Phase transitions and melting of poly(4-hydroxybenzoate)

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Slab-like crystals and needle-like crystals (whiskers) of poly(4-hydroxybenzoate) (poly(4-Hybe)) prepared from 4-acetoxybenzoic acid were studied by means of differential scanning calorimetry and wide-angle X-ray scattering (WAXS) measurements and by microscopy with polarized light. At a heating rate of 20°C min^{-1} the slab-like crystals display phase transitions at 332, 430–440, 510 and 529°C. The whiskers exhibit these transitions at 353, 430–440, 510 and 532°C. The transition of the whiskers at 353°C is not thermodynamically stable and changes upon repeated heating and cooling to the 332°C transition. The endotherm at 510°C seems to indicate the beginning of the melting process reinforced by thermal rearrangements and degradation. Infra-red spectra indicate a nearly complete change of the chemical structure upon heating above 530°C. WAXS measurements conducted with synchrotron radiation up to 500°C confirm that no melting occurs below this temperature. Yet the WAXS patterns indicate melting (at 405°C) of a 1:1 copolyester of 4-Hybe and 4′-hydroxybiphenylcarboxylic acid. Microscopic observation of the poly(4-Hybe) whiskers revealed that these crystals fade away above 500°C in air without forming a melt.

(Keywords: poly(4-hydroxybenzoate); phase transitions; melting point; synchrotron radiation; Fries rearrangement)

INTRODUCTION

During the past two decades poly(4-hydroxybenzoate) (poly(4-Hybe)) has attracted much interest, because it has the ideal structure for a thermotropic and thermostable engineering plastic. However, the high symmetry and regularity of its structure causes an exceptionally high degree of crystallinity, which entails an extremely high melting point and an extremely low solubility in all common solvents. Since the homopolyester is difficult to process, a variety of copolyesters, mainly thermotropic aromatic copolyester, have been synthesized and investigated. Some of them have found application as thermostable engineering plastics with a combination of useful properties[1–5].

Despite numerous studies of poly(4-Hybe) itself and its aromatic copolyesters, the properties of the homopolyester are not yet fully understood. Economy and coworkers[6,7] have demonstrated that poly(4-Hybe) possesses a first-order phase transition at 330–335°C which is not a melting process. Lieser, studying X-ray and electron diffraction patterns of various poly(4-Hybe) samples prepared by Kricheldorf and Schwarz[8–10], revealed that the homopolyester can adopt two different orthorhombic crystal modifications (I and II) at room temperature, which reversibly change to a pseudohexagonal chain packing (modification III) above 330–335°C. Furthermore, it was found that this phase transition may occur at two different temperatures depending on the synthetic method[8], yet any explanation for this phenomenon is lacking so far. Recently Economy *et al.*[11] reported a second phase transition, around 440°C, which is detectable as a weak endotherm in the d.s.c. heating trace of poly(4-Hybe). On the basis of heat-distortion measurements and microscopic studies of oligomers this second phase transition was interpreted as a melting process[11,12]. However, prior to Economy's study, Jackson[2] had reported a melting point at 600–610°C determined by d.s.c. measurements with a heating rate of 80°C min^{-1}. Unfortunately, the d.s.c. traces were not published.

In the present work evidence in favour of a melting process at 510–530°C will be presented along with further details on other phase transitions.

EXPERIMENTAL

Materials

4-Hydroxybenzoic acid, 3-phenyl-4-hydroxybenzoic acid and 4-hydroxybiphenyl were gifts of Bayer AG (Krefeld-Uerdingen, FRG). They were used without further purification. The hydroxy acids were acetylated with excess acetic anhydride in boiling toluene. 4′-Acetoxybiphenyl-4-carboxylic acid was prepared as described previously[13]. Marlotherm-S, a mixture of isomeric benzylbenzenes, was a gift of Hüls AG (Marl, FRG).

Poly(4-hydroxybenzoate)

Whiskers. 4-Acetoxybenzoic acid (1.8 g, 10 mmol) was dissolved in 180 cm^3 Marlotherm-S at 200°C and heated without stirring to 350°C for 7 h under a slow stream of nitrogen. Afterwards the precipitated polyester was isolated by filtration, extracted with hot acetone, filtered off, washed with acetone and dried at 110°C *in vacuo*. Yield: 62%. Acetate end-groups were not detectable in the ^{1}H n.m.r. spectrum of a hydrolysed sample.

Slab-like crystals[8]. A solution of 9 g (50 mmol) 4-acetoxybenzoic acid in ~100 cm^3 Marlotherm-S was condensed for 16 h at 320°C under stirring and worked up as described above. Yield: 91%. A *DP* of ~260 was

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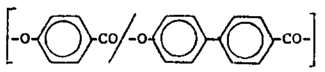
determined from ^1H n.m.r. spectroscopic end-group analyses[8].

Copolyester with 4′-hydroxybiphenyl-4-carboxylic acid (1)

4-Acetobenzoic acid (9.0 g, 50 mmol), 4′-acetoxybiphenyl-4-carboxylic acid (12.8 g, 50 mmol) and 10 mg MgO were heated to 260°C with stirring and under a slow stream of nitrogen. After 1 h the temperature was raised to 300°C and, after an additional hour at 340°C, the vacuum was applied for 1 h. The initially molten reaction product gradually solidified at 300°C. After cooling the reaction product was powdered, extracted with dichloromethane and dried at 110°C *in vacuo*. Yield: 90%. A degree of polymerization of 120 was determined by ^1H n.m.r. spectroscopic end-group analyses after hydrolysis in $CD_3OD/NaOD/D_2O$.



Measurements

The d.s.c. measurements were conducted with a Perkin–Elmer DSC-4 in aluminium pans.

The microscopic characterization was conducted with a Leitz microscope and a Stanton–Redcroft hot stage combined with a temperature programmer.

The WAXS powder patterns at variable temperature were measured with the synchrotron radiation ($\lambda = 1.5$ Å) of the DESY Hamburg[14]. At a heating and cooling rate of 20°C min^{-1} a WAXS pattern was taken every minute with an irradiation time of 10 s.

The i.r. spectra were measured on a Nicolet 20 SXB *FT* i.r. spectrometer with KBr discs.

RESULTS AND DISCUSSION

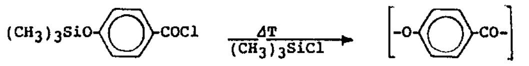
D.s.c. measurements

The characterization of poly(4-Hybe) at high temperatures (>300°C) requires samples of optimum thermostability. It was demonstrated in a previous part of this series[8] that size and perfection of crystallites, and thus the synthetic procedure, had a strong influence on the thermostability of poly(4-Hybe). Recently Yamashita *et al.*[15] have shown that rather long needle-like crystals of poly(4-Hybe), so-called whiskers, are obtainable from 4-acetoxybenzoic acid, when the polycondensation is conducted at low monomer concentration without stirring. For the purpose of the present work such whiskers seemed to be a useful substrate, and thus whiskers were prepared under conditions similar to those described by Yamashita[15]. In addition to these whiskers, so-called slab-like crystals were prepared by condensation of 4-acetoxybenzoic acid at higher concentration under stirring:

(1)

D.s.c. measurements of whiskers and slab-like crystals were conducted at heating rates of 20 and 80°C min^{-1} (*Figure 1*). The slow heating of the slab-like crystals revealed the well known phase transition at 332°C (now labelled α-transition or α-process) and the recently reported weak endotherm at 430–440°C (now labelled β-transition or β-process). Yet continuing the measurement up to 590°C surprisingly also revealed two hitherto unknown strong endotherms at 510°C (γ-process) and 528–532°C (δ-process). Rapid heating shifts all endotherms to higher temperatures, yet this shift is particularly conspicuous for the γ- and δ-processes. This effect is easily understandable if the γ-process is interpreted as unfreezing of the rotation of ester groups, and thus chain segments, and the δ-process as final melting. The melting process is strongly affected by chemical reactions including thermal degradation, and thus will depend strongly on the heating rate. Whatever is the correct interpretation of the γ- and δ-processes, their existence suggests that the endotherm at 430–440°C (β-transition) does not indicate the true melting process.

Heating of the whiskers revealed a similar pattern of endotherms with one characteristic difference. The α-transition occurs at 353°C (at 20°C min^{-1}), i.e. 20°C higher than in the case of slab-like crystals. This temperature difference marks a somewhat different transition to modification III, because repeated heating and cooling between 300 and 400°C leads to complete disappearance of the endotherm at 353°C (now labelled α_2-transition), whereas the endotherm at 332°C (α_1-transition) continually grows in intensity (*Figure 2*). The existence of two α-transitions separated by ~20°C has already been observed for poly(4-Hybe) prepared from 4-trimethylsiloxybenzoyl chloride[8]:



(2)

The results obtained now with whiskers prepared from 4-acetoxybenzoic acid demonstrate that the existence of

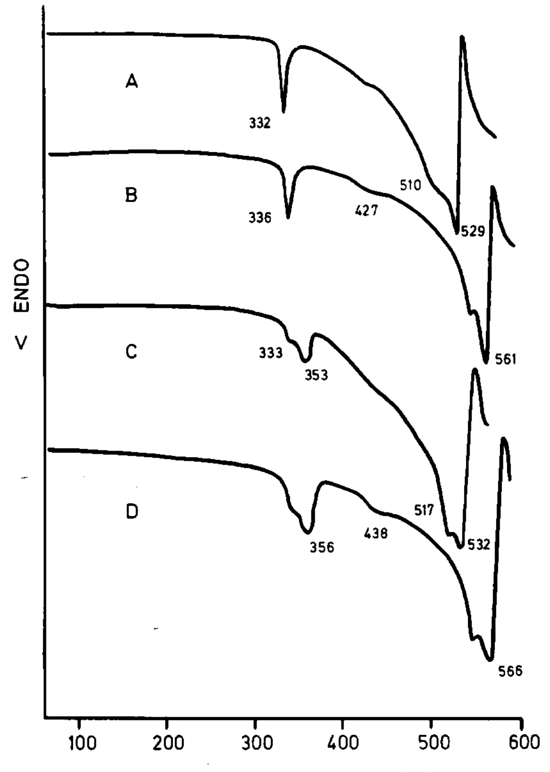


Figure 1 D.s.c. measurements: A, heating of slab-like crystals at a rate of 20°C min^{-1}; B, heating of slab-like crystals at 80°C min^{-1}; C, heating of whiskers at 20°C min^{-1}; D, heating of whiskers at 80°C min^{-1}

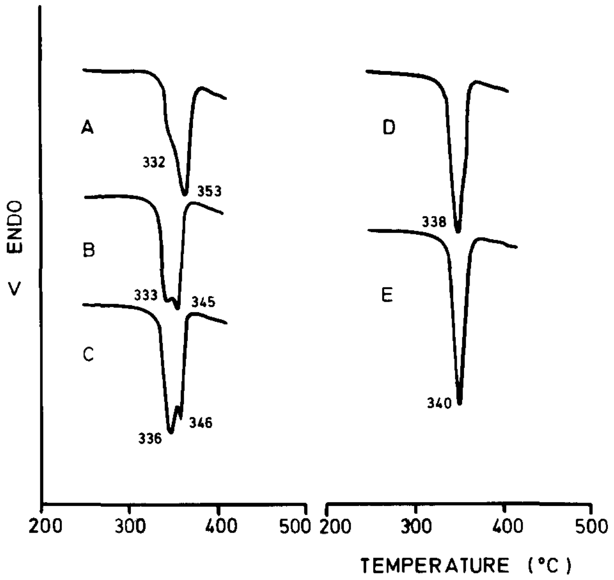


Figure 2 D.s.c. measurements: repeated heating (and cooling) of whiskers between 300 and 400°C at a heating (cooling) rate of 20°C min^{-1}. The exotherm in the cooling traces does not exhibit any change

the α_2-transition has nothing to do with the chemical structure of monomer or end-groups. A detailed study of the α-transition is under investigation, yet a satisfactory explanation cannot yet be offered. In this connection it needs to be emphasized that the coexistence of two α-transitions has nothing to do with the coexistence of two orthorhombic modifications (I and II). As indicated by WAXS measurements (see below) the original whiskers exclusively adopt modification I. After heating up to 400°C and cooling they contain a small fraction of modification II, yet this fraction did not grow when the heating/cooling cycles were repeated.

Microscopic observations and i.r. spectroscopy

When aggregates of slab-like crystals were heated above 500°C, the sample darkened and a melting process was not observed. In contrast to slab-like crystals, whiskers have the advantage that an optical microscope allows one to observe individual crystals (*Figure 3*). Therefore, optical microscopy promised to allow an easy determination of the melting point of poly(4-Hybe). However, when whiskers were heated in air to 590°C at a rate of 80°C min^{-1}, they rapidly vanished between 570 and 580°C without leaving a liquid or solid residue. Since the temperature range of 570–580°C agrees with the δ-process of the d.s.c. measurements conducted at 80°C min^{-1}, the microscopic observation supports the interpretation of the δ-transition as the melting process. When whiskers were heated in air to 500°C and annealed at this temperature, they also vanished without leaving a liquid or solid residue (*Figure 3*). This finding suggests that in addition to oxidative erosion from the surface a degradation mechanism might exist that mainly produces volatile degradation products. A previous study of the thermal degradation of poly(4-Hybe) by Jellinek and Fujiwara[16] had revealed that, *in vacuo*, CO, CO_2, phenol and phenyl-4-hydroxybenzoate are formed as volatile degradation products along with a dark insoluble residue. A brown crosslinked product that could not be hydrolysed with $NaOH/CH_3OH$ was also recovered from the aluminium pans of d.s.c. measurements conducted under nitrogen. Thus it is obvious that heating in air or in the absence of oxygen has different consequences for the degradation mechanism, yet a proper understanding of the degradation mechanisms is still lacking. Nonetheless, the microscopic studies of whiskers in air clearly demonstrated that the whiskers do not melt below 500°C (*Figure 3*), yet they did not enable a clear-cut definition of the melting point.

In order to obtain more information on the γ- and δ-processes, the products recovered from d.s.c. measurements after heating either to 550°C at 20°C min^{-1} or to 590°C at 80°C min^{-1} were characterized by optical microscopy, i.e. spectroscopy and WAXS patterns. Regardless of the heating rate, the WAXS measurements showed that the products heated to 550 or 590°C are mainly amorphous, in contrast to the original whiskers. The microscopic observation revealed that the whiskers had lost their crystalline shape and looked like partially molten, distorted fibres. The i.r. spectra indicated that

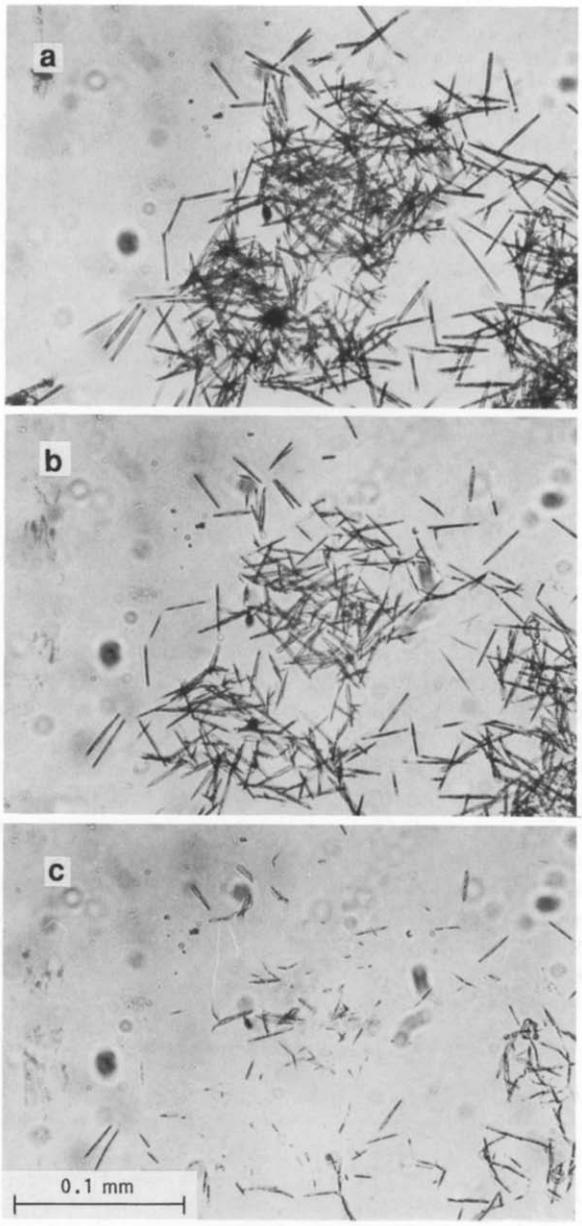


Figure 3 Micrographs of whiskers taken at 500°C: (A) after 10 s, (B) after 2 min, (C) after 3 min

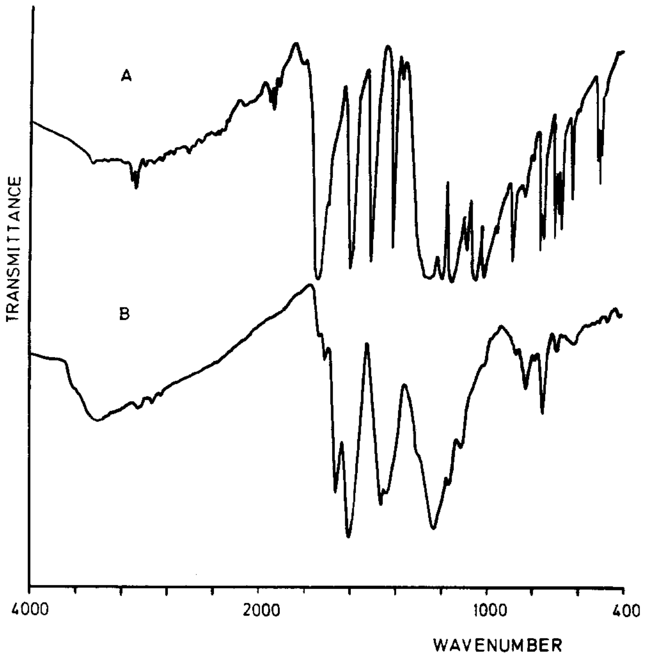
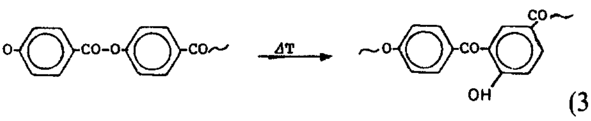


Figure 4 I.r. spectra (measured with KBr pellets): A, poly(4-Hybe) whiskers; B, the same whiskers after heating to 590°C in aluminium pans under N_2 at a rate of $80°C\ min^{-1}$

the chemical structure had almost completely changed (*Figure 4*, curves A and B). The CO band of the ester group ($1740\ cm^{-1}$) has almost disappeared and a new carbonyl band at $1664\ cm^{-1}$ shows up along with a broad OH band at 3000–$4000\ cm^{-1}$.

These spectroscopic features along with the crosslinked structure of these materials may be explained with a thermal 'Fries rearrangement':



(3)

This conclusion is supported by the detection of a dihydroxybenzophenone as a volatile fragment, when poly(4-Hybe) was subjected to pyrolysis mass spectroscopy at 550°C[17]. Unfortunately the lack of a solvent prevented detailed n.m.r. spectroscopic analyses in solution and the ^{13}C n.m.r. cross-polarization/magic-angle spinning (CP/MAS) spectra did not give more information owing to the broad signals. In this connection it is to be emphasized that the whiskers recovered from the d.s.c. pans or from the vacuum oven of the synchrotron radiation beam line (see below) were white crystals, identical with the starting material when heating was stopped at 500°C. Thus it is obvious that a melting process accompanied by rapid rearrangement and degradation reactions occurs between 500 and 550°C, when a heating rate of $20°C\ min^{-1}$ is applied.

WAXS measurements

The synchrotron radiation of the DESY at Hamburg[14] enabled us to measure WAXS patterns with an irradiation time of 10 s. Hence this source of X-ray radiation ($\lambda = 1.50$ Å) allowed us to monitor relatively rapid chemical or physical changes of a crystalline polymer. Unfortunately the maximum temperature that was technically accessible was limited to 500°C. Heating and cooling whiskers in the synchrotron beam at a rate of $20°C\ min^{-1}$ yielded a series of WAXS patterns displayed in *Figures 5–7*. The α-transition at 353°C and the β-transition at 430–440°C are clearly detectable. However, the pseudohexagonal chain packing formed above the α-transition does not disappear up to 500°C.

This interpretation is substantiated by a d.s.c. and synchrotron radiation study of a 1:1 copolyester of 4-Hybe and 4′-hydroxybiphenyl-4-carboxylic acid (**1**). By analogy to the homopolyester of 4′-hydroxybiphenyl-4-carboxylic acid[13], this copolyester possesses a pseudo-

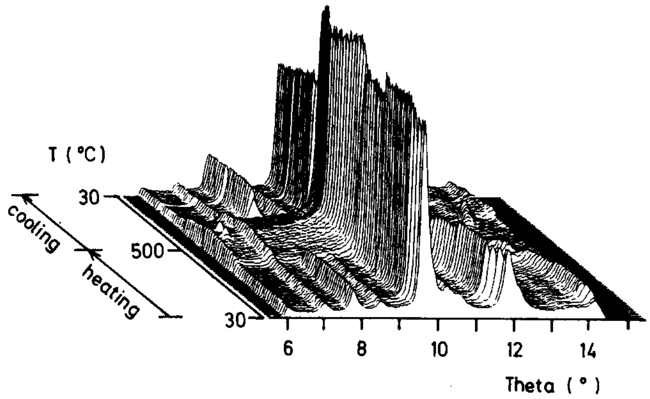


Figure 5 WAXS measurements of whiskers conducted with synchrotron radiation at a heating and cooling rate of $20°C\ min^{-1}$ *in vacuo*

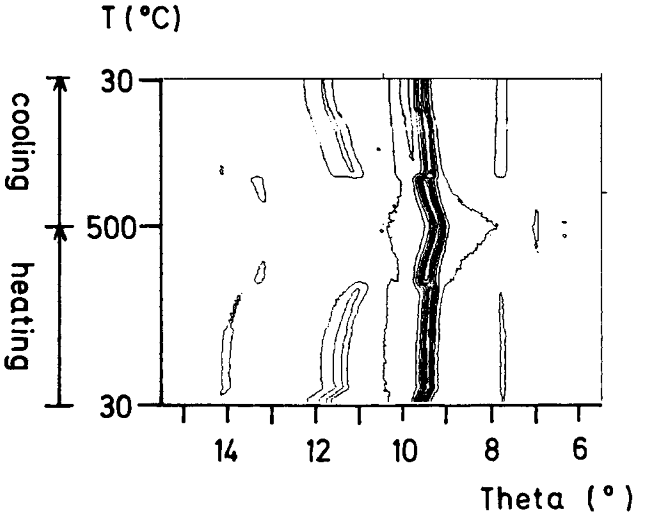


Figure 6 Contour map of the staked plot of *Figure 5*

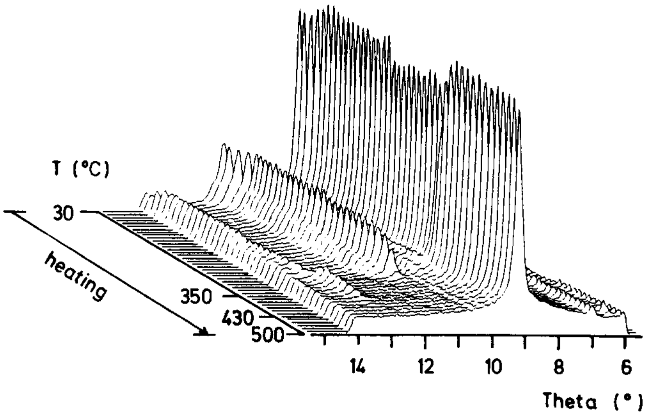


Figure 7 WAXS measurements of whiskers conducted with synchrotron radiation at a heating rate of $20°C\ min^{-1}$

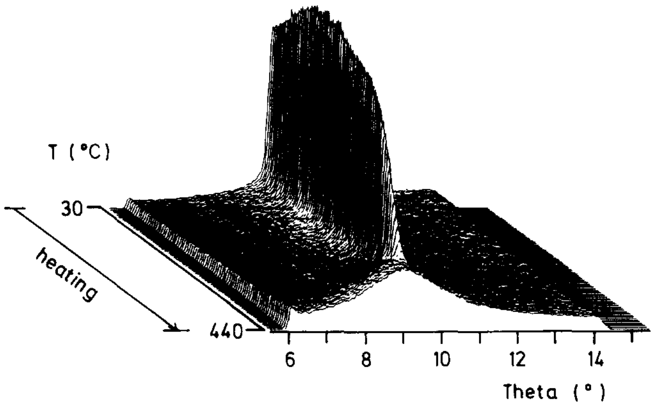


Figure 8 WAXS measurements of a 1:1 copolyester of 4-hydroxybenzoic acid and 4'-hydroxybiphenyl-4-carboxylic acid conducted with synchrotron radiation at a heating and cooling rate of 20°C min^{-1}

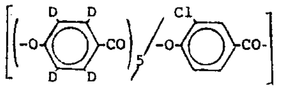
hexagonal chain packing even at room temperature. The d.s.c. heating trace exhibits an endotherm around 405°C and the WAXS patterns clearly show a melting process at the same temperature (*Figure 8*). Above this temperature, optical microscopy reveals the threaded schlieren texture of a nematic melt. These measurements prove that WAXS patterns reliably indicate the melting point of a polymer with pseudohexagonal chain packing. A more detailed study on copolyesters of 4'-hydroxybiphenyl-4-carboxylic acid will be published in a future part of this series.

Another interesting aspect of the WAXS patterns of poly(4-Hybe) whiskers is the existence of a weak reflection at $\theta = 6.95°$, which persists over the full temperature range up to 500°C, without changing position (*Figure 5*). This reflection was indexed as 002 reflection resulting from the periodicity of the ester groups along the chain axis. The existence of this reflection even at 500°C clearly proves that all chains are fully extended and parallel packed up to this temperature. A melting process at 430–440°C is clearly excluded.

The strong reflection at $\theta = 9.5$–$10°$ (4.5–5.0 Å), which represents the lateral distance of directly neighbouring chains, shows a quite different behaviour. As demonstrated by the contour map (*Figure 6*), this reflection continuously moves to smaller angles with increasing temperature. This move indicates a strong expansion of the lateral dimension, presumably resulting from increasing mobility of the aromatic rings. Interestingly, the β-transition at 430–440°C is not detectable from the position or intensity of this reflection. However, the β-process is characterized by the disappearance of a reflection at $\theta = 13.35°$, which appears above the α-transition (*Figure 7*). A reliable interpretation of this reflection is still lacking. For the sake of completeness it is worth noting that a weak reflection at $\theta = 6.35°$ appears above 485°C and disappears at 500°C.

CONCLUSIONS

The good agreement between d.s.c. microscopy and WAXS measurements allows the reliable conclusion that poly(4-Hybe) does not melt below 500°C. The melting process sets in above 510°C, and is immediately followed by degradation and rearrangement reactions. Because the changes in the chemical structure are rapid and almost complete at 560–590°C even at a heating rate of 80°C min^{-1} it is difficult to understand how Jackson[2] could find a T_m at 600–610°C. These results raise the question of the origin of the endotherms at 430–440 and 510°C (as determined at 20°C min^{-1}). In this connection it is worth noting that ^{2}H n.m.r. lineshape analyses of the copolyester **2** were conducted between 30 and 300°C.



This copolyester was synthesized and measured because the incorporation of 3-chloro-4-hydroxybenzoyl units into poly(4-Hybe) depresses the α-transition from 332 to ~260°C[17]. Thus the mobility of aromatic rings in the pseudohexagonal chain packing (modification III) could be measured for the first time. The details of this study will be published separately. Yet in this work it should be noted that the aromatic ring only acquires the freedom to flip (120° or 180° flips), but not the freedom to rotate freely. The unfreezing of free rotation might then be responsible for the β-process. Above 440°C, the chains maintain their parallel packing by dipole–dipole interactions of the ester groups. The unfreezing of rotations of ester groups might then be the origin of the γ-process at 510°C, which is followed by total mobility and chemical rearrangements (δ-process). This scheme of increasing mobility is, of course, still speculative, yet it may be a useful basis for further investigations and discussions.

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