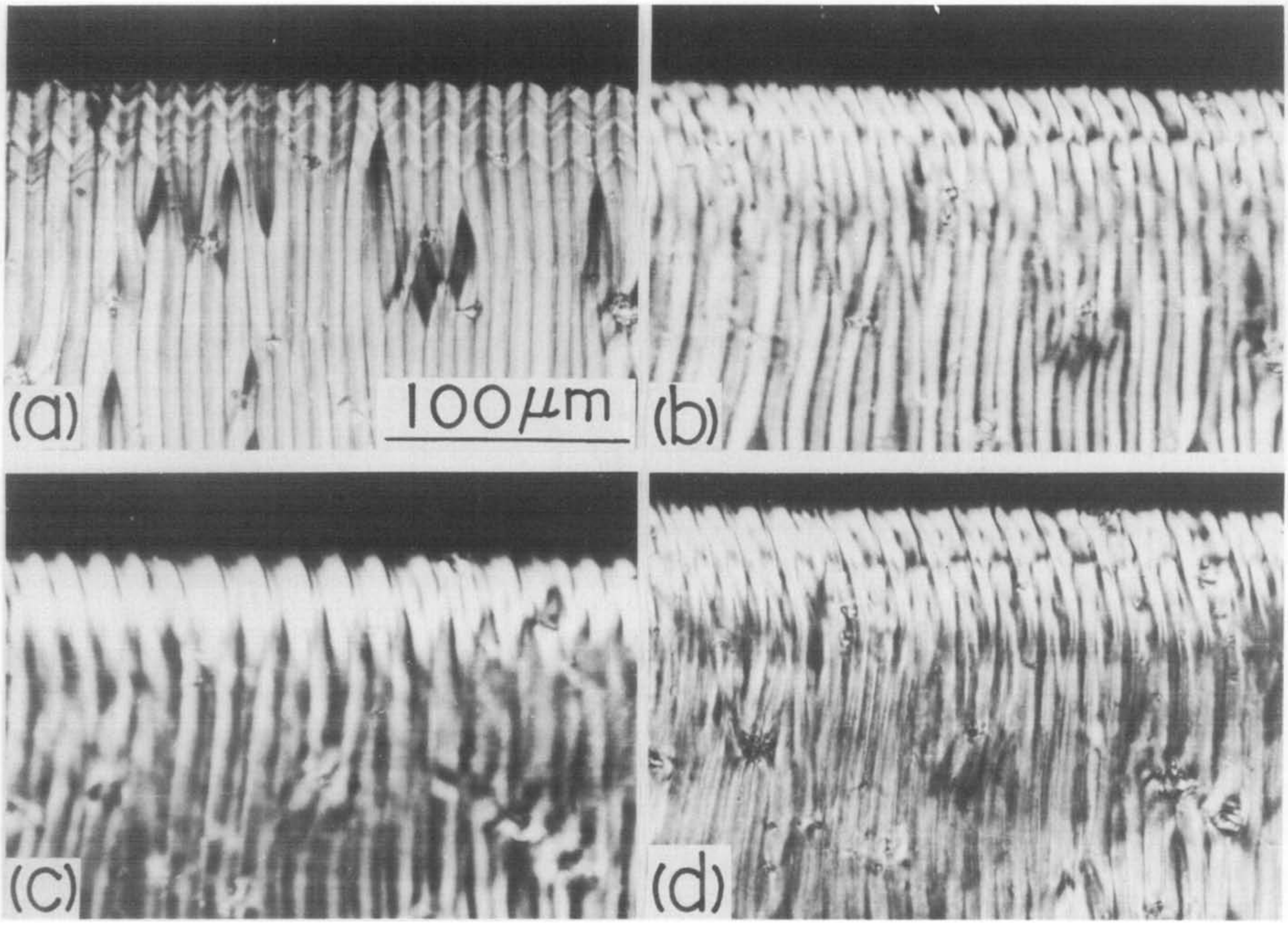


Figure 10 Polarizing micrographs of the P(2,8) oriented film taken at (a) 165°C, (b) 182°C and (c) 274°C. Micrograph (d) was taken on the same film that has been heated to a temperature just below the thermal decomposition temperature of the specimen and subsequently cooled to room temperature

of an oriented specimen that has been heated to temperatures just below the decomposition temperature of the specimen (above 300°C) and then cooled to room temperature. All of these pictures may indicate that the banded texture and its interior structure are quite thermally stable. It means that the thermal motions of each individual molecule may be severely limited even at high temperatures, and do not easily destroy the fibrillar structure and certain other supermolecular structures formed in the preparation of oriented specimens. These results are very similar to those reported for some other main-chain LCPs with rod-like mesogens[12,13].

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