polymer papers

Morphological features and orientational relaxation of films obtained from a liquid crystalline polyester

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Oriented films of an aromatic liquid crystalline polyester obtained from the melt in the mesomorphic state were studied by wide-angle X-ray diffraction, WAXD, polarized light microscopy and infra-red dichroism. The mat structure of the resolidified polymer was found to be in a supercooled liquid crystalline state, not in the crystalline state as in the case of cast films of lyotropic aromatic polyamides. A general picture describing the morphological features of the oriented films at different size levels is depicted. The relaxation of molecular orientation in the mesomorphic state was very slow, and rapid relaxation was only observed near the clearing point.

(**Keywords: aromatic polyester; polymeric liquid crystal; mat structure; orientational relaxation; WAXD; infra-red dichroism**)

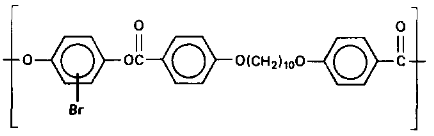
INTRODUCTION

The processing of liquid crystalline polymers in their mesomorphic states is of considerable practical interest because their liquid crystalline organization makes it possible to retain high orientation of the macromolecules in the final products. For example high strength and high modulus fibres are now produced by solution spinning of lyotropic aromatic polyamides. It is important, therefore, to study the morphology of such polymers in the oriented states, which are obtained from processing in their mesomorphic state.

A 'pleated' or mat structure has been observed in Kevlar fibres and in oriented aromatic polyamide films, and the morphological features of these materials have been studied by different authors using various techniques[1–6]. Recently, we and others have reported on the same texture in films of polymers exhibiting thermotropic liquid crystal behaviour[7,8]. In the present report we report on the morphology of oriented films of an aromatic polyester containing a triad ester mesogenic group and a decamethylene flexible spacer in the main chain. Films of this polymer were studied in order to give a general picture of the morphological features of their mat structure on different size levels. The results of orientation relaxation of the oriented films are also described.

EXPERIMENTAL

The polymer studied was an aromatic polyester derived from bromohydroquinone and 4,4′-dicarboxy-1,10-diphenoxydecane, which has the following structure:



The preparative procedures for the polymer have been described previously[9]. The polymer has a melting transition at 163°C and an isotropization transition at 270°C as determined by d.s.c. Oriented films were obtained by shearing the molten polymer in the liquid crystalline state between aluminium foil and a glass slide at about 180°C and subsequent quenching with liquid nitrogen. The thickness of the films was 10–20 μm.

The Ni-filtered CuKα radiation (40 kV, 30 mA) was used for WAXD measurements and the angular dependence of diffraction was recorded on a Regaku automatic X-ray diffractometer type D/max IIIB operating in the transmission mode. Diffraction patterns were also recorded on flat films with pinhole collimation. In order to get high scattering intensity, about 20 pieces of film were stacked together with their shearing directions parallel to each other.

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An Olympus polarizing microscope equipped with a hot stage was used to study the morphological changes of the mat structure in the heating process.

Infra-red dichroism measurements were performed with a Perkin–Elmer type 180 infra-red spectrophotometer. A temperature controllable sample cell with rock salt windows was used to study the temperature dependence of the dichroism. The heating rate was 10°C min^{-1}, and the temperature was kept constant for 20 min at each experimental point.

RESULTS AND DISCUSSION

In our previous report[8] we studied oriented films of the same polymer by use of polarized light microscopy, small-angle light scattering, birefringence and infra-red dichroism. It was found that the stripes of the mat structures observed in the films were composed of fibrils arranged in a zig-zag manner containing polymer chains packed in a highly ordered, parallel alignment. In order to obtain more detailed information about the molecular packing and the nature of the mat structure, in general, the oriented films were analysed by WAXD, and the WAXD patterns of films obtained from the melt under shear and by solution casting are shown in *Figure 1*. The diffraction pattern of the former (a) is entirely different from that of the same polymer in the crystalline state (b). *Figure 2* plots the 2θ dependence of the diffraction intensity along the equator for film specimens with mat structures. Only two diffraction rings are observed, at 2θ values of about 7.0° and 21.0°.

The non-crystalline nature of the mat structure is consistent with the results of our previous infra-red dichroism studies[8] and also indicates the existence of a random orientation of the rotational position of the molecular chains. The 2θ position of these diffraction peaks are almost the same as those which were obtained for unoriented specimens formed from the melt in the nematic phase[10]. In the latter case the solidified films were shown to have a liquid crystalline morphology by polarized light microscopy. Apparently, therefore, the mat structures obtained from casting lyotropic polyamide solutions and solidifying thermotropic polyester melts are different in nature. That is, poly(*p*-phenylene terephthalamide) crystallizes during precipitation from an anisotropic solution, while our aromatic polyester retains its mesomorphic order during solidification.

The outer ring in the WAXD pattern of a polymeric liquid crystal is generally considered to be caused by the diffraction related to the average lateral distance between parallel neighbouring molecules. This interpretation is also evidenced in our polymer from the azimuthal dependence of the intensity of the outer ring. The WAXD pattern in *Figure 3* was obtained at $2\theta = 21°$ with the meridian parallel to the shearing direction of the films.

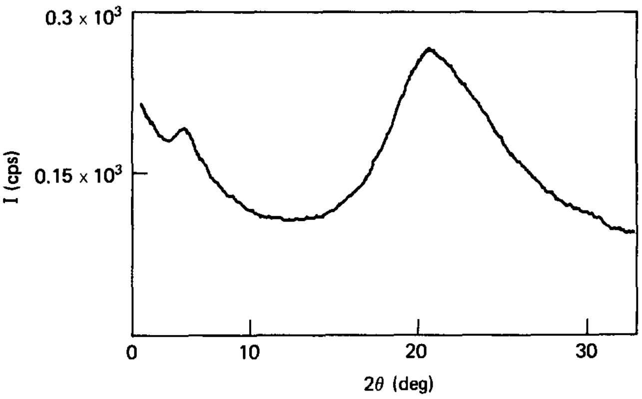

Figure 2 2θ dependence of diffraction scanned along the equator for film specimens with mat structures

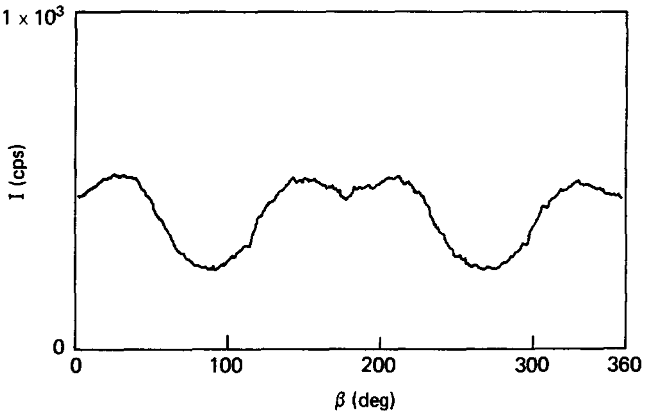

Figure 3 Azimuthal dependence of the diffraction intensity at $2\theta = 21°$ for film specimens with mat structures

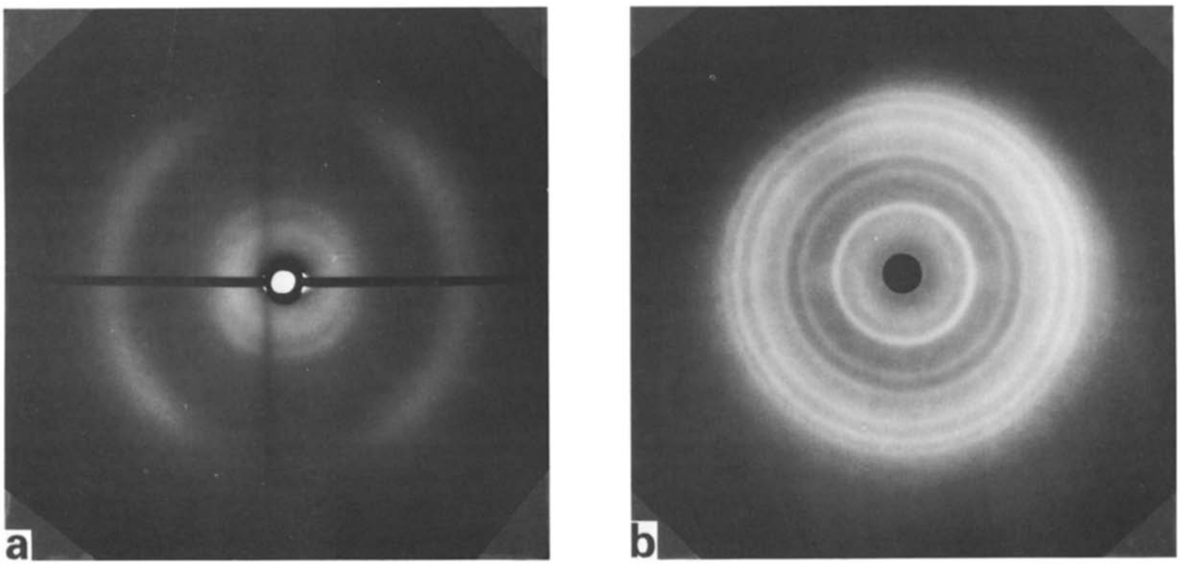

Figure 1 WAXD patterns of: (a) oriented films having a mat structure (the shearing direction is vertical); (b) solution cast films

The figure shows that the outer ring was split into four spots which were distributed symmetrically with respect to the equator ($\beta = 0°, 180°$) and to the meridian and were grouped around azimuthal angles of 30°, 150°, 210° and 330°. These results agree very well with our previous suggestion of a parallel alignment of molecules in directions deviating from the shearing direction by about ±30° (ref. 8). The average lateral distance between the parallel molecules, estimated from the outer ring, was about 4.7 Å, based on the De Vries modification of the Bragg equation[11]. The inner ring implies the existence of a periodic spacing of about 14.1 Å, but the assignment of this diffraction is not clear. Usually an additional diffraction ring at small 2θ values was reported for liquid crystals of smectic and cybotactic nematic mesophases[12]. It is supposed to be related to the spacing between smectic or smectic-like layer planes, and is located in the directions along the parallel molecular chains. However, for these oriented films with mat structures the azimuthal dependence of the inner ring intensity, shown in *Figure 4*, is similar to that of the outer ring, which may indicate that it is also related to a lateral spacing between parallel molecules.

From these observations and our previous results, a general picture describing the morphological features of oriented films of this polymer on different size levels can be depicted. Microscopy reveals that the oriented films obtained in those experiments are composed of parallel stripes or bands of several microns width which are extended in the direction perpendicular to the shearing direction, as seen in *Figure 5a*. Parallel aligned fibrils of several thousand Å diameter and tens of microns in length lie in the film plane and travel through the stripes in a regular zig-zag manner. The fibrils make an angle of about ±30° with the shearing direction, as shown in *Figure 5b*. The fibrils are composed of molecules packed in a parallel alignment with their axes parallel to the fibril axes, as shown in *Figure 5c*. However, the rotational positions of the rod-like molecules with respect to the orientation axis are almost random. That is, the films contain an oriented mesomorphic order with an average lateral distance between polymer molecules of about 4.7 Å, as represented in *Figure 5d*.

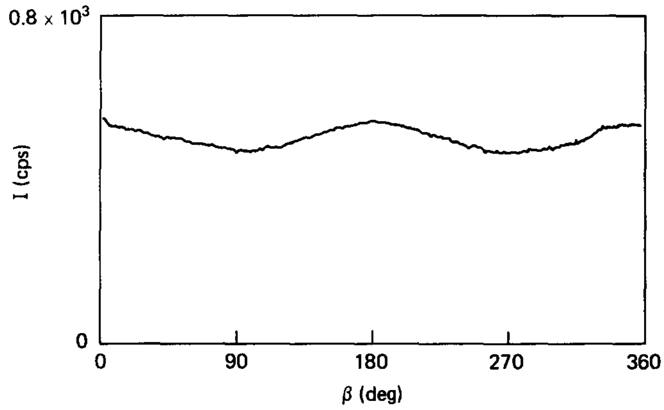

Figure 4 Azimuthal dependence of the diffraction intensity at $2\theta = 7°$ for film specimens with mat structures

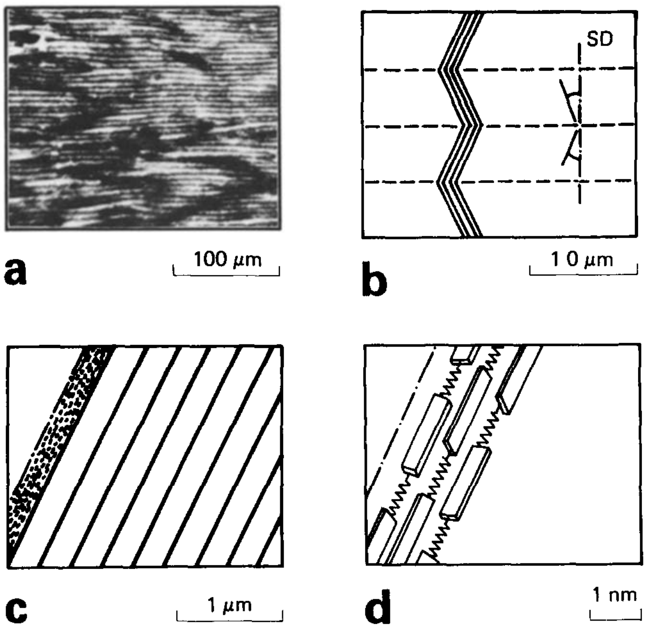

Figure 5 Morphological features of an oriented film in which the shearing direction is vertical: (a) photomicrographs of the mat structure observed with a polarized light microscope; (b), (c) and (d) structural models of the mat structure at different size levels

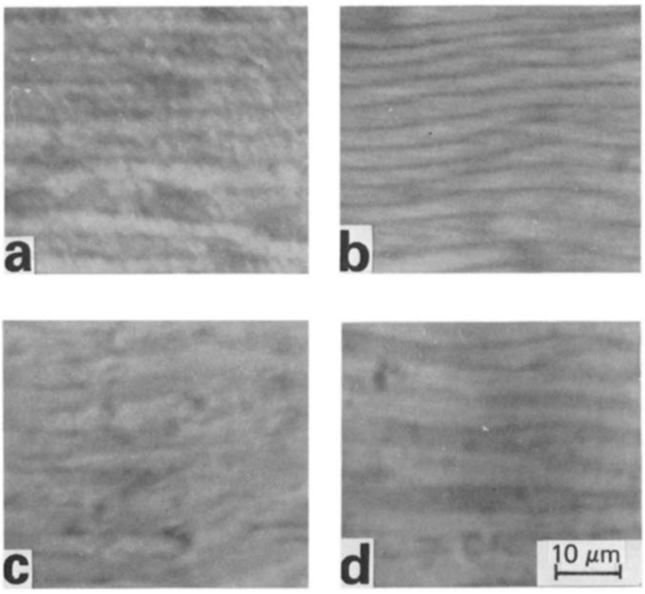

Figure 6 Polarized light photomicrographs of the mat structure of a film at different temperatures (a) room temperature, (b) 170°C, (c) 220°C and (d) 270°C

The stability of the mat structure has also been studied by polarized light microscopy. *Figure 6* presents photomicrographs of a sample of the oriented film at different temperatures. It is seen that the oriented films retain their parallel stripe morphology during the heating process up to a high temperature, until the beginning of the mesomorphic-to-isotropic transition. However, the birefringence of the stripes decreased with increasing temperature, especially at temperatures higher than 250°C, and the boundary regions between stripes showed a lower contrast.

The relaxation of molecular orientation in the heating process was measured from the infra-red dichroism of two bands at 1605 and 2920 cm^{-1}. The 1605 cm^{-1} band is related to the skeletal vibration of the benzene rings, while the 2920 cm^{-1} band is related to the C–H stretching vibration of the methylene groups in the spacer groups. The absolute value of the absorbance difference, $|A_S - A_L|$, of the two bands was determined to characterize the change in orientation of both the mesogenic units and the flexible spacers with the results shown in *Figure 7*. A_S is the absorbance of the specimen for the radiation

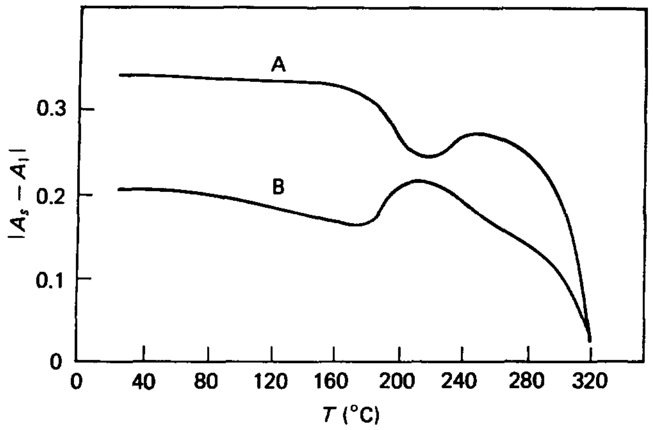

Figure 7 Temperature dependence of $|A_S - A_L|$ for the bands at: A, 1605 cm^{-1}; B, 2920 cm^{-1}

polarized in the shearing direction, and A_L is that for the radiation polarized in the lateral direction.

The values of $|A_S - A_L|$ for both bands begin to decrease rapidly at about 280°C, which is much higher than the melting point of the polymer (163°C) and approach zero at about 320°C, which is well above the transition from anisotropic melt to isotropic melt (270°C). The slight decrease in the value of $|A_S - A_L|$ for the 2920 cm^{-1} band at temperatures below the melting point is probably related to the onset of some molecular motions of the flexible spacers at about 50°C[10]. In this temperature range the $|A_S - A_L|$ value of the 1605 cm^{-1} band remained constant. This result implies that the axes of the mesogenic units did not change their orientation during crystallization from the mesomorphic state, or, if they did, the change was so small as not to be detectable by i.r. dichroism.

For an amorphous polymer, relaxation of molecular orientation usually takes place rapidly above its glass transition temperature. For a crystalline polymer the crystallites will prevent orientation relaxation of polymer segments not only in the crystalline regions, but also in neighbouring amorphous regions. In contrast, the molecular motion of polymer segments in the liquid crystal state appears to be very limited, and the macroscopic orientation of the polymer which was initiated by external effects, such as shear, does not relax for extended periods of time, if at all, while the polymer retains mesomorphic order.

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