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Crystallization of random aromatic copolyesters containing flexible spacer chains and side-groups

Z. He and G. R. Mitchell*
Polymer Science Centre, J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 2AF, UK
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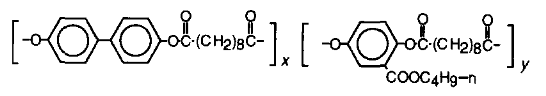
The crystallization behaviour of a series of random copolymers of varying chemical composition is reported. For polymers containing a high proportion of alternating rigid aromatic units and flexible spacers, conventional liquid crystalline and crystalline phase behaviour is observed. The introduction of a substantial fraction of a second shorter rigid unit containing side-chains leads to a broad endotherm in the d.s.c. scan covering some 150°C. Subsequent isothermal crystallization at any point within the broad endotherm leads to the generation of sharp endotherms at temperatures just above the recrystallization temperature. We attribute this behaviour to the crystallization of clusters of molecules containing similar random sequences. Such crystals are non-periodic along the chain direction.

(Keywords: crystallization; random copolymers; d.s.c.)

Introduction

The crystallization of apparently uncrystallizable random copolymers[1–3] or other random systems, such as atactic homopolymers[4], has attracted considerable attention over the last few years. Much of this has been stimulated by the synthesis of liquid crystal forming random copolyesters, in which the random copolymer nature was designed to reduce the high crystal melting point of such wholly aromatic polyester systems[5]. Such wholly aromatic polyesters depend, for their improved room temperature properties, on both the high level of anisotropy induced through the formation at elevated temperatures of liquid crystal phases, and on the development of a strengthening network of crystallites. The mechanism for the formation of these crystallites has been the subject of considerable study[1–3]. In this contribution we report the observations made of a particular random copolymer prepared as part of a larger programme concerned with the development of processable high performance materials[6]. This copolymer differs from those studied previously in that it does not form a liquid crystal phase and that it is built up from a rather flexible polymer chain. We show that the development of a crystalline structure at room temperature may occur in such a material through the crystallization of molecules containing similar but random sequences of the two chemical units, in a similar manner to the non-periodic layer crystallites proposed by Windle *et al.*[1]. In this case the considerable variety in chemical composition leads to a substantial variation in the melting points of the copolymers.

Experimental



[I] [II]

Materials. A series of random copolyesters containing units I and II were prepared through an interfacial copolymerization of the biphenyl-based monomer, I, and II formed from 1-butyl-2,5-dihydroxy benzoate and sebacoyl chloride. The synthesis and characterization of these materials is described more fully elsewhere[6]. The composition of each of the copolymers is shown in *Table 1*. End-group analysis using i.r. spectroscopy shows the average degree of polymerization of these materials to be low, typically around 5–10. X-ray scattering studies of the diffraction peaks arising from intramolecular correlations[7] show these materials to be random copolymers[6].

Methods. The phase behaviour of these materials was investigated using a combination of differential scanning calorimetry (d.s.c.) and optical microscopy techniques. The d.s.c. measurements were performed using a Perkin–Elmer DSC2-C with a scanning rate of 20°C min^{-1}. Optical microscopy was performed using a Zeiss Jenalab-Pol microscope together with a Linkam TH600 hot-stage.

Results and discussion

The d.s.c. scans for each of the copolymers prepared are shown in *Figure 1*. The scans correspond to samples that had been previously cooled from the melt (~300°C) at 20°C min^{-1}. It can be seen that there is considerable variation in the phase behaviour, both in terms of the number of phase transitions and their breadth. The homopolymer PB10CB0, formed from the biphenyl-based unit I, and the PB9CB1 copolymer both exhibit a liquid crystal phase range above 210°C. Homopolymers of the biphenyl-based unit I have been the subject of a number of studies[8–12]. It is generally agreed that smectic liquid crystal structures are formed in this temperature

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* To whom correspondence should be addressed

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Table 1 Composition of copolymers

Polymer code	Feedstock composition (y)	Measured composition^a (y)
PB10CB0	0.00	0.00
PB9CB1	0.10	0.23
PB5CB5	0.50	0.48
PB2CB8	0.80	0.77
PB0CB10	1.00	1.00

^{a} Measured using ^{1}H n.m.r. and i.r. spectroscopy
y is the fraction of unit II

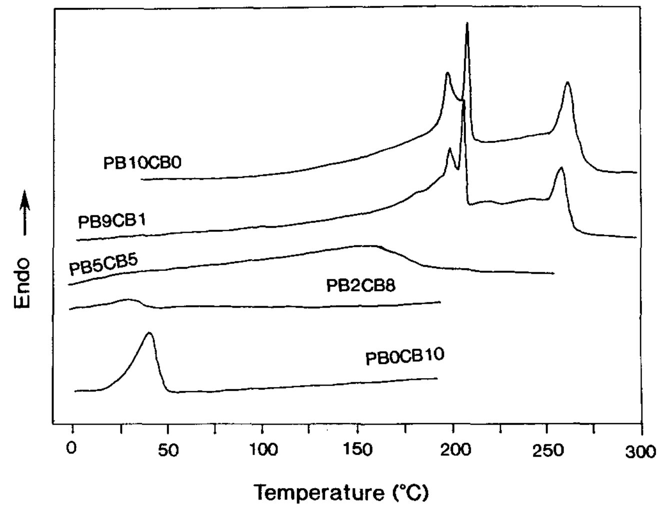

Figure 1 D.s.c. scans for each of the copolymers (see *Table 1*) for samples that had been cooled at 20°C min^{-1} from ~300°C

range. At lower temperatures the homopolymer forms a semicrystalline structure. The other copolymers studied here do not exhibit liquid crystal phases; clearly the enhanced flexibility introduced by both the hydroquinone unit (also a shorter 'rigid' unit) and the accompanying side-chains has been sufficient to destabilize the liquid crystal phase. The homopolymer PB0CB10, prepared from the side-chain carrying hydroquinone unit, forms a semicrystalline phase at room temperature, which melts at the relatively low temperature of ~40°C. A similar but modified behaviour is exhibited by the copolymer PB2CB8, which contains predominantly the hydroquinone unit.

The focus of this paper is the phase behaviour of the copolymer PB5CB5, which exhibits a broad endothermic transition from 60 to 200°C in the d.s.c. scan, as shown in *Figure 1*. At room temperature the copolymer sample is semicrystalline. Electron microscopy of etched samples reveals characteristic semicrystalline spherulitic or parallel lamellar-like morphologies, according to the crystallization conditions. Such structures are similar to those displayed by poly(ether ether ketone) (PEEK)[13] but on a scale about three times that of PEEK. It is noticeable that this broad transition starts just above the sharp melting endotherm for the homopolymer PB0CB10 and terminates just below the transition of the homopolymer PB10CB0 from the crystalline phase to the liquid crystalline phase. Isothermal crystallization at any temperature within the broad range of the endotherm results, upon cooling and subsequent reheating in the d.s.c., in a sharp endotherm at a temperature just above the isothermal crystallization temperature, as shown in *Figure 2*. It should be noted that there is a dip in the endotherm trace just before this sharp feature, but in general the overall shape of the broad transition is retained. In other words the fraction of material that would have melted at temperatures lower than the isothermal crystallization temperature has recrystallized in substantially the same form as the initial sample.

Figure 3 shows a plot of the temperature corresponding to the sharp endotherm against the isothermal crystallization temperature. It can be seen that there is a constant offset (10–20°C) of the melting point of the recrystallized component of the copolymer from the isothermal crystallization temperature. The relative independence of the isothermal recrystallization process from the broad range of the transition is shown more dramatically in *Figure 4*, which shows a d.s.c. scan for a sample that had been previously subjected to a step-isothermal recrystallization. In this procedure the sample was held at a sequence of temperatures for the fixed periods of time shown. It may be noted that there is some variation in the shape of the 'sharp' endotherms produced by the isothermal recrystallization. Analysis of the total endotherm shows that the enthalpy change associated with this broad transition was approximately constant, irrespective of the nature and detail of the isothermal recrystallization procedures, and was 70% of the value shown for the homopolymer of I, suggesting broadly similar values of crystallinity.

There are three particular features that relate to the observed phase behaviour of the copolymer PB5CB5.

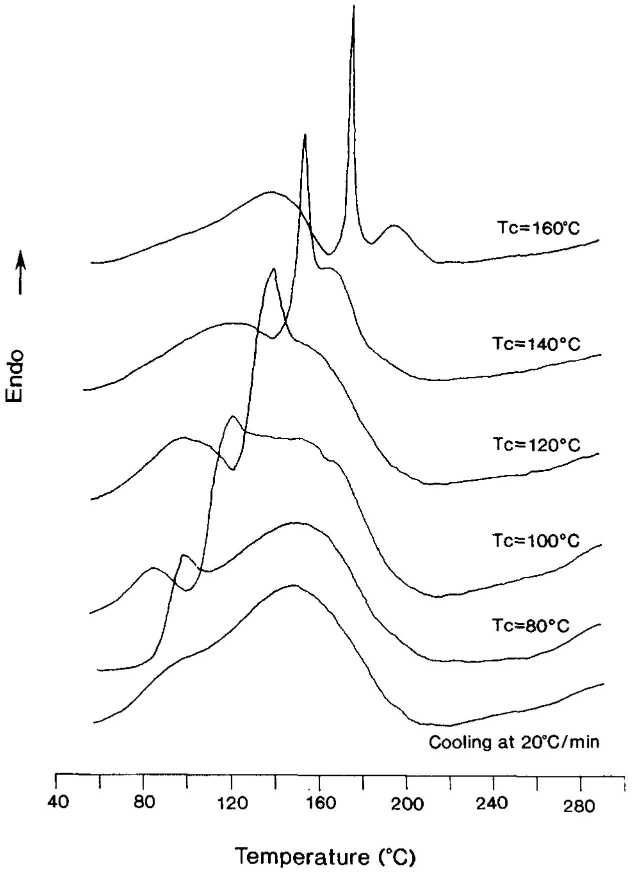

Figure 2 D.s.c. scans for the copolymer PB5CB5 (see *Table 1*) previously cooled at 20°C min^{-1} from ~300°C and held at the indicated temperature for 12 h

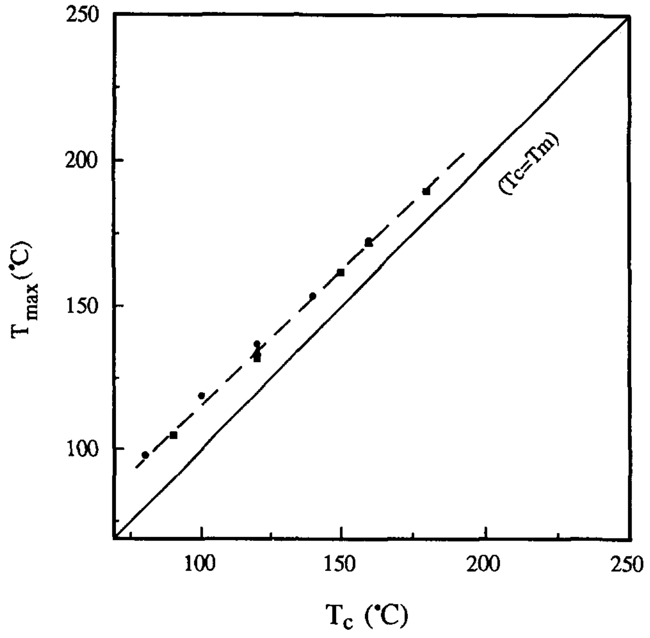

Figure 3 Plot of the temperature corresponding to the sharp maxima observed in the d.s.c. scans following isothermal crystallization against the isothermal crystallization temperature

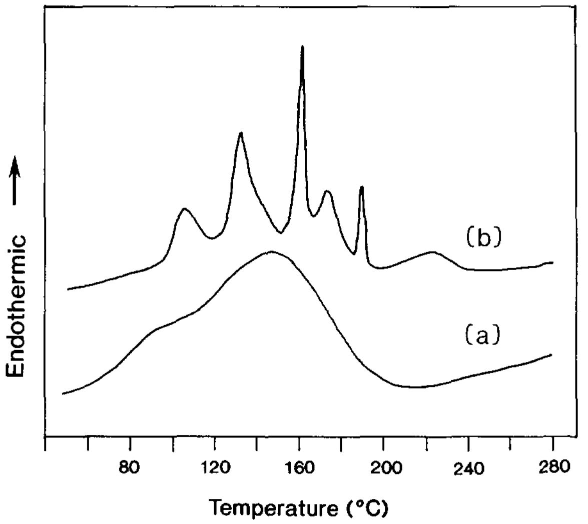

Figure 4 Comparison of the d.s.c. scans for samples of PB5CB5 which had been previously (a) cooled from ~300°C at 20°C min^{-1} and (b) subjected to a step isothermal crystallization at 180, 150, 120 and 90°C for 12 h at each temperature

The first is that such a random copolymer crystallizes at all. The second feature is the broadness of the endotherm, which covers the temperature range between the transitions displayed by the homopolymers. The third feature is the subsequent unusual isothermal recrystallization behaviour. Crystallization in a number of random systems involving either tacticity (for example poly(vinyl chloride) (PVC)[4]) or chemical composition (for example liquid crystal forming random copolyesters based on benzoic and naphthoic acids[1–3]) has been observed. The nature of crystallization in PVC remains the subject of some debate[4], while Windle *et al.*[1] have introduced the concept of non-periodic layer crystallites to explain the behaviour of a number of wholly aromatic copolyesters, which are of particular interest because they also exhibit liquid crystal phases at elevated temperatures. Non-periodic crystallites are those crystals that are formed by the segregation of identical or near-identical random copolymer sequences of the chemical units which make up the copolymer. It is envisaged that in the highly oriented structure the chains can shuffle longitudinally to 'match' these sequences. Although such chains are positioned laterally on a lattice, there is no periodicity in the chain direction. In essence, the unit cell in the chain direction is that of the crystal thickness. There is some electron microscopy evidence to support the formation of such entities[14,15], the number and perfection of which may be enhanced by isothermal crystallization procedures.

The second feature of the crystallization behaviour of the copolymer PB5CB5 is the broadness of the endotherm, which extends over ~140°C. The fact that this endotherm spans the temperature range between the melting points of the homopolymers suggests directly that it is due to compositional variation. It must follow, therefore, that the crystals which form and exhibit an intermediate melting point have an intermediate composition, that is the crystals are formed by molecules which contain similar but random sequences of the two monomer units. For a 50/50 copolymer system, the average run length of a sequence that includes only one of the chemical units is three. In a polymer system such as PB5CB5, with a relatively low degree of polymerization, although the overall composition is equivalent to a polymer of infinite molecular weight, individual molecules will exhibit defined identifiable sequences of the two chemical units. For example the sequences –BABAB– and –AABBB– have the same chemical composition but clearly will have different interactions. In other words, the system is made up of a broad range of molecular species with a changing sequence distribution. There is a finite chance of molecules with a degree of polymerization of 5 exhibiting an –AAAAA– or –BBBBB– sequence. It is the variation in the properties of partially segregated clusters of such random chain sequences that leads to the wide range of melting points observed. The end-points of the phase transition are the homopolymer structures. The fact that the melting points of these crystals appear to vary more or less linearly with composition, as may be judged by the span of the endotherm, shows that the melting points of such non-periodic crystals are not directly influenced by the 'random' distribution of the chemical units.

The third feature of the crystallization behaviour of the copolymer PB5CB5 is the relationship between the sharp peaks in the d.s.c. scans and the relevant isothermal recrystallization temperatures. A similar relationship has been found from the secondary crystallization of other polymers[13,16–18]. Secondary recrystallization experiments abound in polymer science and date from early experiments by Wunderlich *et al.*, which were concerned with the further crystallization of the amorphous component of a semicrystalline polymer[16]. More recently, multiple transitions and secondary crystallization have been subjects of intense interest in relation to PEEK[13,17,18], in which one school of thought attributes the two transitions to different morphologies arising as a consequence of infilling after the initial dominant lamella growth[13]. However, in contrast to the behaviour observed in this work with PB5CB5, these secondary peaks are generally small compared with the main transition. Another example of multiple transitions is that of branched polyethylene in which, in general, the branched segments are excluded from the crystals on the basis of their chemical composition[19]. This leads to crystals of differing thicknesses and therefore different melting points, which are defined by the degree of branching. This multiple-transition phenomenon is somewhat similar to that observed for PB5CB5, although in this work the breadth of the endotherm envelope is an order of magnitude larger than that shown by branched polyethylene.

In this work isothermal crystallization serves to perfect the crystals that melt out at the selected crystallization temperature, by enhancing the level of segregation and increasing the size and degree of perfection of the crystals. The sharpness of the features in the d.s.c. scans of the isothermally crystallized samples is a measure of these two possibilities, although doubtless there must be some further spread resulting from distributions in molecular weight. The fact that the crystals with melting points lower than the isothermal crystallization temperature reform on cooling, as may be seen from the shape of the endotherm, is evidence that the variation in these crystals, as observed through the melting point, has a chemical composition origin rather than physical or morphological basis. Thus in the particular case of the 50/50 copolymer, PB5CB5, crystallization takes place through the formation of crystals made of clusters of similar but random sequences of the two monomer units. These crystals are similar in basis to the oligomer series prepared by Chan *et al.*[20] as analogues to the random copolymers of benzoic and naphthoic acids. However, in this case the range of copolymer sequences is the natural product of the random copolymerization process. Here, it is anticipated that largely whole molecules are matched rather than the restricted lengths of sequences in the wholly aromatic copolymers studied by Windle *et al.*[1], in which the degree of polymerization is substantially higher. A consequence of the differences between the biphenyl-based unit I and the side-chain bearing hydroquinone unit II, is that the substantial compositional variations in the different crystals lead to marked variations in their melting points. These observations highlight the class of polymers, perhaps much broader than previous realized, which are capable of developing significant levels of crystallinity.

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