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The existence of a mesophase in poly(ethylene naphthalate)

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Poly(ethylene naphthalate) (PEN) is a polymer with potentially useful industrial properties. During a study of the morphology and properties of drawn PEN fibres it became apparent that an ordered structure existed in some specimens that was not the well-known crystalline form. This structure is considered to be a mesophase in which substantial lengths of individual chains are fully extended but do not pack laterally in crystalline register. The existence of this intermediate phase is strongly dependent upon processing conditions and could have implications for the properties of commercially produced fibres, since it appears to be stable and not easily converted to the crystalline form at elevated temperatures. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Poly(ethylene naphthalate) (PEN) is a polyester whose preparation was first reported[1] as long ago as 1948. There has, however, been increasing interest in its commercial exploitation since recent indications[2,3] that the dicarboxylic acid monomer may soon become available in large-scale quantities. This short communication has been submitted to report the observation of a mesophase structure that has been observed under certain processing conditions. The research forms part of a more substantial research project at Leeds University on the structure and properties of oriented PEN fibres.

Experimental

The starting point for the present research was a series of melt-spun PEN fibres at two levels of number-average molecular weight, 21 850 and 20 110, respectively. In each case a range of wind-up speeds from 500 to 3000 m min^{-1} was adopted. Each type of spun fibre was then drawn at 120°C to a range of draw ratios. For the purposes of this communication, wide-angle X-ray diffraction patterns were recorded photographically for each spun sample and each drawn sample.

Results and discussion

Drawing produced the expected result of increasing both orientation and order in all samples, as seen from inspection of the X-ray diffraction patterns. In some cases the order was clearly crystalline in nature, but in others, e.g. the lowest molecular weight sample spun at the lowest wind-up speed, the diffraction pattern after drawing differed from that reported for conventional semi-crystalline PEN as reported elsewhere[4]. The key feature of these unusual diffraction patterns, an example of which is shown in *Figure 1*, is a number of relatively sharp azimuthal reflections consisting of short straight lines normal to the draw direction. A three-dimensional crystalline structure in a relatively poorly oriented sample would show each reflection as a circular arc, but the fact that the reflections are straight lines rather than arcs indicates that the ordering giving rise to the reflections is essentially one-dimensional. For comparison, a similar X-ray photograph of a sample that has undergone a two-stage drawing process is shown in *Figure 2*. Sharp spots show a predominantly conventional crystalline structure but still with a hint of the horizontal lines on the azimuth, suggesting that the mesophase coexists with the crystalline component. This pattern is consistent with the α-form described by Mencik[5].

Thus in a number of different samples we have seen that a fraction of the material of each sample has a morphology which is neither fully crystalline nor amorphous, yet still exhibits spatial order. We refer to this as a mesophase that normally coexists with the conventionally ordered material and, of course, the disordered material to a greater or lesser degree.

A diffractometer scan of the sample whose diffraction pattern was given in *Figure 1* is shown in *Figure 3*. A series of clear peaks is seen which is interpreted as several orders of a reflection corresponding to the chain repeat length. The order is noted against each peak. Analysis of the diffractogram gives a value for the repeat length of 13.0 ± 0.1 Å. The odd numbered orders are considerably more intense than the even orders. The reflection near 28° is not thought to arise from the mesophase since, in other samples which do not show the photographic characteristics of a mesophase, it appears strongly on its own.

In summary, low wind-up speed samples of both molecular weights showed little, if any, crystalline structure and little or no orientation before drawing, very much as one might expect. At higher wind-up speeds the lower molecular weight samples showed evidence of

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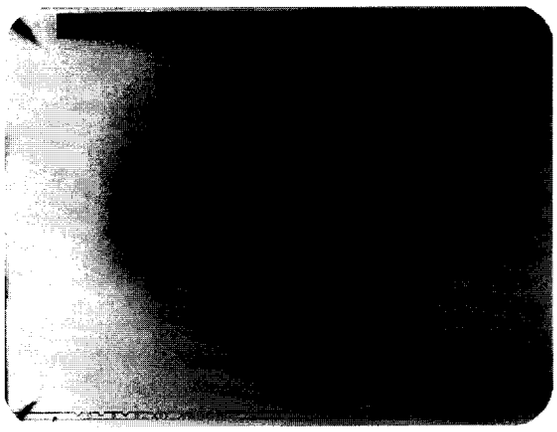

Figure 1 Diffraction pattern of PEN sample showing mesophase structure

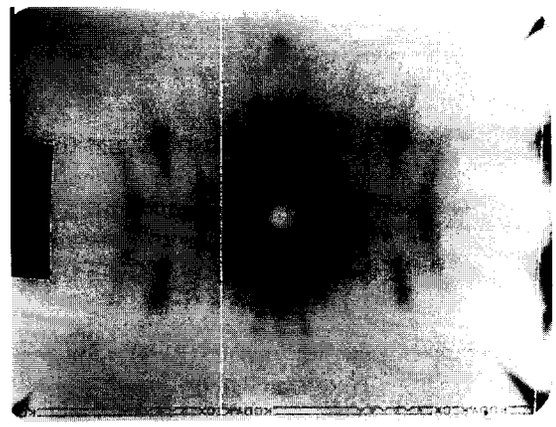

Figure 2 Diffraction pattern of highly crystalline, oriented PEN sample

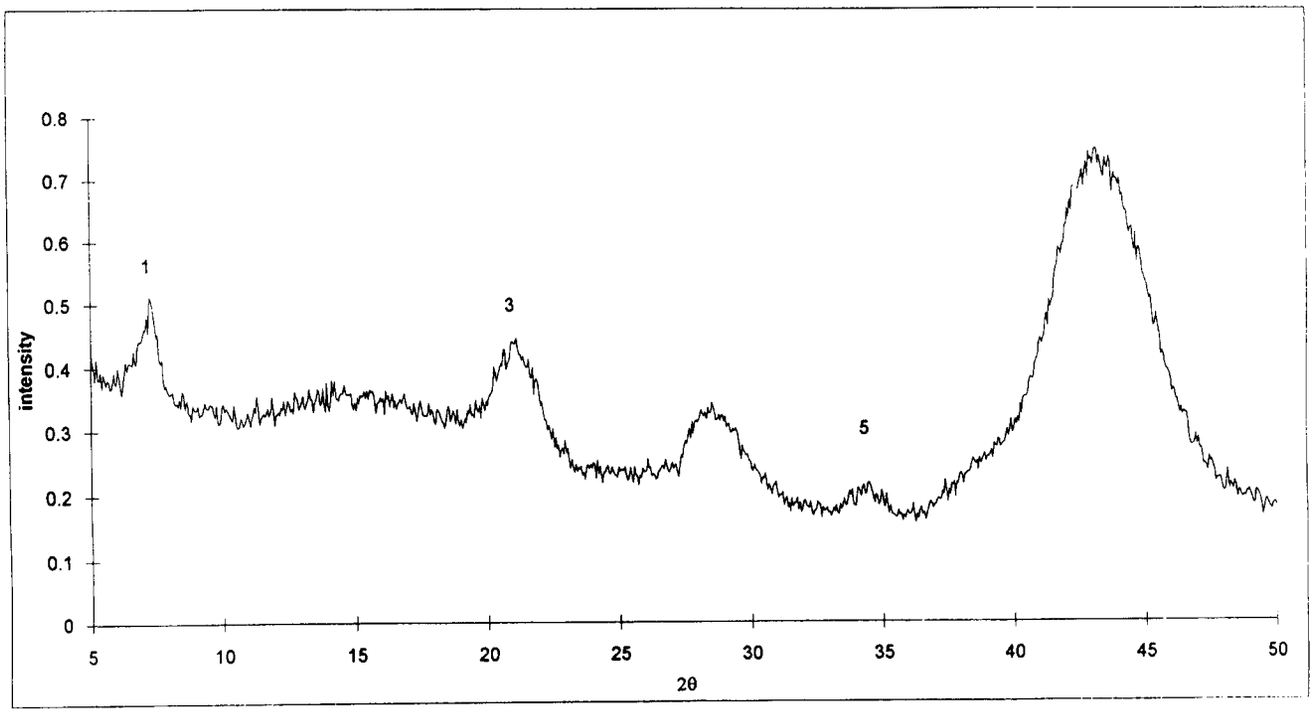

Figure 3 Meridional diffractometer scan of low-molecular-weight sample showing mesophase structure: intensity *versus* Bragg angle 2θ

an oriented crystalline component arising, presumably, from crystallization occurring due to higher stresses in the thread line. The higher molecular weight samples showed a smaller degree of order, but still showed some evidence of the mesophase when spun at the highest wind-up speeds.

A surprising feature is the stability of the mesophase. The sample used to produce *Figure 1* was annealed at 180°C for 30 min and, although there was evidence of crystalline material appearing, the mesophase reflections hardly changed in intensity. This has implications for the mechanical properties of PEN fibres, details of which will be presented in a subsequent paper.

Acknowledgements

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