JOURNAL OF MATERIALS SCIENCE 17 (1982) 2661–2670

Phase transformations in the thermotropic liquid crystal polymer: 60/40 PABA/PET

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Microstructures observed in 60/40 PABA/PET co-polyester in transmitted polarized light are reported. The microstructure changes as a function of temperature. Between 190 and 340° C the optical textures are similar to those seen in small molecule liquid crystals in the smectic C modification; above 340° C the textures are typical of nematic structures. At 420° C the specimen is totally isotropic and begins to degrade. Rapid cooling to below 190° C can quench in the high temperature phases, including the isotropic one. DSC traces show endotherms identifiable with the onset of mobility at 190° C, the transition from smectic C to nematic-like textures at 340° C and the development of the isotropic phase in the range 350 to 420° C. The "smectic C" to "nematic" transition in texture is associated with the appearance of a transient microstructure, known as a "myelin" texture, and reported here for the first time in a liquid crystal polymer.

1. Introduction

Mesomorphic, or liquid crystal, polymers appear to have unique mechanical and flow properties. This is encouraging their development, with the objective of the straightforward manufacture of high modulus mouldings, and in an attempt to facilitate processing operations in general. In some systems, described as lyotropic, the liquid crystalline properties are achieved only in the presence of a suitable solvent which is introduced at an appropriate stage of the manufacturing cycle. Despite the rather cumbersome processing requirements, the lyotropic route is used in the successful range of aromatic polyamide fibres pioneered by Du Pont as "Kevlar". In contrast to lyotropic systems, thermotropic polymers show liquid crystal-like properties over a particular temperature range without the addition of any solvent. They are also comparatively cheap. It is thus possible that conventional processing routes can be used to produce products with high and controlled levels of mechanical anisotropy.

The term "liquid crystal" when applied to polymers defines a state which has one or more of the following characteristics in common with low molecular weight liquid crystals:

(a) anisotropy of properties, for example optical anisotropy in the absence of three-dimensional crystalline order [1, 2];

(b) anomalously low solution or melt viscosity [2, 3];

(c) possibility of inducing significant molecular orientation by magnetic or electric fields [2, 4];

(d) production of characteristic nmr line shapes [5];

(e) miscibility with a known small-molecule liquid crystal [6];

(f) an endotherm, detectable by differential scanning calorimetry (DSC) at the temperature where a thermotropic mesophase first flows freely, and again where this phase is replaced by an isotropic one [6].

It is widely recognized that liquid crystal-like properties can be induced in a polymer by the incorporation of suitable rigid mesogenic groups into the molecule. These groups may either be included in the main chain, although usually separated by less rigid groups, or they may occur as side groups attached to the main chain directly or via a less rigid sequence. The polymer studied and reported on here is a main chain mesomorphic co-polyester. It consists of 40 mol% poly(ethylene

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terephthalate) (PET) and 60 mol% *p*-acetoxybenzoic acid (PABA) as a random co-polymer; its chemical structure and preparation will be described in the next section.

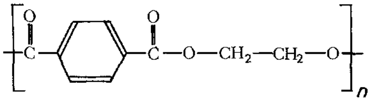
This paper presents a comparison of optical textures exhibited by the polymer at different temperatures with textures previously reported for low molecular weight liquid crystals. On this basis, the textures seen in the polymer are identified as "nematic" and as "smectic C"; terms which, when associated with small molecule liquid crystals, imply molecular arrangements as shown in Fig. 1. Whereas it is relatively easy to visualize how the co-polyester chains might adopt the nematic arrangement, it is not clear, as will be stressed again later, how they could conform to the smectic C structure as envisaged for small molecule liquid crystals. Transitions recorded by DSC are discussed, and each optically observable transition is paired with a DSC endotherm.

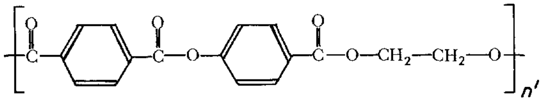
The work follows on from optical studies performed on the co-polyester by Mackley *et al.* [7]. We are grateful to Dr Mackley for his encouragement, and for his gift of the material used in our investigations.

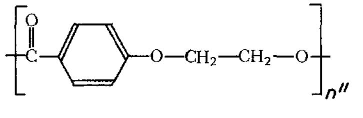
2. Experimental procedure

2.1. Material

The polymer used was manufactured by Tennessee Eastman Kodak. It was synthesized [3] by reacting PABA with both PET (in other words breaking into the PET chain) and itself, and then condensing together the segments thus formed. The resultant co-polyesters contain sequences of the form shown below:







The ethylene terephthalate and PABA residues are reported [3, 5] to occur in random sequence.

The material was supplied as 2 mm diameter chopped extrudate.

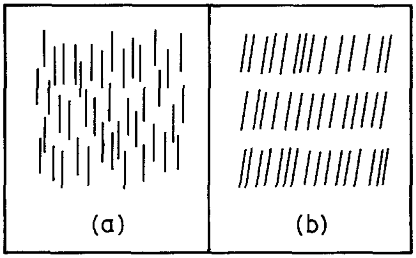


Figure 1 Sketch depicting molecular organization associated with nematic (a) and smectic C (b) modifications of small molecule liquid crystals. Each line represents a short rod-like molecule.

2.2. Techniques

Slices 10 μm thick were microtomed from as-received material, and were heated between glass microscope slides in a hot stage. Unless otherwise stated, microstructures reported and discussed below were observed in transmission between crossed polars. DSC plots were produced using a Du Pont 990 system, specimens being heated in an atmosphere of dry argon at a rate of 20° C min^{-1}.

3. Results

3.1. Effect of temperature on microstructure

The texture within the liquid crystal polymer varies as a function of temperature. The transitions observed are outlined in Fig. 2. Below 340° C the equilibrium microstructure as seen between crossed polars is shown in Fig. 3. It consists of discrete groups (or knots) of dark extinction bands, separated by regions of generally low contrast. Such microstructures are well documented for low molecular weight liquid crystals and are referred to as "interrupted schlieren" textures [8–10]. At temperatures above 190° C the texture is mobile. The microstructure of Fig. 3 is discussed in greater detail below.

Above 340° C the microstructure is distinctly different, as can be seen in Fig. 4 which shows a specimen quenched from 350° C. The network of extinction bands is now continuous and fills the field of view. In the terminology of low molecular weight liquid crystals it is a "continuous schlieren" texture. As the temperature is increased further, a second, optically isotropic, phase is nucleated. It first appears at about 350° C, and grows until the entire specimen is isotropic at 420° C; at this temperature, sample degradation is becoming significant, with some occurrence of internal bubbles. The biphase region has been reported

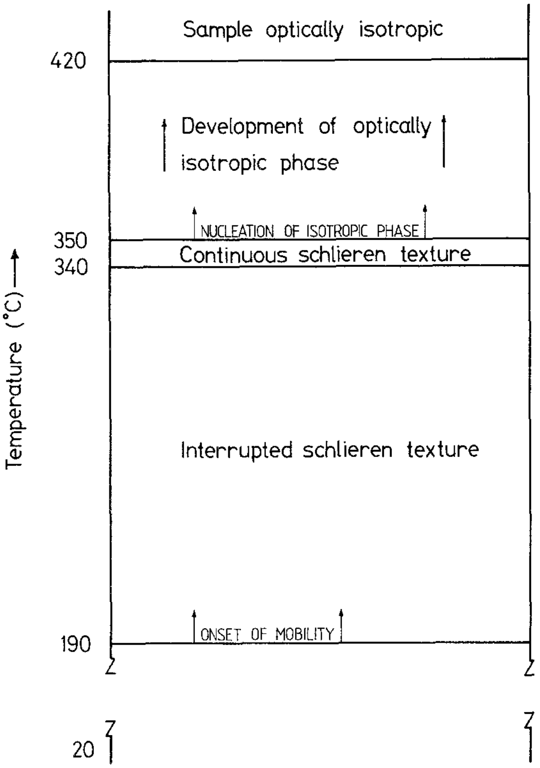


Figure 2 Diagram indicating the stability regimes of, and transitions between, different phases in the co-polyester.

previously for both this material [7] and other thermotropic co-polyesters [11].

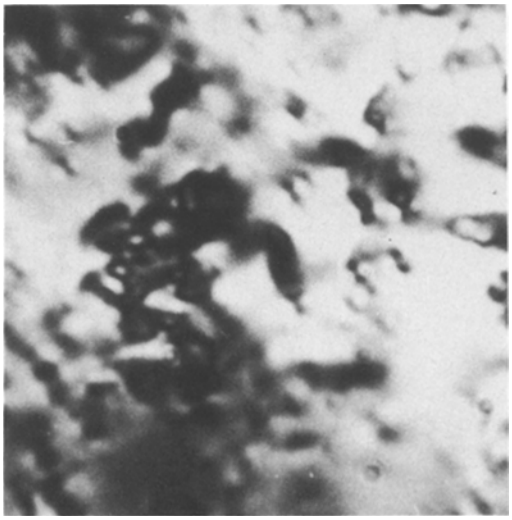


Figure 3 Light micrograph of a 10 μm thick section of the co-polyester quenched from 250° C, showing an interrupted schlieren texture. (X 2400 between crossed polars.)

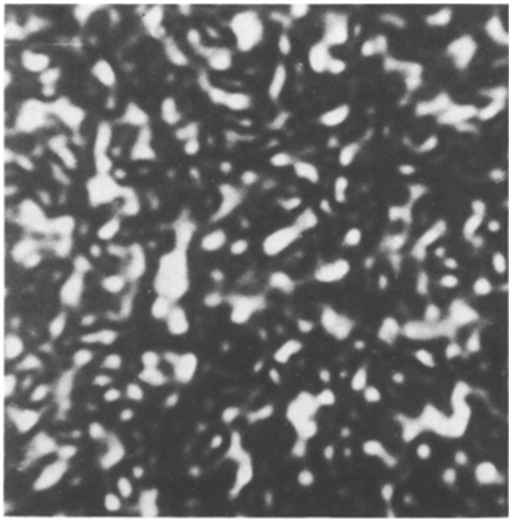


Figure 4 Microstructure observed under similar conditions to Fig. 3, except that the sample was quenched from 350° C. The schlieren texture is now continuous and is typical of that observed at elevated temperature (X 2400).

A DSC trace of the material is shown in Fig. 5. The transition at 70° C suggests a glass transition in that there is a discontinuous increase in specific heat. It agrees closely with the lowest temperature transition discussed by Menczel and Wunderlich [12] for the same material. The onset of mobility at 190° C corresponds to a marked endothermic peak. It is possible that this peak represents "melting out" of regions of local order which, at low temperatures, pin the microstructure. Similar peaks have been observed for other related thermotropic polymers [13] and their relationship to reinforcing elements in the structure noted. The peak at 250° C does not appear to correlate with a change either in microstructure or in mobility, and its position is not reproducible to within better than ± 5° C. Its possible origins are discussed below. The small peak at 340° C marks the change from interrupted to continuous schlieren texture. The growth of the optically isotropic phase between 350 and 420° C corresponds to a broad, yet substantial, peak. However, its profile above 400° C is apparently influenced by the degradation process, which destroys the smoothness of the plot and eventually leads to a pronounced exotherm.

All the mesophases observed can be "quenched-in" by cooling the sample rapidly to room temperature. This route, previously suggested [7, 14, 15], was exploited so as to avoid the necessity for high temperature, high magnification microscopy wherever possible. The isotropic phase requires particularly rapid cooling if it is to be preserved to room temperature, and it can only be "quenched-in" in thin samples. Quenching larger samples into water produces an optically isotropic surface layer,

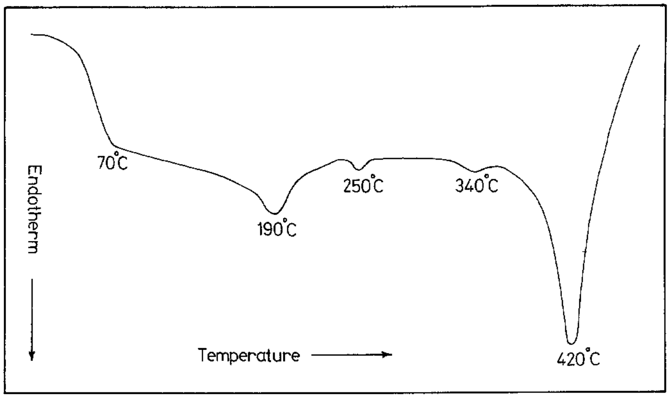


Figure 5 DSC trace of the as-received copolyester. Heating rate 20° C min^{-1} in dry argon.

but the finite thermal conductivity limits the cooling rate in the centre and allows the mesophase to reform (Fig. 6). The surface layer is glassy and particularly brittle, but it returns to the equilibrium liquid crystal structure if heated above 200° C.

3.2. Structure below 340° C

Fig. 3 shows the interrupted schlieren texture, which is the most common microstructure seen below 340° C. The distribution of the individual extinction bands within the discrete groups depends on the orientation of the sample relative to that of the crossed polars. There is a particular arrangement of extinction bands in which four of them radiate from a point. These bands rotate about the point as the polars are rotated; the sense of rotation may be the same as, or opposite to, that of the polars, but the angular velocity is the same. Fig. 7 shows an area in which two such points occur, and illustrates the rotation of the associated dark brushes as the polars are rotated anticlockwise in 10° increments. The accompanying map, prepared from the photographs, shows possible spatial variation of the orientation of the local optical director in the specimen plane. (Since it is not possible to tell whether a particular extinction band results from the local optical director being parallel to the polarizer or parallel to the analyser, a map comprising the set of lines orthogonal to those drawn here would be equally valid). As discussed by Mackley *et al.* [7], these "centred textures" are associated with the existence of disclinations of strength ± 1 running vertically between the glass slides. The orientation distribution of local optical directors, as plotted, follows patterns suggested by Frank [16] for the trajectory of the director about such disclinations. Disclinations of strength ± 1/2, also discussed by Frank, were not seen below 340° C.

In a few specimens, a different type of texture was observed in the temperature range below 340° C (Fig. 8). It consisted of comparatively large regions (~ 50 μm) of fairly uniform contrast,

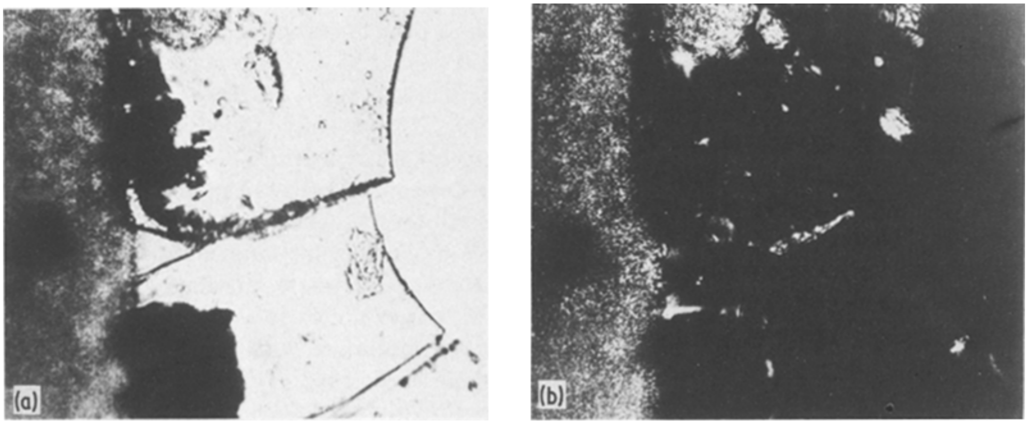


Figure 6 Slice through sample quenched in water from the isotropic phase. The surface regions (centre) are a brittle glass, while the interior (left) shows a continuous schlieren texture which is not fully resolved at this magnification (X 2000). (a) Plane polarized light, (b) crossed polars.

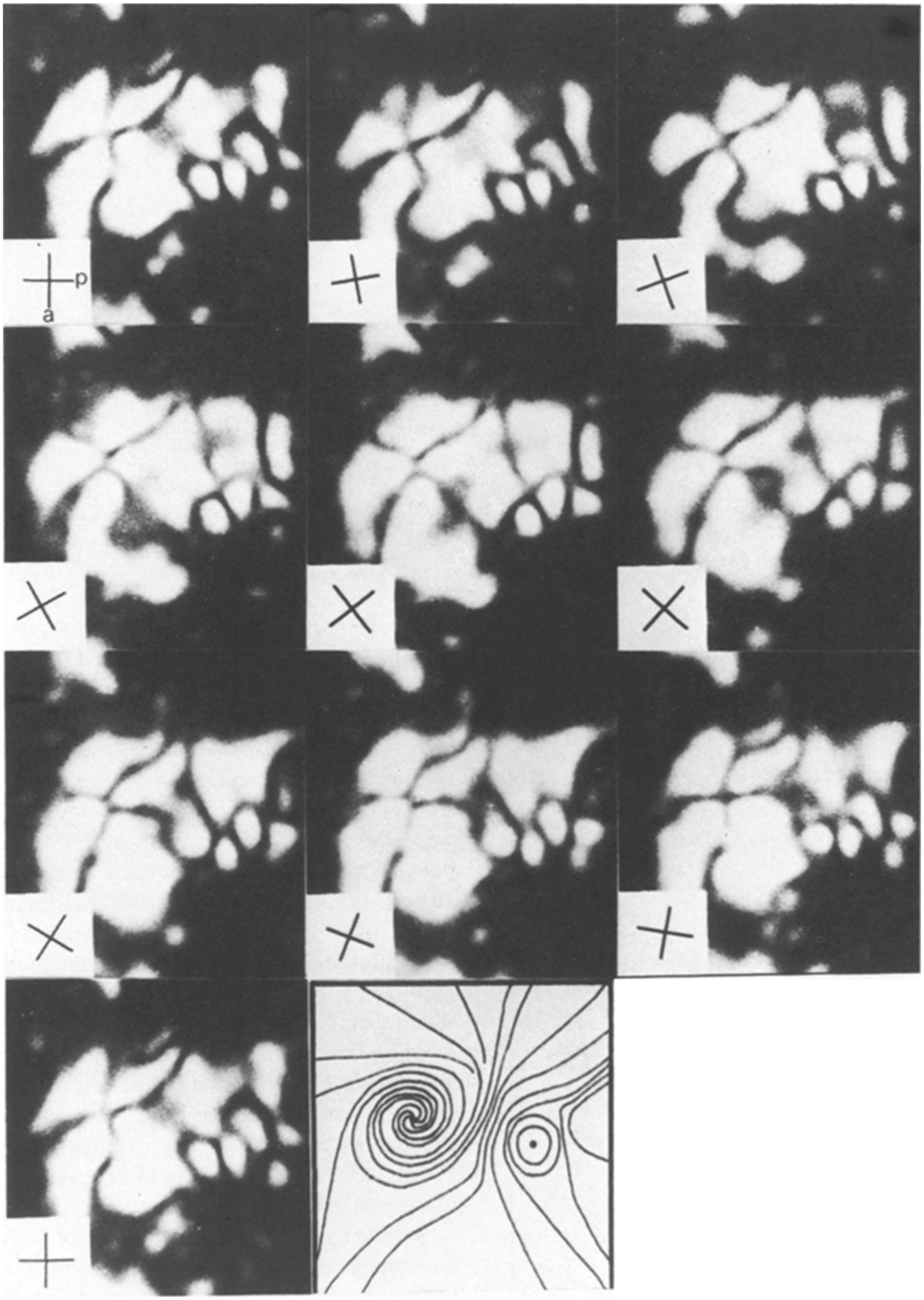


Figure 7 A series of micrographs of a 10 μm thick section of material quenched from 250° C, showing extinction bands organized as four-fold "brushes" which rotate in the same direction and at the same rate as the crossed polars. The director map indicates the presence of two disclinations at the centres of the circular features. Both are of strength + 1 and lie normal to the section (× 3500).

indicating homogeneity of alignment, with the boundaries between them visible as well-defined walls (so-called "inversion walls of the second kind" [9]). The walls are faintly visible even in unpolarized light. Fig. 9, which is a map of local optical director orientation, substantiates this description.

The presence of interrupted schlieren textures and disclinations of strength ± 1 but not ± 1/2, and the occasional observation of a texture con-

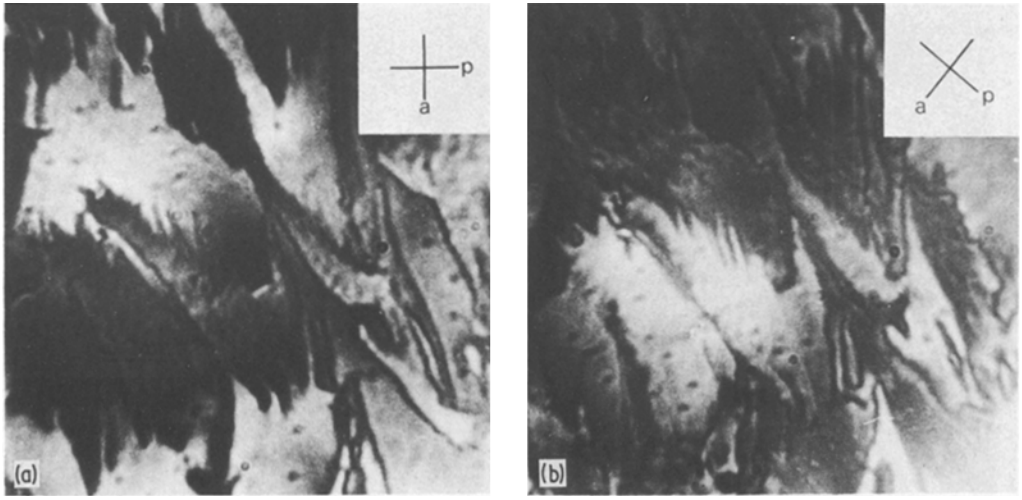


Figure 8 Regions of homogeneous molecular alignment separated by well-defined inversion walls of the second kind. This texture is not typical; however, when it does occur it is only seen below 340° C. (× 1800, crossed polars, rotated by 40° in (b), 10 μm section quenched from 250° C.)

sisting of large areas of homogeneous alignment are all characteristic of low molecular weight liquid crystals in the smectic C modification [9]. It thus appears that, whatever its detailed molecular arrangement might be, this polymer shows optical textures which, below 340° C, are strikingly similar to those seen in small molecule liquid crystals with smectic C structure.

3.3. Structure above 340° C

At 340° C, the optical texture changes. The network of extinction bands extends throughout the whole specimen, to give a continuous schlieren texture (Fig. 4). Both four-brush (as also seen below 340° C) and two-brush singularities can be identified above the 340° C transition. The latter features indicate the presence of disclinations of strength ± 1/2. Fig. 10 shows an area which contains four such disclinations. The pairs of extinction bands rotate with an angular velocity twice that of the crossed polars, in either the same or opposite sense. The accompanying map shows possible arrangements of the local optical director around the disclinations. The ± 1/2 disclinations are relatively more numerous than those of strength ± 1. This observation is in line with the predictions that ± 1/2 disclinations are energetically more stable than the ± 1 type [17, 18].

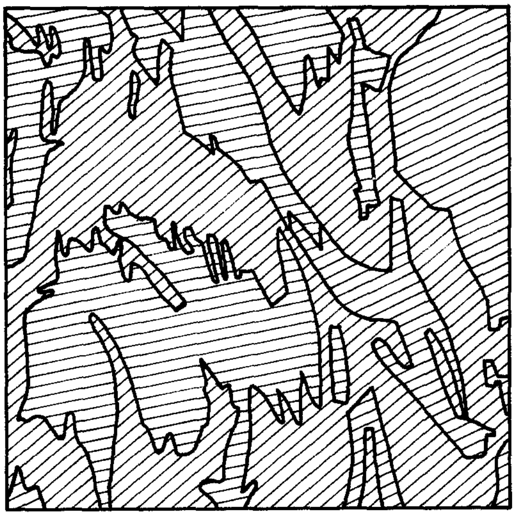


Figure 9 A director map of the region shown in Fig. 8.

The presence of a continuous schlieren texture, and both ± 1/2 and ± 1 disclinations in the microstructure, is typical of low molecular weight nematic liquid crystals [9]. It thus seems that, above 340° C, the mesophase is at least an analogue of the nematic structure.

Another route in the preparation of the various mesophases is to quench from the isotropic phase to form a glass, and then to re-form the equilibrium structures by reheating to the appropriate temperature range. Heating the glass above 200° C but below 340° C leads to the nucleation and growth of the discontinuous schlieren texture typical of small molecule smectic C structures. Heating in the range just above 340° C often leads to the growth of the typical nematic analogue texture, although, occasionally, a strikingly different texture appears. It is shown in Fig. 11. The disclinations of strength

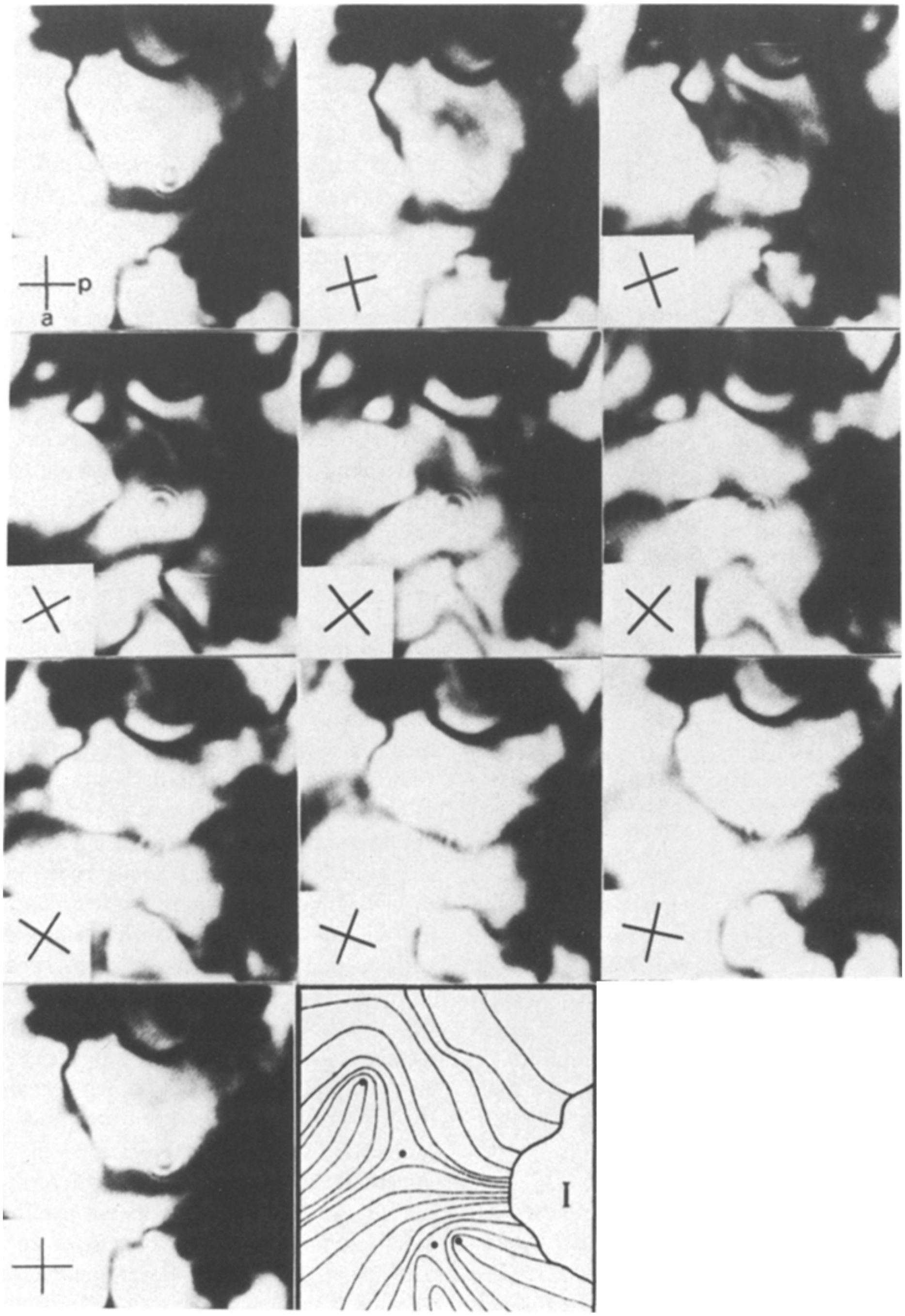


Figure 10 A series of micrographs showing disclinations of strength + 1/2 and — 1/2 at different angular settings of the crossed polars. These disclinations are only seen in equlibrium mesophases above 340° C; they can be readily identified in the director map generated from the micrographs. (X 3500, 10 μm section quenched from 360° C. I = isotropic.)

± 1, as indicated by the confluence of four extinction bands, are arranged along inversion walls, but there is no special distribution of ± 1/2 disclinations. This structure has also been seen in low molecular weight nematics [19].

3.4. Transition texture

Specimens held at the 340° C transition temperature develop a unique structure which often occupies the regions between areas of typical smectic C and nematic textures (Fig. 12). Such

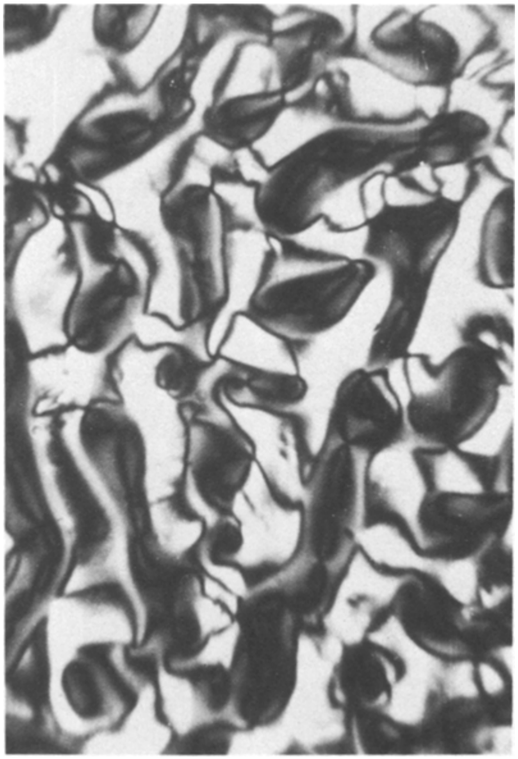


Figure 11 The microstructure resulting from the nucleation and growth of a mesophase at 350° C in previously quenched isotropic material. Disclinations of strength ± 1 and ± 1/2 can be identified. (X 2100, crossed polars, 10 μm section.)

structures, although not seen before in liquid crystal polymers, have been reported for low molecular weight materials [9, 10] held at the smectic–nematic transition. The transient texture is seen during both heating and cooling cycles. It has been referred to as a "myelin" texture, in deference to similar patterns seen in lyotropic extracts from the sheaths of nerve fibres.

4. Discussion

Optical textures observed in the co-polyester can be identified by analogy with textures seen in known low molecular weight liquid crystal modifications. Below 340° C, the microstructure is typical of a small molecule smectic C, while above 340° C, textures characteristic of nematics are seen. At 340° C, an appropriate transition texture is observed. The sequence of apparent phases – smectic at lower temperatures and nematic at higher temperatures – is consistent with that observed in small molecule materials which exhibit both modifications. The close correspondence between the optical microstructures of the polymeric and conventional liquid crystals only fails when one considers the transition to the isotropic phase. Small molecule liquid crystals have a well-defined "clearing point", but, in the co-polyester, the transition occupies a range of temperatures, within which there is an equilibrium two-phase microstructure. Co-existence of mesomorphic and isotropic phases has been seen in other co-polyesters. In particular, the similarity to relatively well-understood behaviour of lyotropic polymers [20] has been pointed out [11], the segregation of flexible links in the thermotropics being likened to the development of solvent-rich phase in the lyotropic.

It should be stressed, however, that the close correspondence between optical textures is not in itself sufficient proof that the local molecular arrangement in polymer liquid crystals is the same as that generally accepted for small molecule materials. Whilst we are able to ascertain possible variations in local optical director orientation, and hence to account for observed textures, we have not identified either of the orthogonal optical directors with the molecular axis itself; in fact, there is some evidence which suggests that this straightforward supposition is open to question. In any case, it is not easy to visualize how co-polyester molecules, with the mesogenic groups incorporated in the main chain, could be arranged to give an apparent smectic C structure, although models for polymers with mesogenic side groups with smectic ordering have been proposed [21].

It is possible that the optical textures seen below 340° C, which are so reminiscent of small molecule smectic C structures, may, in fact, indicate the presence of a biaxial nematic phase [22]. Biaxial nematics have been proposed for low molecular weight materials [23–27] although apparently they have never been seen, possibly because small molecules with the required level of axial asymmetry would crystallize too readily. The proposal that the lower temperature phase may be biaxial nematic, rather than smectic C, is more compatible with nmr [5] and electric field induced flow instability observations [28], both of which have been interpreted as implying a nematic phase at all temperatures where the material is liquid crystal-like.

It is also important to stress the possible effects of the glass slides used to contain the specimens during microscopy. Surface properties are recognized as being important in influencing the type of

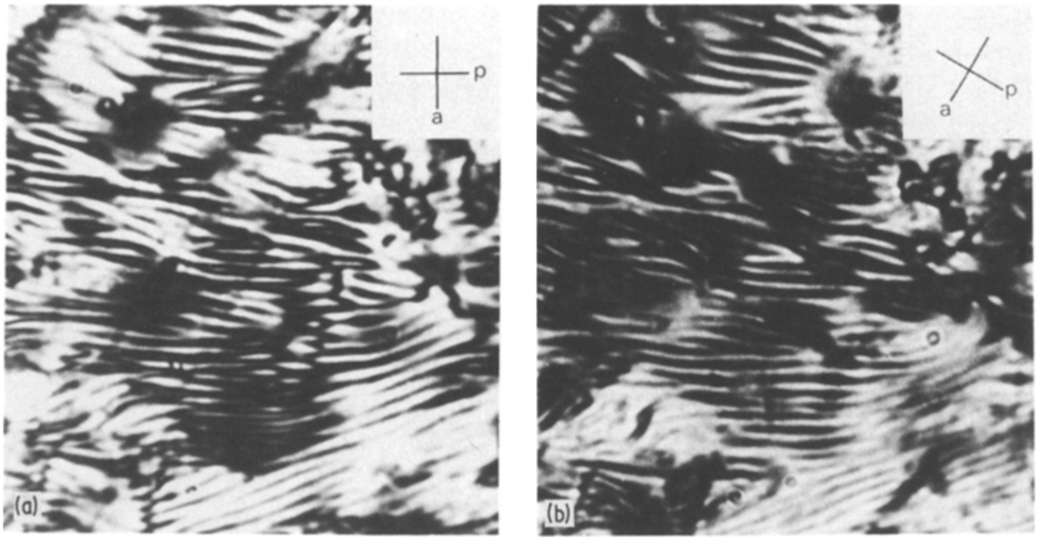


Figure 12 Transient myelin texture associated with the phase transformation ("smectic C"–"nematic") at 340° C. (× 2400, crossed polars rotated by 30° in (b), 10 μm section quenched from 340° C.)

texture obtained with particular small molecule liquid crystal modifications [17, 29]. In order to check if the textures seen in sections heated between glass slides are also typical of bulk material given a similar thermal history, a series of thicker specimens, supported by a glass slide on one side only, was examined. Slices microtomed from the centre of such material show a dependence of mesophase texture on temperature broadly similar to that described above: interrupted schlieren textures occur if the polymer is quenched after heating to below 340° C, while continuous schlieren textures only form above 340° C. Textures consisting of large areas of homogeneous alignment (e.g. Fig. 8) are not seen, however. Also, the unique extinction band configurations associated with disclinations running vertically through the specimen could not be found. It seems then that the role of glass surfaces is two-fold:

(1) the associated surface effects sometimes induce a homogeneous area texture which may not be favoured in the bulk;

(2) disclinations are encouraged to align normal to the surfaces, and the resultant distribution of extinction bands allows these disclinations to be characterized easily in terms of strength and sign.

The DSC results raise several questions. While certain peaks can be linked with optically observed transitions, there is little indication as to what the associated structural changes are, although each endotherm probably represents some increase in level of molecular freedom. The difficulty in visualizing the structural reorganization associated with the 340° C transition has already been mentioned. (Regarding this peak, too, there is analogy with small molecule liquid crystals: they show a DSC endotherm at a smectic C–nematic transition.) The 190° C peak, corresponding to optically observed onset of microstructural mobility, presumably involves "melting out" of some form of stabilizing order, as suggested for other co-polyesters [11], but its structural implications are uncertain. The 250° C endotherm has not been correlated with any optically observable transition. However, it may result from loss of correlation between segregated PABA segments, since, firstly the co-polyester contains more PABA residues than PET residues, and secondly, if one was dealing with correlation between PET residues, the endotherm would be expected to occur at a temperature lower than the melting point of PET homopolymer [30], which is 245° C [3].

The significance of the 70° C glass-like transition also begs careful assessment, since, at room temperature, as-received polymer is manifestly plastic in nature.

5. Conclusions

(1) The co-polyester shows liquid crystal-like optical textures between room temperature and 420° C. Above 350° C these textures co-exist with an optically isotropic phase which increases in volume fraction up to 420° C.

(2) Below 340° C, the optical textures are in-

distinguishable from those shown by conventional (small molecule) liquid crystals in the smectic C modification. They are characterized by the presence of disclinations of strength ± 1, but absence of any of strength ± 1/2.

(3) Above 340° C, the birefringent phase shows an optical texture with disclinations of strength ± 1 and ± 1/2, as is typical of conventional liquid crystals in the nematic modification.

(4) The transition from smectic C to nematic type textures is marked by the appearance of regions of "myelin" texture, previously referenced only for small molecule materials.

(5) Although the microstructure is mobile (as is the material) above 190° C, all optical textures can be preserved by quenching to room temperature.

(6) It is possible to quench the isotropic phase in thin sections only, when it forms a particularly brittle glass.

(7) There is evidence that the optical texture is modified in detail by contact with glass microscope slides, in that disclinations tend to be normal to the surfaces, and associated patterns of extinction bands are more readily apparent. Furthermore, the occasional appearance of homogeneous area textures in the temperature range below 340° C also suggests a specific polymer–glass interaction.

(8) DSC traces show endothermic peaks at 190° C, corresponding to the onset of mobility; at 340° C, at the transition between smectic C and nematic type textures; and around 400° C, associated with the increasing fraction of isotropic phase. A further endotherm at 250° C could not be correlated with any observable change in optical texture. A transition typical of a glass transition is apparent at 70° C.

Acknowledgements

The authors with to thank Dr M. R. Mackley and Mr G. R. Mitchell for stimulating discussions and encouragement, Professor R. W. K. Honeycombe for the provision of laboratory facilities and the Science and Engineering Research Council for a studentship (CV).

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Received 14 December 1981
and accepted 4 February 1982