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Correlation of observations made by DSC and hot-stage optical microscopy of the thermal properties of a monotropic liquid-crystal polyester

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Abstract

The polyester formed by condensation of 4,4′-bis(6-hydroxyhexoxy)biphenyl (BHHBP) and isophthalic acid has been reported to show many interesting and intriguing thermal properties. By optical microscopy, we established that the polymer shows monotropic liquid-crystalline behaviour. Thus, on heating, no mesophases are formed and the crystal melts directly to the isotropic state; on cooling, however, the material transforms from the isotropic melt to a nematic and smectic A mesophase before crystallizing. However, the DSC *heating* scan of this polymer was very complex, showing an exotherm and two endotherms; further, unlike the phenomenon of cold crystallization, the exotherm occurred *between* the two endotherms. If there is only a single phase transition (crystal–isotropic) on heating, then the multiple peaks need to be explained.

In this work, we have shown that the multiple peaks in the heating scan are solely related to the thermal history of the sample. The nascent polymer and quench-cooled material showed multiple peaks during heating, whereas slowly crystallized polymer showed a single melting endotherm. By quench cooling from the isotropic melt, it was not possible to obtain the material in an amorphous form, because this polyester had a propensity for fast ordering.

In the previous work, on *cooling*, we only found two instead of three DSC peaks. Here, we have attempted to see if three peaks (corresponding to I–N, N–S_A and S_A–K) can be resolved by going to very slow cooling rates (0.1°C min^{-1}). It was found that even at such low cooling rates, I–N and the N–S_A transitions could not be separated into distinct peaks. This is in accord with optical microscope observations which indicated that the transformation to the smectic phase from the nematic was never complete and was overtaken eventually by crystallization. This kind of incomplete phase transformation appears to be a feature of this monotropic liquid-crystalline polymer.

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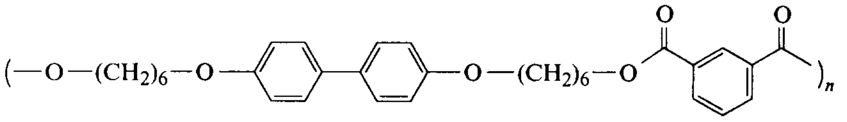
1. Introduction

The polyester formed by condensation of isophthalic acid and 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP) has interesting thermal properties. The polyester is shown below (Scheme 1).

In the earliest reports on various condensation polymers formed with the diol BHHBP [1, 2] it was stated that the above polyester formed a smectic A liquid-crystal phase. Subsequently, a more detailed investigation [3] showed that this polyester formed not only a smectic but also a nematic liquid-crystal phase. Moreover, it was shown that the mesophases were monotropic in character and were observed only on cooling and not on heating [3]. The phase sequence on cooling was proposed to be $I \rightarrow N \rightarrow S_A \rightarrow K$ and $K \rightarrow I$ on heating (I = isotropic, N = nematic, S_A = smectic A, K = crystal). In another investigation, it was demonstrated that deformation of this polyester in the smectic melt state led to an extraordinary chain orientation perpendicular to the flow direction or the fibre axis [4].

These phases of the polyester were established principally by hot-stage microscopy and differential scanning calorimetry (DSC). The DSC results could on the whole be interpreted according to the phase sequences shown above, but there were still certain intriguing aspects which had not been resolved properly. For example, the heating scans of the polyester were complex, showing multiple endothermic peaks, even though it was argued that there is only one phase transition ($K \rightarrow I$). At heating rates of 5°C min^{-1} or lower, it was found that there were two endothermic peaks with an exothermic peak lying between them [2]. This is reproduced in Fig. 1a. Although an exothermic peak before and endothermic peak is quite common on heating semi-crystalline polymers, owing to "cold crystallization", an exothermic peak between two endothermic peaks was more unusual and difficult to explain. We postulated that this may be a result of partial melting, followed by recrystallization to a more perfect form, followed by remelting of the perfected form at a higher temperature. Preliminary annealing experiments were cited as supporting this proposal but sufficient experimentation had not been conducted at the time to be definitive about the nature of the multiple peaks observed in the heating scan [2]. Further, on cooling, two exothermic peaks were found; these started to overlap as the cooling rate was lowered. However, as the phase sequence cited above shows, on cooling there are three transitions and hence



Scheme 1. The polymer formed by condensation of isophthalic acid and 4,4'-bis(6-hydroxyhexoxy) biphenyl.

one might have expected three exothermic peaks. Because of the closeness of the transitions, we assumed that the first exothermic peak at 105°C in the DSC represented, in fact, the formation of both the mesophases, whereas the second exothermic peak at ~ 70°C was a result of crystallization (see Fig. 1a).

In this work, we have concentrated on the DSC results and tried to resolve the two complexities mentioned above. Firstly, in order to establish whether the multiple peaks in the heating scan arise purely as a result of thermal history (rather than multiple phase transitions), the heating scans of the nascent polymer were compared with quench-cooled material and also with polymer that had been slowly or isothermally crystallized. Secondly, on cooling, an attempt has been made to see if three exothermic transitions could be resolved by using lower cooling rates than those tried previously. Lower cooling rates should enhance peak resolution, albeit at the expense of sensitivity.

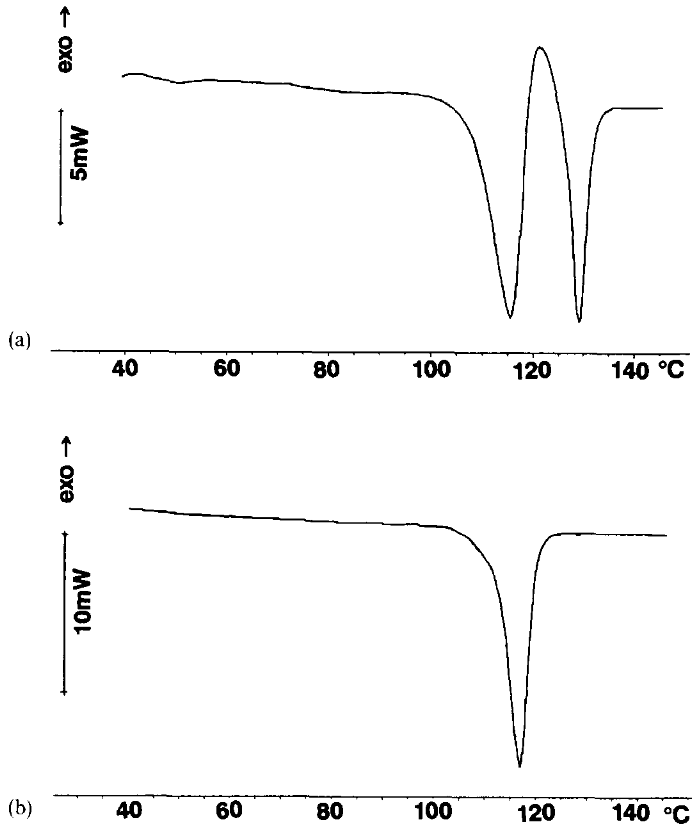


Fig. 1. DSC heating scans of polymers with different thermal histories: (a) nascent reactor polymer (heated at 5°C min^{-1}); (b) heating scan at 5°C min^{-1} of slowly crystallized polymer (formed by melting the nascent polymer and cooling from 150 to 30°C at −5°C min^{-1}); (c) heating scan at 5°C min^{-1} of polymer isothermally crystallized at 100°C for 5 h; (d) heating scan at 5°C min^{-1} or polymer isothermally crystallized at 105°C for 5 h; (e) heating scan at 5°C min^{-1} of polymer isothermally crystallized at 110°C for 5 h; (f) quench-cooled polymer heated at 5°C min^{-1}.

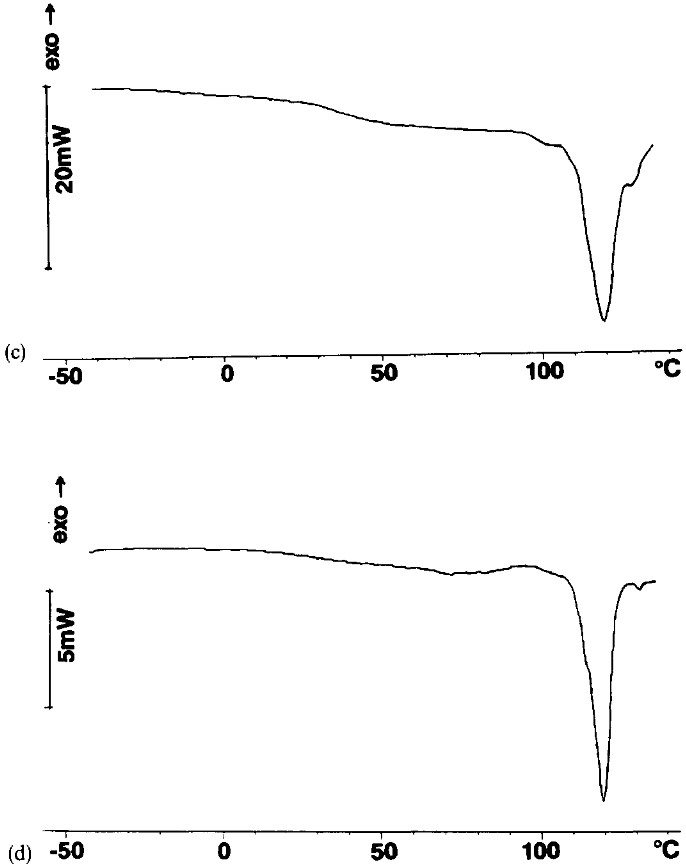


Fig. 1. (*Continued*).

Hot-stage microscopy experiments were conducted in parallel using the same conditions (crystallization temperatures and times, heating and/or cooling rates) to provide a visual backup in the interpretation.

2. Experimental

2.1. Synthesis and characterization of monomer and polymer

2.1.1. 4,4′-bis(6-Hydroxyhexoxy)biphenyl (BHHBP)

The reaction scheme for the synthesis of the monomer BHHBP is shown below (Scheme 2). The details of preparation of the monomer may be found in the previous work [2].

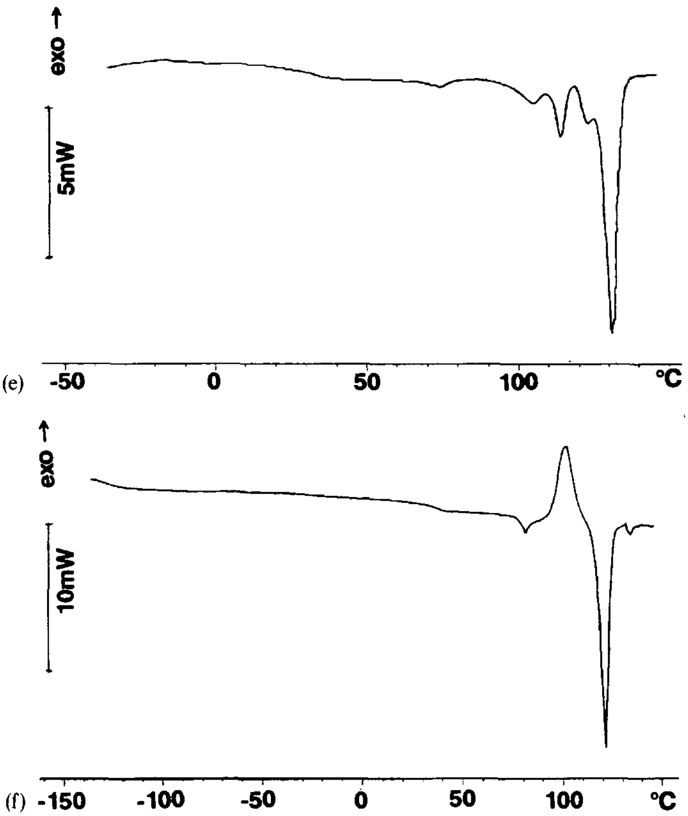
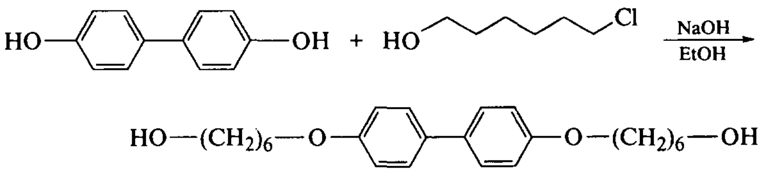


Fig. 1. (*Continued*).

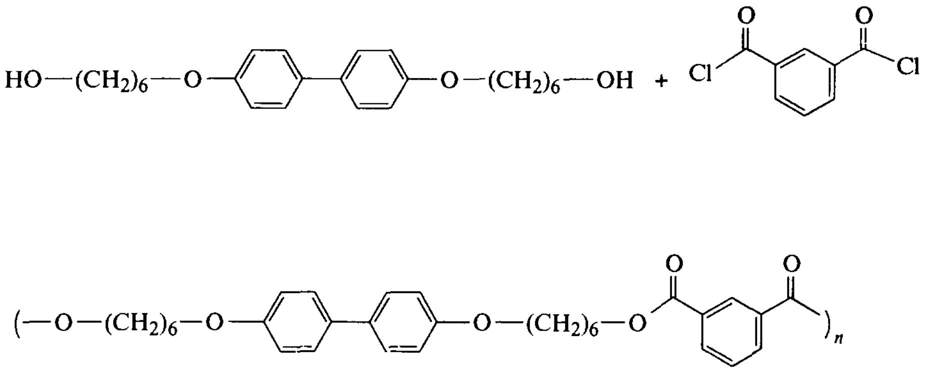


BHHBP smectic monomer

Scheme 2. The synthesis of BHHBP.

2.1.2. *Polyester of BHHBP and IA*

The same polyester sample that was employed in the previous investigations [2–4] was used in this work. The reaction scheme for the synthesis of the polyester of BHHBP and isophthalic acid (IA) is shown below (Scheme 3). The details of preparation of the polyester are given in a previous paper [2]. The polymer was purified by repeated dissolution in dichloromethane followed by reprecipitation in methanol. The purified



Scheme 3. Reaction of BHHBP and isophthalic acid.

polymer (referred to as the nascent polymer in the paper) showed perfect extinction at the clearing point under the polarizing microscope whereas the unpurified polymer showed some birefringent specks in the isotropic melt. Therefore purification of the polymer is important.

2.2. *Differential scanning calorimetry (DSC)*

Calorimetric measurements were performed using a Mettler DSC 30 and TC 11 controller. This is a heat-flux type of DSC. Data storage and analysis were performed using an IBM microcomputer running Graph Ware TA-72 under QNX. The DSC cell was calibrated for temperature and enthalpy response according to the melting points and heats of fusion of pure indium. The samples were encapsulated in hermetically sealed pans and the scans were conducted under a static air atmosphere.

In order to find if the heating scans are dependent on the thermal history of the polymer, the same sample was used for all the experiments. Degradation was established not to be a problem providing the sample was not heated above about 150°C, as all features could be reproduced for a particular thermal history with the same sample. For both heating and cooling experiments, a 20 mg sample and a 40 μL pan were used.

2.2.1. *Heating scan of nascent and slowly crystallized polymer*

The heating scan of the nascent polymer was recorded.

Heat from 30°C → 150°C at 5°C min^{-1} (heating scan of nascent polymer, Fig. 1a).

Cool from 150°C → 30°C at − 5°C min^{-1} (to form slowly-crystallized polymer).

Heat from 30°C → 150°C at 5°C min^{-1} (heating scan of slowly-crystallized polymer, Fig. 1b).

2.2.2. *Heating scans of isothermally crystallized polymer*

In order to understand the origin of the multiple peaks found in the heating scan shown in Fig. 1a, an isothermally crystallized sample was produced. Four isothermal crystallization temperatures were tried (100°C, 105°C, 110°C and 115°C). The procedure used for isothermal crystallization was as follows:

Heat 30°C → 150°C at 5°C min^{-1} (destroy thermal history of nascent polymer).

Cool from 150°C → 100°C (or 105°C, 110°C, 115°C) at −5°C min^{-1}.

Hold isothermal at 100°C (or 105°C, 110°C, 115°C) for 5h (isothermal crystallization).

Quench to −50°C.

Reheat −50°C → 150°C at 5°C min^{-1} (heating scan of isothermally crystallized polymer, Fig. 1c–1e).

2.2.3. *Heating scans of quench-cooled polymer*

The quench-cooled sample was produced in order to measure the glass transition and compare its heating scan with that of the nascent polymer.

Heat from −100°C → 150°C at 5°C min^{-1}.

Hold isothermal at 150°C for 1 min.

Remove pan from DSC cell and immerse in liquid nitrogen (to produce quench-cooled sample).

Set DSC cell at −100°C and allow 10 min to equilibrate.

Reinsert pan in DSC cell and hold isothermal at −100°C for 10 min.

Heat from −100°C → 150°C at 5°C min^{-1} (heating scan of quench-cooled sample, Fig. 1f).

2.2.4. *Cooling scans and effect of cooling rate*

In order to check whether three exothermic transitions could be resolved on cooling, the isotropic melt was cooled at the lowest possible cooling rates attainable. DSC scans were thus performed at cooling rates of −5, −0.7, −0.3, and −0.1°C min^{-1}.

The following sequence was used for the first cooling rate:

Cool from 150°C → 30°C at −5°C min^{-1}.

In the above sequence, the sample was heated very rapidly to the starting temperature of 150°C (for isotropization).

For the very slow cooling scans (−0.7, −0.3 and −0.1°C min^{-1}), the following procedure was used in order to reduce the length of the experiment. Again, the sample was heated very rapidly to the starting temperature of 150°C for isotropization, and was cooled in two stages as shown below.

Cool from 150°C → 120°C at −5°C min^{-1} (there are no transitions in this interval and a faster rate cuts time).

Cool from 120°C → 70°C at −0.7°C min^{-1} (or −0.3, −0.1°C min^{-1}).

2.3. *Optical microscopy*

Optical observations were made with a Zeiss Axioplan polarizing microscope equipped with long working distance objectives. The samples were heated and cooled with a Linkam hot-stage and associated temperature controller. Very small powdered fragments of the polymer were placed between two glass cover slips and heated to 150°C (i.e. about 20°C above the isotropization temperature). The melt was very viscous and did not form a thin layer spontaneously. Hence the melt between the glass plates was sheared with a circular motion in the isotropic state. The isotropic melt (150°C) was then continuously cooled at about -0.7°C min^{-1} to room temperature (20°C). The textural changes were recorded photographically as a function of temperature.

In order to see if an amorphous polymer could be prepared, the polymer was melted at 200°C (about 70°C above isotropization) between two thin cover slips, and removed with tweezers from the heating block of the Linkam hot-stage and immersed in liquid nitrogen. The quenched polymer film that was sandwiched between the coverslips was examined at room temperature by eye for turbidity, and with the polarizing microscope for birefringence.

3. Results and discussion

3.1. *Effect of thermal history on heating scan*

3.1.1. *Nascent polymer and well-crystallized polymer formed by slow cooling*

As stated earlier, we proposed that the mesophases in this polymer are monotropic in character and hence are only observed on cooling [2]. On heating, the crystal transforms directly to the isotropic melt, without any liquid crystal phase being formed. Yet, the DSC heating scan of the nascent reactor polymer (Fig. 1a) does not show a single melting endotherm, but manifests two endotherms with an exotherm in between. We have tentatively attributed this to crystal annealing effects [2]. It was suggested that the scan in Fig. 1a could be interpreted in terms of partial melting, recrystallization and remelting [2]. It has been proposed by Fischer et al. [1] that chain-folding can occur in polymers containing the monomer BHHBP, hence it is conceivable that during annealing, chain-folded crystals with a lower melting point convert to a higher melting, extended-chain crystal form. Thus, isothermal annealing of the nascent polymer for a prolonged time at a temperature below the crystal melting point should increase crystal size; hence, it should reduce crystal-perfectioning transformations occurring during the heating scan. In our initial work [2], one such annealing experiment was reported. The nascent polymer was heated to 115°C and annealed for 1h and after cooling to 30°C the sample was reheated at 1°C min^{-1}. The heating scan of the annealed polymer showed only a major melting peak at 130°C with a small shoulder at a lower temperature [2].

The fact that there is only a crystal–isotropic transition on heating can be shown by another experiment demonstrated here. If instead of annealing the nascent polymer, it is first melted and *cooled slowly* at -5°C min^{-1}, a well-crystallized material is obtained. When the well-crystallized polymer is reheated at 5°C min^{-1}, only a single melting endotherm is observed (Fig. 1b, compare with Fig. 1a). This clearly indicates the thermal history of the sample (i.e. nascent polymer versus slowly crystallized polymer) affects the heating scan.

3.1.2. *Isothermally crystallized sample*

Here, a well crystallized sample was produced not by isothermal annealing [2] or slow cooling from the melt but by an *isothermal crystallization from the melt state*. This was achieved by cooling from the isotropic state at 150°C to the crystallization temperature (100°C, 105°C, 110°C or 115°C) and holding for 5 h at this temperature. After this, the sample was rapidly cooled and was reheated from −50°C to 150°C at 5°C min^{-1}.

The heating scan of the sample crystallized at 100°C (Fig. 1c) shows a single peak at 120°C with a shoulder at 130°C. The isothermally crystallized sample melts at a slightly higher temperature than the slowly crystallized polymer (Fig. 1b) because of its even larger and more perfect crystals. After isothermal crystallization at 105°C, the heating scan in Fig. 1d was obtained. This also shows a major endotherm with peak at 120°C; however, a small but distinct peak at 130°C is also noticeable. This at first is puzzling, but it merely means that the true crystalline melting point of the extended chain crystal is probably near 130°C. If the polymer is crystallized at a higher temperature, such as 110°C, then the heating scan shows apparently renewed complexities (Fig. 1e). The dominant endotherm is now at 130°C (instead of 120°C), but there are several smaller peaks preceding it. The smaller peaks appear to be a sequence of alternating endotherms and exotherms, suggesting that the transformation takes place by a series of almost discrete melting and recrystallization steps. Crystallization at higher temperatures such as 115°C also led to heating scans similar to that in Fig. 1e (not shown). Thus, it still seems that there is only a single $\text{K} \rightarrow \text{I}$ transition and the equilibrium crystal melting temperature is just above 130°C.

Optical microscope observations were also consistent with the DSC findings. An isothermally crystallized sample (110°C for 10 h) was produced under similar conditions between glass cover slips; this showed a banded spherulitic texture (Fig. 2). On heating, the birefringence diminished at about 125°C and the spherulites melted and

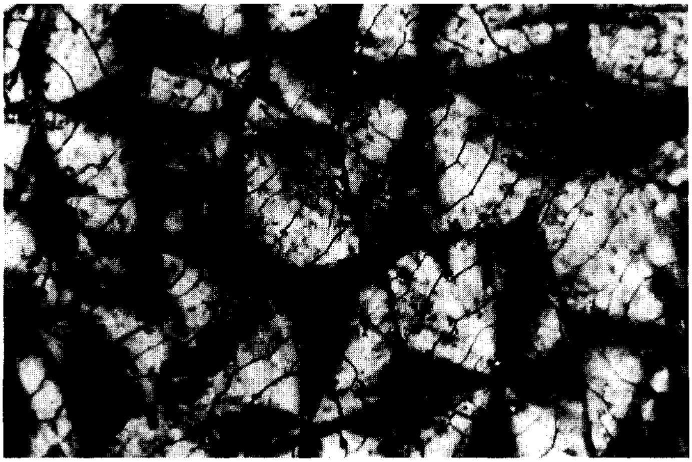


Fig. 2. Banded spherulitic texture of a sample that had been isothermally crystallized at 100°C for 10 h.

transformed to the isotropic melt at 133°C; there were no intervening smectic or nematic textures on heating.

3.1.3. Quench-cooled polymer

These experiments were conducted to probe further the effect of thermal history on the heating scan of the polymer, and to establish the glass transition temperature. The material was prepared by heating to the isotropic state (150°C) and quenching the molten polymer by dropping the DSC pan in liquid nitrogen. The quenched material was transferred from the liquid nitrogen to the DSC cell which had been equilibrated at −100°C. It was interesting to compare the heating scan (at 5°C min^{-1}) of the quench-cooled polymer with the nascent polymer and the slowly or isothermally crystallized material. This is shown in Fig. 1f. On heating the quench-cooled material, a weak glass transition was observed between 30 and 40°C. After the glass transition, again an endotherm occurs before the exotherm and this is followed by the main melting endotherm as well as a very small endothermic peak near 130°C. Thus, the quench-cooled material is similar to the nascent polymer. It appears that partial melting, reorganization and remelting occur. This behaviour ought to be contrasted with that of quench-cooled poly (ethylene terephthalate) where after the T_g, a cold crystallization exotherm is observed followed by the melting endotherm.

Visual observations were also conducted on quench-cooled material. It was found that even material formed by quenching from 200°C (i.e. about 70°C above the isotropization temperature) was turbid instead of clear. In contrast, quench-cooled poly(ethylene terephthalate), which is a slowly crystallizing polymer, is generally transparent. Fig. 3 shows that the quenched material was birefringent when viewed between crossed polars, though no recognizable features such as spherulites could be seen. We may contrast the behaviour of this polyester with poly(ethylene terephthlate)

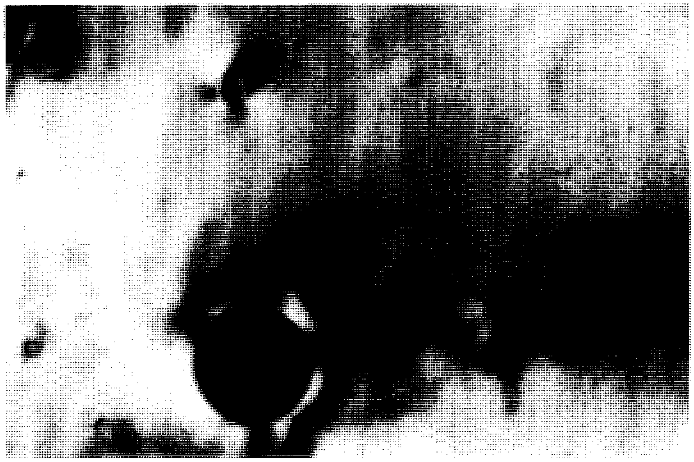


Fig. 3. Optical texture of quench-cooled polymer at room temperature, between crossed polars. The birefringence indicates quench cooling in liquid nitrogen does not produce an amorphous polymer. The circular black region is void.

which crystallizes slowly. On quench-cooling the latter polyester from the melt, an amorphous (non-birefringent) polymer is indeed obtained, and this crystallizes on heating above the glass transition. In contrast, the current polyester is able to order itself very quickly and hence an amorphous material is not easily obtainable. Its behaviour seems to be more akin to a rapidly crystallizing polymer such as polyethylene rather than poly(ethylene terephthalate). In fact, we have found similar behaviour with other segmented liquid crystalline polymers containing flexible spacers such as the family of polyesters formed by the condensation of 4,4′-biphenyl dicarboxylic acid and aliphatic diols.

3.2. Cooling rate experiment

In our previous study [3], we proposed that on cooling the following phase transition sequence occurs $I \rightarrow N \rightarrow S_A \rightarrow K$. However, after further intensive study we find that these transitions appear to overlap and what is observed depends on the cooling rate. On cooling from the isotropic melt using a relatively fast cooling rate of $-10°\mathrm{C\ min^{-1}}$, one finds a rapid emergence of small batonnets at 110°C (Fig. 4a). These coalesce but the focal conic domains are hard to see because of their small size. In contrast, if a cooling rate of $-0.7°\mathrm{C\ min^{-1}}$ is used, a nematic Schlieren texture is observed at 112°C; however, superimposed batonnets and focal conic domains are also found (Fig. 4b). It was not clear whether the smectic phase appears by conversion of the nematic or whether it is formed simultaneously. On further cooling, the batonnets never seemed to grow any further and coalesce as they do in molecular and, indeed, many polymeric liquid-crystals. That is, the full conversion to the smectic phase did not seem to occur. Eventually, as the temperature drops to about 100°C, crystallization starts and this is recognised by the growth of spherulites. These features are embodied in the single micrograph in Fig. 4b — it can be seen that all three textures (nematic, smectic and crystalline) are simultaneously present.

In our previous DSC investigation, we only observed two, rather than three, exothermic peaks on cooling, even at the lowest cooling rate ($0.5°\mathrm{C\ min^{-1}}$) tried [3]. This is shown in Figs. 5a and 5b. We decided that the higher temperature peak at 105°C could not be resolved further and must be a result of two overlapping mesophase transitions [3], while the lower temperature peak was the crystallization exotherm. Comparing Figs. 5a and 5b, it can be seen that on reducing the cooling rate from $-5°\mathrm{C\ min^{-1}}$ to $-0.7°\mathrm{C\ min^{-1}}$, the isotropic–mesophase peak does not shift but the crystallization peak moves to higher temperature and starts to overlap with it.

Generally, using lower cooling rates in the DSC should lead to higher peak resolution, but this has to be balanced against a loss of sensitivity (i.e. there is increased noise at very low rates). It was thus hoped that by going at even slower cooling rates than tried previously, it would be possible to see the splitting of the higher temperature (isotropic–mesophase) peak. Figs. 5c and 5d show the DSC scans recorded at cooling rates lower than that shown previously. Lowering the cooling rate from $-0.7°\mathrm{C\ min^{-1}}$ to $-0.3°\mathrm{C\ min^{-1}}$, does not lead to splitting of the mesophase peak (Fig. 5c); instead, there is now a *single*, broad peak due to crystallization. At the lowest cooling rate of $-0.1°\mathrm{C\ min^{-1}}$ (Fig. 5d) there is a single and relatively narrow crystallization peak. The

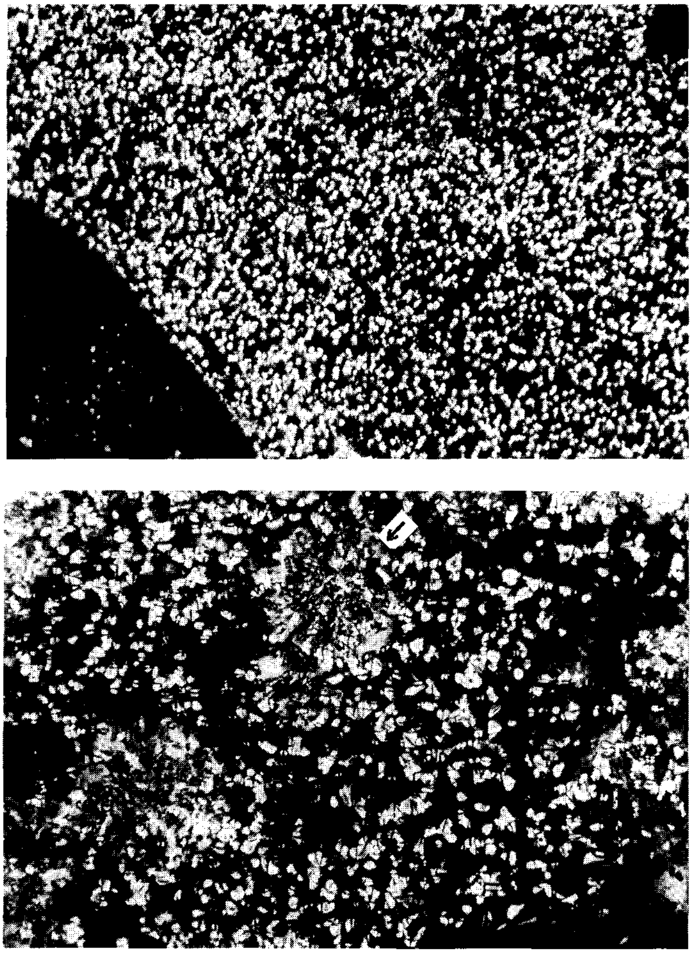


Fig. 4. Optical textures obtained on cooling the isotropic melt from 140°C at different cooling rates: (a) fast cooling at $-10°C\ min^{-1}$ leads to a profusion of batonnets emerging at 110°C from the isotropic phase; (b) slow cooling at $-0.7°C\ min^{-1}$ leads to a Schlieren texture of the nematic, batonnets of the smectic A phase, and spherulites (arrow) due to crystallization. The photograph was recorded at 100°C. Though the Schlieren texture and batonnets first appear at 112°C, the conversion from the nematic to the smectic was never complete even at 100°C, at which point crystallization started.

fact that only a single peak is observed at the lowest cooling rates is due to the monotropic nature of the liquid-crystal phases in this polymer — the mesophase is not thermodynamically stable and the crystalline state is the only truly stable form below the melting point. Hence, as the cooling rate is lowered, the supercooling needed to observe crystallization is reduced, and crystallization occurs directly.

Though we have not been able to resolve the higher temperature peak of Figs. 5a and 5b into the I–N and N–S_A transitions as hoped, the sequence in Fig. 5 is actually consistent with what is seen in the microscope: the nematic and smectic phases appear almost *concurrently*, and not consecutively, and also the conversion to the smectic state from the nematic is not complete before crystallization starts (Fig. 4b). One may still ask if this inability to observe complete mesophase transitions is due to limitations of our DSC and indeed the hot-stage used for the microscope, or is an intrinsic property of the material. Where the instrumental response could be a problem is in maintaining an accurate linear temperature ramp, particularly near an exothermic transition. Terry et al. have observed somewhat similar behaviour with another segmented polyester, that formed by condensation of *p,p'*-bibenzoic acid and 1,8-octamethylenediol [5]. This polymer has a single monotropic smectic phase. With heat flux DSC, partial overlap of the two transitions (I–S_A and S_A–K) was observed, whereas with a power-compensation DSC instrument, these were completely separated [5]. Thus, there was definitely an instrumental factor involved [5]. In the microscope, on cooling from the isotropic melt, batonnets were formed which developed partially into focal conics; this process was never complete and stopped after some time, after which crystallization occurred [6]. For this polymer, the microscope behaviour, which suggested two overlapping

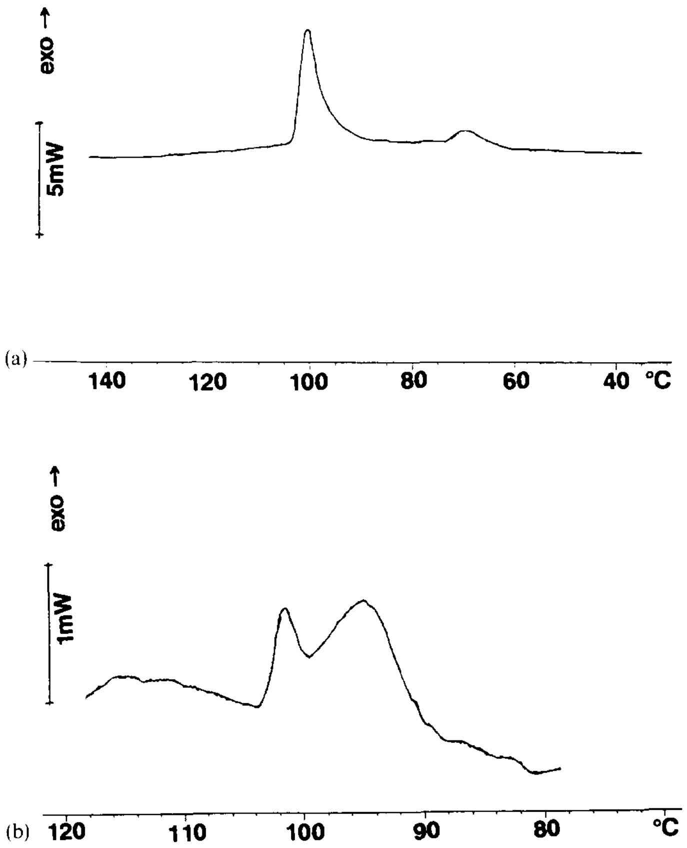


Fig. 5. DSC cooling scans: (a) −5°C min⁻¹; (b) −0.7°C min⁻¹; (c) −0.3°C min⁻¹; (d) −0.1°C min⁻¹.

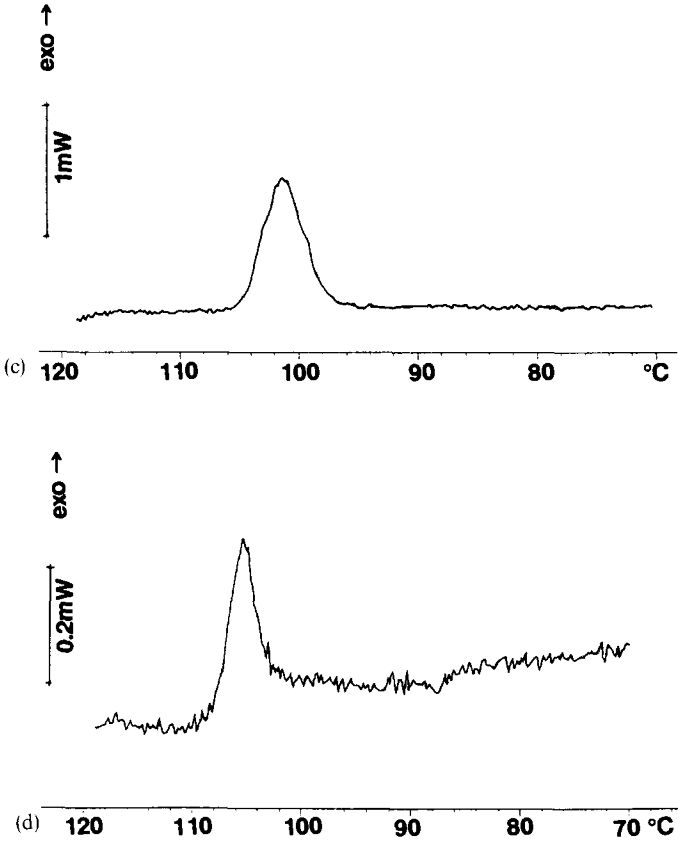


Fig. 5. (*Continued*).

transitions, was in accord with what was seen in heat-flux DSC, rather than power-compensation DSC [5].

Hence, it is possible that instrumental response also affects the *observed* behaviour of the monotropic liquid crystal polyester of this work, but the incomplete conversion of the mesophase may also be a material property. On very slow cooling, the batonnets of the smectic phase appear and grow quite fast initially, but later their growth rate is impeded. It is possible that a certain number of chain segments can build themselves into the stratified smectic layer with ease initially, but this becomes difficult later and the remaining chain segments are not able to extricate themselves from the entangled isotropic state. Such a situation would clearly not arise with molecular liquid-crystals.

4. Conclusions

In this paper we have conducted further investigations on the thermal properties of the polyester formed from the condensation of BHHBP with IA. In previous work, we proposed that this polymer shows monotropic liquid-crystal phases [3]. From optical microscope observations, it was believed that on cooling the phase transition sequence was $I \rightarrow N \rightarrow S_A \rightarrow K$ and on heating was $K \rightarrow I$. However, unlike the case of molecular compounds with liquid crystal phases, the DSC scans of these material were not straightforward, in that there was not a simple correlation between the number of peaks and phase transitions. Hence, we set out to resolve two issues—why multiple peaks including an exothermic one occurred in the *heating* scan [2] and why on the cooling scans reported previously [3], only two instead of three peaks were found.

From the heating scans, the following are the conclusions:

(1) Multiple endotherms and exotherms can be observed with this polyester, but these are not due to multiple phase transitions.

(2) The number of peaks observed in the heating scans depends solely on the thermal history of the polymer.

(3) The nascent polymer and the quench-cooled material showed two endotherms with an exotherm in between. The most probable reason for this is partial melting, recrystallization and remelting.

(4) A sample crystallized by slow cooling from the isotropic melt showed a single, endothermic peak at ~ 120°C.

(5) Isothermally crystallized samples showed either a single, broad, melting endotherm at 120°C with a shoulder at 130°C, or a dominant endotherm at 130°C and smaller, multiple endotherms near 120°C; this depended on the isothermal crystallization temperature. The equilibrium crystal melting temperature is ~ 130°C.

(6) Likewise, optical observation of the isothermally crystallized sample revealed a well formed banded spherulitic texture, which melted to the isotropic state at 133°C, without forming any intervening smectic or nematic textures.

(7) The findings reported here confirm the view that the crystal melts directly to the isotropic, and the liquid-crystal phases of this polyester are monotropic.

DSC cooling experiments at very low rates (-0.3 and $-0.1°\mathrm{C\,min^{-1}}$), which yield better peak resolution but which are normally not attempted because of the time required and the loss of sensitivity, were carried out to see if three peaks could be resolved in accord with the phase sequence $I \rightarrow N \rightarrow S_A \rightarrow K$, proposed previously [3]. The following are the conclusions from the cooling experiments:

(1) Instead of seeing three peaks, on lowering the cooling rate below $-0.7°\mathrm{C\,min^{-1}}$, one sees just one peak. This is because crystallization now occurs almost directly from the isotropic melt. This is in accord with the monotropic nature of the mesophase.

(2) The DSC cooling experiments are consistent with the microscope observations, where it was found that the nematic and smectic phases always occurred concurrently on cooling rather than consecutively. This appears to be a feature of this polymer.

(3) In light of the above, and even though instrumental factors may also play a role, for practical purposes, it may be better to write the phase sequence on cooling as $I \rightarrow N/S_A \rightarrow K$.

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