Morphological studies of oriented films obtained from aromatic polyester fractions

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The banded texture and its thermal stability in oriented films of aromatic polyester with different molecular weights have been investigated. Banded texture has been observed for all the fractions used and its perfection improved with increasing molecular weight of the fractions. It was found that the bandwidth and the angle between the optical axis of the bands and the shear direction both depend on the molecular weight. The banded texture was found to be stable up to temperatures very close to T_i. A 'memory effect' of banded texture has been observed: the banded texture in oriented specimens disappears due to isotropization at temperatures above T_i and may reappear during cooling and liquid crystallization. The formation of the banded texture is discussed as the result of forced relaxation due to elasticity in the sheared specimens.

INTRODUCTION

One of the morphological characteristics of liquid-crystal-forming polymers obtained by shear or elongational flow in their mesomorphic state is the so-called banded or mat-like texture observed under a crossed polarizing microscope[1,2]. The banded texture has been reported for both lyotropic and thermotropic main-chain polymeric liquid crystals and the morphological features have been studied by various techniques in different laboratories[1-13]. In our detailed studies with oriented films of an aromatic polyester a general picture was given to describe their morphological features on different size levels[11-13].

Studies on the formation process of banded texture were reported only in few cases[14-18]. Usually a cone and plate rheometer was used and the texture changes were monitored by an optical method during the experiment. Kiss and Porter[14] 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, band texture developed only after cessation of shear. Marsano *et al.*[18] observed banded texture in hydroxypropyl cellulose aqueous solutions after cessation of shear in the shear rate range $0.1-150\,\mathrm{s}^{-1}$. They found that the time for formation after shear was a decreasing function of shear rate and shear time. Navard[16] obtained similar results for hydroxypropyl cellulose at low shear rate and possibly the bands were present during shearing with a shear rate of $\approx 200\,\mathrm{s}^{-1}$, the region of negative N_1. Optical texture for thermotropic copolyesters was observed under shear of oscillatory mode by Graziano and Mackley[15], and banded texture was found for high molecular weight

fractions during the relaxation process after shear cessation. Marrucci[19] has attempted to give a theoretical description based on rheological concepts of low molecular weight liquid crystals and conventional polymers and some tentative explanations of the banded texture have been made. However, the mechanism and the details of the formation process of banded texture are still far from clear and more experimental facts about this banded texture are needed. In this work the influence of molecular weight on the banded texture for a thermotropic aromatic polyester has been investigated.

EXPERIMENTAL

The aromatic polyester used was synthesized by solution polycondensation of monomers 1,10-bis(chloroformylbenzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene and has the following structure:
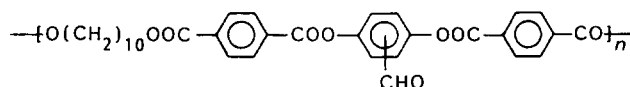
Fractions were obtained by precipitation from solution in 1,1,2,2-tetrachloroethane by adding ethanol as the precipitant. The synthesis and fractional procedures have been described elsewhere[20]. The intrinsic viscosity of the fractions in tetrachloroethane at 40°C and their transition temperatures obtained from differential scanning calorimetry measurements are given in *Table 1*.

Oriented film specimens were prepared by shearing the mesomorphic polymer melt between two slides and subsequently quenching to room temperature. The specimens were sheared at temperatures ≈ 10°C above the T_m of the polyester samples at shear rates of magnitude of

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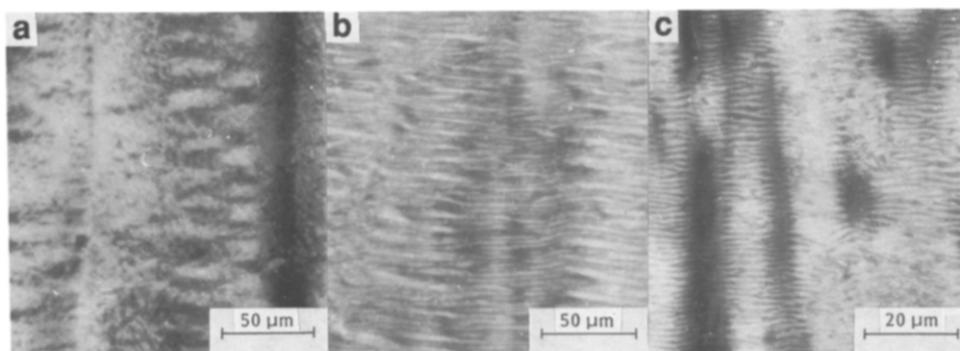* To whom correspondence should be addressed

Figure 1 Polarizing micrographs of oriented films for (a) fraction 2, (b) fraction 4 and (c) fraction 6. The shearing directions are vertical
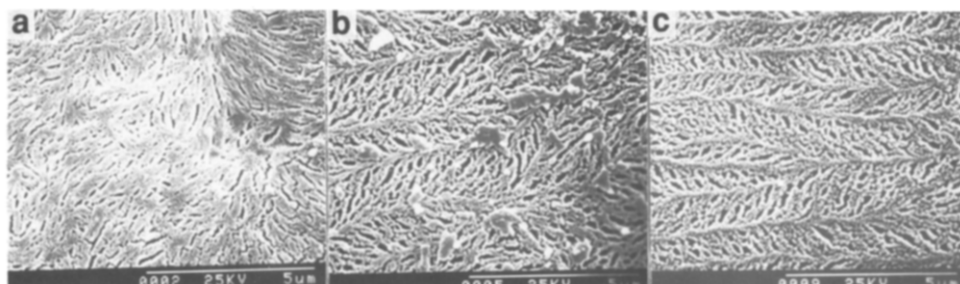

Figure 2 Scanning electron micrographs of oriented films for (a) fraction 2, (b) fraction 4 and (c) fraction 6. The shearing directions are vertical

Table 1 Polyester fractions

Fraction	$[\eta]$ (dl g^{-1})	T_m (°C)	T_i (°C)
2	0.254	162	176
4	0.355	167	189
6	0.591	162	185

Table 2 Band characteristics

Fraction	Bandwidth[a] D^* (μm)	$D^\#$ (μm)	Direction of optical axis θ (deg)
2	≈8	6.8	10
4	≈3	4.0	18
6	≈1	1.1	23

[a] D^*, estimated from microscopic observations; $D^\#$, average value from SALS measurements

order 10^2 s^{-1}. The morphology of these oriented specimens was studied by using an Olympus polarizing microscope and a JEOL scanning electron microscope type JSM-U3. The film surface was treated by etching with an argon plasma technique before scanning electron microscope observations. The ionic current and voltage for etching were carefully controlled and the specimen stage was cooled by circulation of cold water. Light scattering experiments were conducted with a 632.8 nm wavelength He–Ne gas laser. The H_v scattering patterns were recorded photographically. Infrared spectra of the specimens were obtained by using a Bruker IFS-113V Fourier transform infrared spectrometer. 64 scans at a resolution of 2 cm^{-1}were signal-averaged and stored on a magnetic disc system.

RESULTS AND DISCUSSION

Polarizing micrographs composed of parallel bands with alternate brightness extended in the direction perpendicular to the shear direction were observed for all three fractions (*Figure 1*). However, the difference in band structure among the fractions is evident. For higher molecular weight samples, fractions 4 and 6, the banded texture is usually perfect and regular and bands of clear boundaries may have great extension and cover almost the entire view field. Fraction 2, however, shows an imperfect banded texture. The bands are not regular in shape and have very short extensions. These results are consistent with the fact that banded texture is not known to occur in small molecule liquid crystal systems. This indicates that the molecular weight may be one of the prime factors in band formation.

Banded texture can be characterized by the width of the bands, which increases with decreasing molecular weight of the fractions (*Figure 1*). The data for bandwidth estimated from polarizing micrographs are given in *Table 2*. Similar results about bandwidth were obtained from the scanning electron microscope observations given in *Figure 2*. Typical grating diffraction patterns were obtained for these oriented films with a laser beam incident perpendicular to the film. *Figure 3* shows the H_v patterns for the three fractions. By taking into account an additional phase difference π between beams from adjacent bands besides that usually calculated from geometrical considerations, the average value of bandwidth D over the scattering volume was determined from the position of the scattering intensity maximum θ_m according to the equation[11]:

$$D = \lambda/2 \sin \theta_m$$

where λ is the wavelength of the laser beam. Results are also listed in *Table 2*. They are reasonably consistent with those from microscope observations.

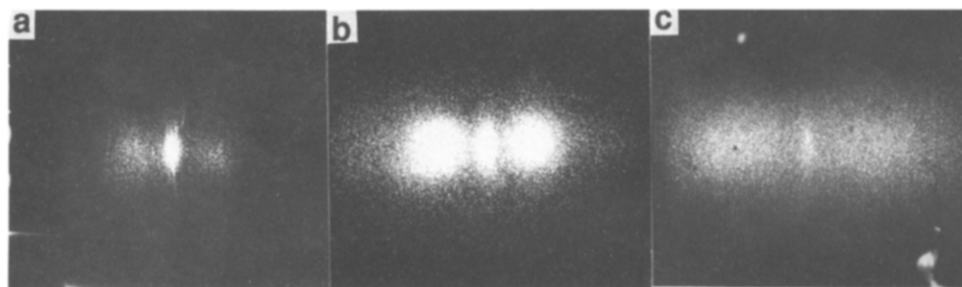Another characteristic of the banded texture is the

Figure 3 Small angle light scattering (SALS) H_v patterns of oriented specimens for (a) fraction 2, (b) fraction 4 and (c) fraction 6. The shear direction is horizontal and the specimen to photographic film distance was 14, 10.5 and 4 cm, respectively

directions of the optical axes of the bands, which may deviate from the shearing direction alternately by an angle of $+\theta$ or $-\theta$ from band to band. It has been shown[11,13] that these optical axis directions coincide with the orientation directions of macromolecules and fibrils in each band. The fibrils are composed of polymer molecules packed in a parallel alignment with their axes parallel to the fibril axis, and they travel through the bands in a regular zigzag manner. The fibrils and their parallel alignment in the bands for fractions 4 and 6 can be seen in *Figure 2*, while the orientation of fibrils in specimens of fraction 2 is not regular due to imperfection of its banded texture. The θ values were determined from the extinction positions of bands under the crossed polarizing microscope. Listed in *Table 2* are the average θ values for samples of different molecular weight. Although the experimental data for each fraction have some dispersity, especially for the low molecular weight fraction, a tendency of optical axes to deviate more from the shearing direction with increasing molecular weight was observed.

Information about molecular orientation in the oriented specimens was obtained from infrared dichroism measurements. The spectra for one of the fractions are given in *Figure 4*, where A_S and A_L are absorbances for radiations polarized in the shearing direction and lateral direction, respectively. Data on the ratio A_S/A_L for some π bands are given in *Table 3*. The 1017, 1580 and 1242 cm^{-1} bands have been assigned to the C–H in-plane bending and skeletal stretching of aromatic rings and C–O–C stretching modes, respectively. The transition moments of these bands are supposed to be along the backbone of the molecular chain. From the absorbance ratio the average orientation direction of molecules can be estimated and the angle between the orientation direction and the shearing direction for the three fractions is also listed in the table. It was found that the angle of deviation of molecular orientation from the shearing direction increases with increasing molecular weight of the fractions. These values of deviation angle for molecular orientation are significantly larger than those for optical axes given in *Table 2*. This is because not all the portions of the specimens are well oriented during the manually controlled shearing procedure and data from infrared spectroscopic studies are related to the situation of all the molecules in the volume of measurement, not only molecules included in the bands. Note that a comparison of infrared dichroism data for different fractions indicates that A_S/A_L for fraction 2 is usually larger than the values for the other two fractions. This implies that molecules of fraction 2 may be oriented under shear as well as
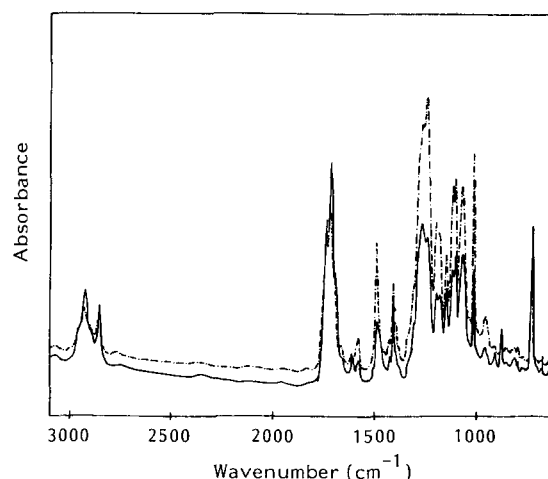

Figure 4 Infra-red spectra for an oriented film of fraction 6. — · — · —, A_S; ——, A_L

Table 3 Data from infrared dichroism measurements

Fraction	Wavenumber (cm^{-1})	A_S/A_L	θ (deg)	$\bar{\theta}$ (deg)
2	1017	3.52	28.1	30.8
	1242	2.94	30.2	
	1580	2.19	34.0	
4	1017	2.54	32.1	32.9
	1242	2.66	31.5	
	1580	2.00	35.0	
6	1017	1.97	35.5	36.9
	1242	1.91	35.9	
	1580	1.50	39.2	

molecules of the other fractions; they may remain to some extent oriented individually with respect to the shear direction after shear cessation, but do not usually form the special regular oriented structure, banded texture, which occurs for higher molecular weight fractions.

The thermal stability of the banded texture has been studied for all the fractions under the polarizing microscope. Results are similar for the three fractions and consistent with those obtained for another aromatic polyester[13]. *Figure 5* shows the polarizing micrographs for a film specimen of fraction 4 at different temperatures. The banded texture remains almost unchanged during the melting transition. It becomes weakened at temperatures very close to T_i and disappears at T_i. Micrographs for oriented films which have been heated to temperatures $\approx 20°C$ above their T_i and then cooled to room temperature are given in *Figure 6*. It is clear from these

micrographs that during the cooling process not only does the transition of liquid crystallization occur, but also the banded texture reappears, although its perfection and contrast are less than those in the film before the heat treatment. This implies some kind of memory effect of banded texture. Once the macroscopic ordering of parallel alignment of molecules and fibrils is formed, it is very difficult to destroy it by thermal relaxation even at high temperatures at which the mesomorphic order is not observed.

Most of the results obtained from studies on the band formation process in the literature indicate that the specimens are first oriented in the shear direction and banded texture is formed after shear cessation immediately or in a short period of time. The stability of the banded structure shown in our observations may imply that the banded texture could hardly be the result of free thermal relaxation from the shearing orientation state, but is probably the result of forced thermal relaxation due to elasticity in sheared specimens. This means that the zigzag rearrangement of fibrils from their straight orien-

ted state occurs under crushing along the orientation direction. A contraction effect has been proposed by Nishio et al.[10] to explain the formation of banded texture in hydroxypropyl cellulose solutions after shear. Marrucci[19] suggested that the banded texture is formed under the influence of Frank elasticity, and the orientation angle θ reflects the competition between Frank and polymer elasticities. Our results of the perfection and θ values for banded texture indicate that the elasticity effect should increase with increasing molecular weight of the samples. The elastic energy stored during shearing gives the driving force for band formation, and it can be dissipated mainly in the destruction of structure at the boundaries between bands. The higher the initial elastic energy term, the greater is the percentage of band boundary regions in the specimens. This may explain the decrease of bandwidth with increasing molecular weight of the samples and the shear effect observed in this work and reported in a previous paper[12], if a positive influence of molecular weight and shearing on the elastic energy can be considered as reasonable.

The rheological behaviour of polymeric liquid crystals is a problem of interest for further investigations, but to our knowledge the positive effect of molecular weight and shearing on the elastic behaviour of conventional polymer melts is well known.

ACKNOWLEDGEMENT

Figure 5 Polarizing micrographs for oriented films of fraction 4 at different temperatures: (a) 110; (b) 165; (c) 180; and (d) 188°C

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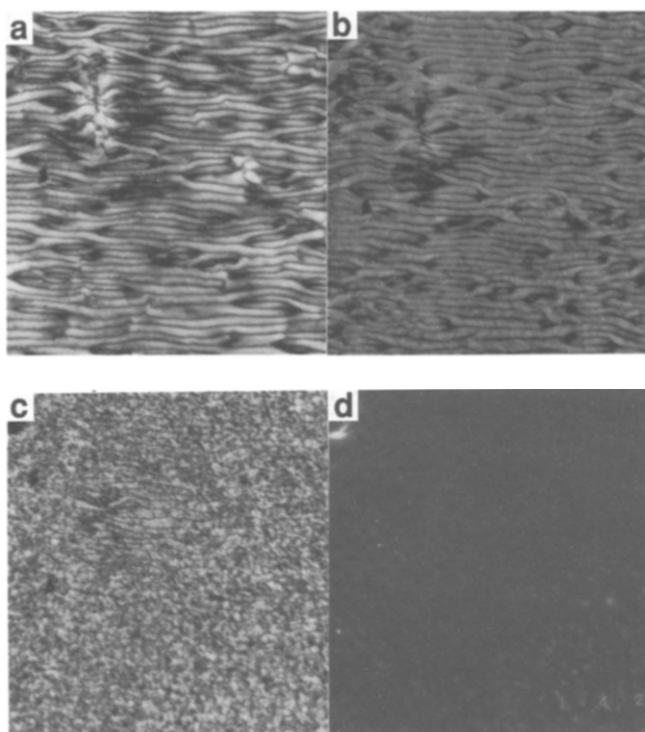10 Nishio, Y., Yamane, T. and Takahashi, T. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 1053
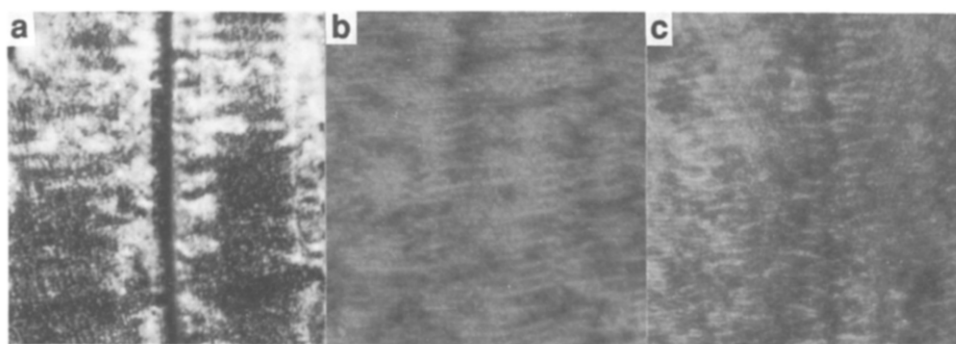
Figure 6 Polarizing micrographs of oriented specimens which have been heated to temperatures above T_i and then cooled down to room temperature: (a) fraction 2; (b) fraction 4; (c) fraction 6

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