The crystal lamellar morphology of an aromatic polyketone with unusual crystallization and melting behaviour*

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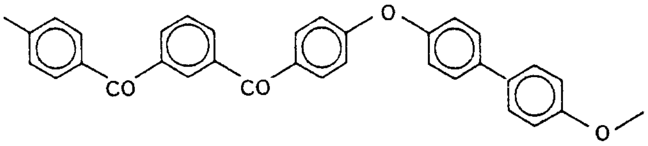
Wide-angle and small-angle X-ray scattering and differential scanning calorimetry are used to elucidate the lamellar morphology of an aromatic polyketone (designated PK99). PK99 has three unusual crystallization and melting characteristics. First, there is a coupled melting and recrystallization process at around 260°C, well below the final melting point of 306°C; this process suggests two crystal forms. Secondly, there are two maxima in the growth rate *versus* temperature characteristics. Thirdly, the melting point is relatively low compared with the T_g (158°C). WAXS shows that above and below the 260°C process there is no essential difference in the crystal packing. However, WAXS and SAXS data do show small step differences in crystal perfection and in lamellar thickness. The lamellar thicknesses are comparable to the periodic repeat length. This produces a new situation not normally observed in other crystalline polymers, where more than one type of lamellae can be formed containing different chain sequences. The unusual characteristics can be explained in terms of these different types of lamellae.

(Keywords: aromatic polymer; polyketone; crystal morphology; crystallization; melting behaviour; X-ray scattering; differential scanning calorimetry)

INTRODUCTION

There is considerable interest in the aromatic polymer poly(ether ether ketone) (PEEK) and its variants for applications as high-temperature materials. The phenyl rings in PEEK itself are all *para*-linked, but other reported variants also contain *meta*-phenyl or biphenyl units[1–3]. This paper is concerned with one particular variant labelled 'PK99', which is a homopolymer and exhibits very unusual crystallization and melting behaviour. We believe that this behaviour results from the interrelation of the chemical repeat length with the crystal lamellae thickness, and that it highlights a new aspect of lamellar morphology affecting polymer crystallization. PK99 incorporates both biphenyl and *meta*-phenyl units regularly spaced along the chain:



The preparation of PK99 and a description of its unusual crystallization effects are described in a previous paper[4]. In this present paper we will concentrate on the crystal lamellar morphology of the polymer and construct a model to explain its unusual behaviour.

There are three unusual features to note. First, depending on its prior thermal history, d.s.c. heating scans of PK99 reveal an unusual coupled melting and recrystallization process at around 260°C, well below the final melting temperature. The behaviour strongly suggests the presence of two distinct crystal species and that when one of the species melts it is replaced by the second higher-melting structure. As well as this, observations of isothermal crystallization as a function of temperature show two distinct maxima in the crystallization rate instead of the usual single maximum. This suggests that the homopolymer can partake in two separate crystallization processes. The third feature of interest is that the normal upper d.s.c. melting temperature of 306°C is unusually low relative to its T_g of 158°C. For instance, the ratio $T_g/T_m(\mathrm{K}) = 0.75$ is significantly greater than the ratio 0.68 for PEEK. This combination of transitions is relevant to practical applications, since it provides the advantage of a higher operating temperature combined with lower melting and processing temperatures. Normally this can only be achieved by resorting to copolymerization[5,6].

This paper is concerned with samples of PK99 that have been fabricated under controlled isothermal conditions chosen so as to help distinguish the differences in morphology above and below the unusual 260°C transition. D.s.c. and X-ray diffraction techniques are used to elucidate the nature of the crystal morphology and to arrive at an explanation of the unusual behaviour. The paper also includes complementary data collected at the Daresbury synchrotron showing the development of small-angle X-ray scattering from the lamellar structure while heating at d.s.c. heating rates. Further associated studies on the crystal structure of the polymer will be reported separately.

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EXPERIMENTAL

Specimen preparation

The synthesis of PK99 has been described in a previous publication[4]. The polymer was compression moulded and quenched to give clear, amorphous sheets with a thickness of approximately 300 μm. Small pieces (approximately $20 \times 10\,mm^2$) were cut from the sheets and crystallized isothermally at 200, 230 and 260°C for a time of 1 h. This was done by sandwiching the sample between aluminium foil and then lightly clamping in a small press that had been previously heated to the required crystallization temperature. After 1 h the samples were quenched in water.

Because of the reduced rate of crystallization, it became impracticable to crystallize isothermally much above 260°C. Therefore, in order to extend the range of thermal conditioning, additional samples were also prepared by post-annealing. They were made by first isothermally crystallizing at 260°C as above and then heating in a press to the annealing temperature for 1 h, before quencing into water.

A summary list of the samples prepared is shown in *Table 1*.

Differential scanning calorimetry

D.s.c. scans were obtained from 10 mg samples by heating at 20°C min^{-1} in a Perkin–Elmer DSC-4.

Wide-angle X-ray scattering

X-ray scans were obtained in the symmetrical transmission mode using a slit configuration of 1/6°, 4°, 4° on a Philips diffractometer.

Small-angle X-ray scattering

The SAXS scattering profiles were collected on a Kratky camera. The scatter was desmeared and corrected with the isotropic Lorentz factor ($4\pi s^2$). The position of the diffraction maximum was used to deduce the 'long period' using the Bragg relationship. Selected samples were also examined using a scanning hot stage fitted on to the SAXS line 2.1 of the SERC Daresbury synchrotron source. The particular objective was to obtain evidence of the mechanisms occurring during the unusual 260°C transition.

RESULTS

Differential scanning calorimetry

D.s.c. scans of all samples, including the quenched, the isothermally crystallized and the post-annealed samples, are shown in *Figures 1* and *2*. Certain of the features in these thermograms are similar to those seen in PEEK, while other features including the unusual process around 260°C are novel.

The quenched amorphous sample in *Figure 1a* shows a clear T_g step at 158°C. This is followed by a very sharp crystallization process at 260°C and then a clear final melting peak at around 306°C.

In the isothermally crystallized samples, the T_g process has become predictably less distinct. All these samples show a small melting endotherm about 12–15°C above the isothermal crystallization temperature. This process is equivalent to the low-temperature process that is observed with PEEK samples that have been isothermally crystallized. It can be interpreted as the onset of melting of crystals that had formed during the previous crystallization process, and marks the beginning of a continuous recrystallization process occurring during the temperature scan[7]. All these samples also show a sharp final melting around 360°C as in the quenched sample. The feature that is novel and is not seen in PEEK is the event around 260°C, which occurs in all those samples which have been crystallized below 260°C. It appears to consist of a melting process around 255°C followed immediately by a sharp crystallization process at 260°C. The features does not occur in the sample initially crystallized at 260°C or those which were post-annealed. It suggests the disappearance of one crystal form followed immediately by the replacement with another type of crystal. Accordingly, one would infer that the type of crystal formed depends on whether crystallization is above or below 255°C.

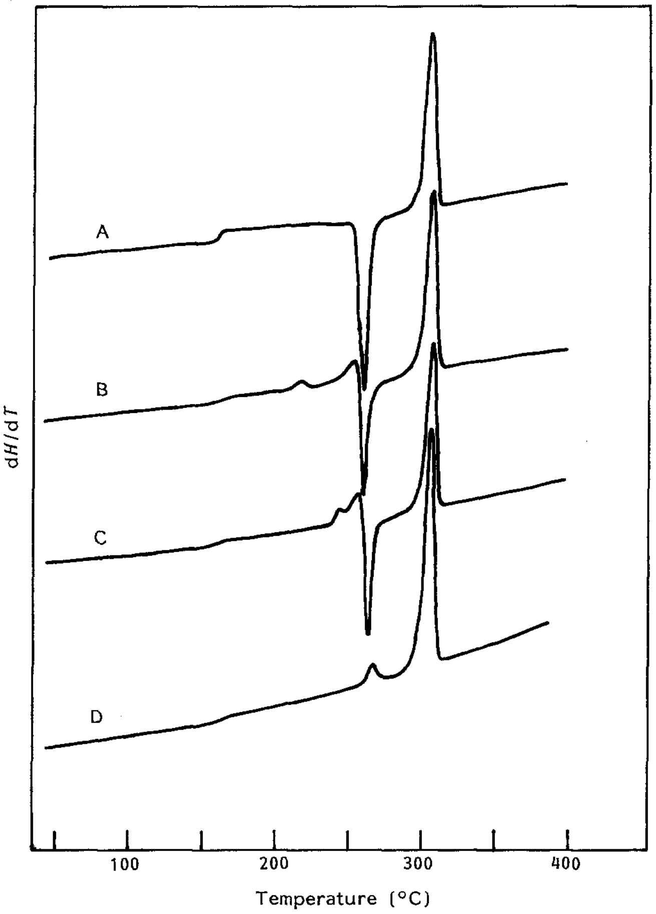

Figure 1 D.s.c. scans of quenched amorphous sample (a) and samples isothermally crystallized at (b) 200°C, (c) 230°C and (d) 260°C

The post-annealed samples show other interesting effects. The 290°C sample (*Figure 2a*) shows a recrystallization process as a shoulder on the main melting peak. The 300°C annealed sample (*Figure 2b*) shows one single final melting peak at 308°C, indicating the absence of any significant recrystallization during the scan. However, the 310°C annealed sample shows a major melting process around 318°C as well as a minor process at the normal 308°C position. There is a possibility with this sample that the 308°C peak is associated with parts of the sample that remained molten during the annealing procedure and which then recrystallized during the quenching and subsequent reheat. A comparison of the peak areas of the curves for the 290 and 300°C samples

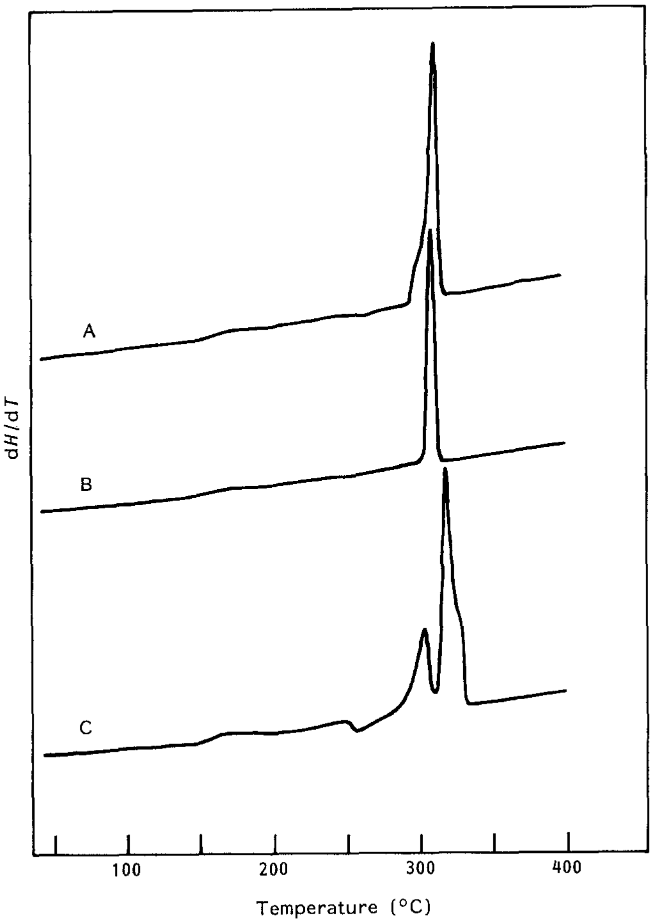

Figure 2 D.s.c. scans of samples post-annealed at (a) 290°C, (b) 300°C and (c) 310°C

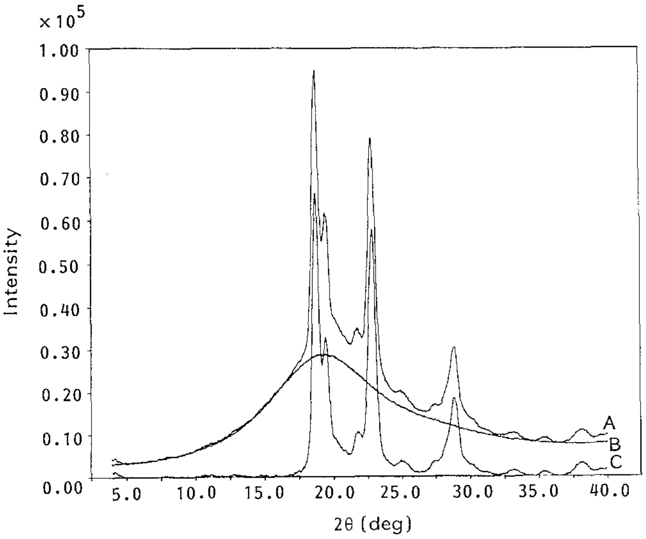

Figure 3 WAXS profiles for sample post-annealed at 310°C: (a) original data; (b) fitted profile from quenched amorphous sample; (c) profile from crystalline component derived by substracting (b) from (a)

with the corresponding X-ray crystallinity estimates discussed below indicates that the heat of fusion of PK99 is about 125 J g^{-1}, i.e. slightly lower than the 130 J g^{-1} found for PEEK[8].

Wide-angle X-ray scattering

Figure 3 shows an example of the observed X-ray scatter from one of the crystallized samples. It shows characteristic crystalline peaks superimposed on a broad halo from the amorphous regions of the polymer. In order to help with the analysis, the observed scatter from the quenched amorphous sample has been scaled and fitted as in curve b in *Figure 3* and then subtracted to give the profile of the crystalline component shown as curve c. *Figure 4* shows a superposition of such deduced crystalline components for a selection of the samples. The curves show a gradual improvement in the resolution of the diffraction peaks as the temperature of crystallization is increased, consistent with crystals of larger size and improved perfection. There is no obvious evidence with increasing temperature of the appearance of any new peaks from alternative crystal cells. However, there is a clear trend for the peaks to shift to higher scattering angles consistent with a systematic reduction in lattice spacing. Such peak shifts have also been seen in PEEK and can be associated with crystals of greater perfection[9].

The areas above and below the fitted amorphous curve (as shown in *Figure 3*) were used to estimate the crystallinity of the samples giving the values listed in *Table 1*. *Figure 5* shows the crystallinity plotted as a function of crystallization and annealing temperature. There is a gradual increase in crystallinity with temperature with a suggestion of a slight jump in value at 260°C. The sample post-annealed at 310°C shows a lower crystallinity, probably due to the quenching interrupting the completion of the crystal annealing process.

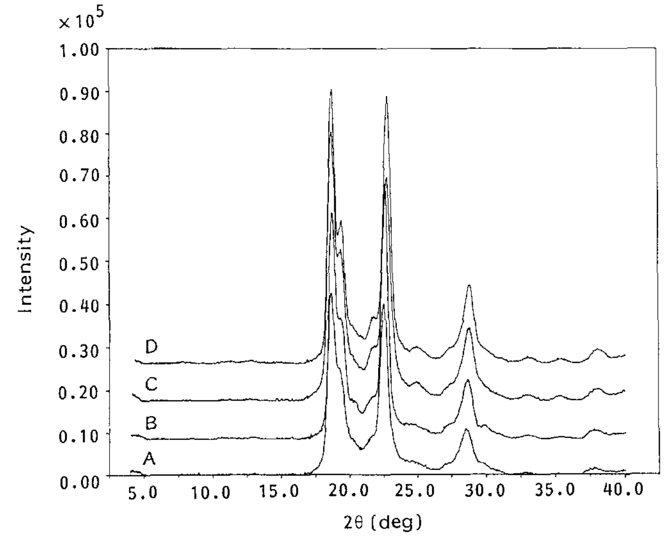

Figure 4 WAXS profiles for the crystalline components of samples crystallized at (a) 200°C, (b) 230°C, (c) 260°C and (d) post-annealed at 300°C

Table 1 Sample details and X-ray data

Preparation treatment	Treatment temperature (°C)	Crystallinity (%)	Long period (Å)	l_c (Å)
Isothermal	200	30.0	116	34.8
	230	31.7	119	37.7
	260	36.8	138	50.8
Annealed	290	37.0	147	54.4
	300	37.5	152	57.0
	310	34.0		

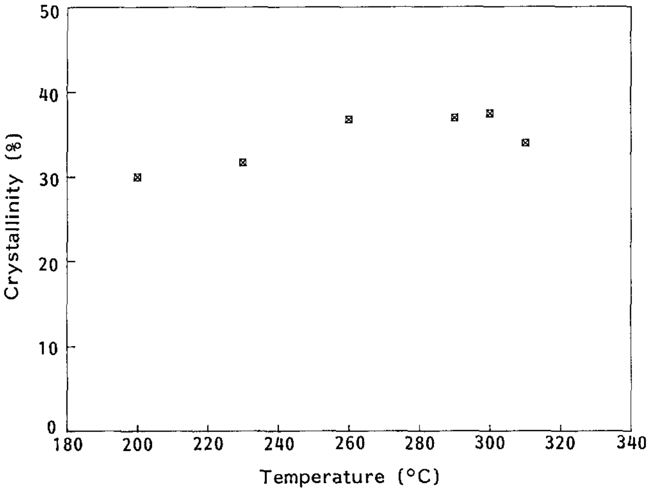

Figure 5 X-ray crystallinity as a function of temperature of crystallization or post-annealing

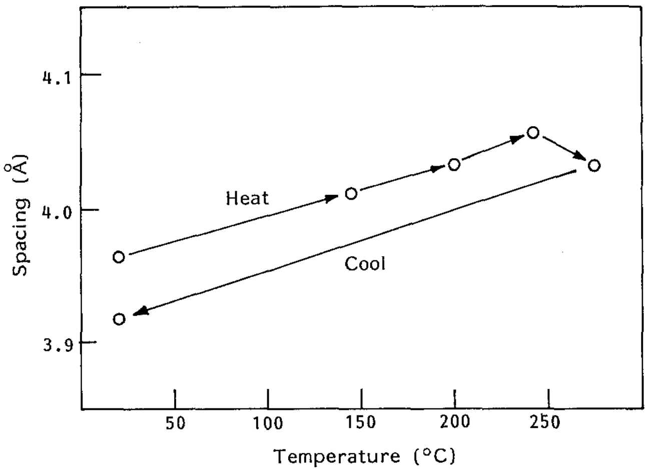

Figure 6 Variation of spacing of {2 0 0} reflection during X-ray hot-stage experiment on sample originally crystallized at 200°C

To help elucidate the change in structure with temperature, a sample that had previously been isothermally crystallized at 200°C was also examined in a laboratory X-ray hot stage. The sample was heated in several stages to 275°C to record the WAXS pattern and then cooled to room temperature. Although the character of the diffraction profile was observed to remain the same, there were significant changes in the peak positions. These shifts can be partly attributed to thermal expansion and partly to changes of the crystal perfection. As an example, *Figure 6* shows a plot of the Bragg spacing of the {2 0 0} peak at around 23°C. On heating up to 240°C there is a gradual increase in spacing consistent with thermal expansion. However, when heated further to 275°C there is a distinct reduction in spacing, indicating a sudden change in the nature of the crystals. On cooling to room temperature, the spacing reduces owing to thermal shrinkage to a value below that of the original crystals.

Small-angle X-ray scattering

The long periods deduced from the SAXS are listed in *Table 1*. If one assumes that the crystalline morphology is entirely in the form of lamellae, then one can multiply the long period by the crystallinity to obtain an estimate for the thickness l_c of the lamellar crystals.

A plot of l_c as a function of crystallization and annealing temperature is shown in *Figure 7*. As in the case of crystallinity, l_c shows an increase with increasing temperature although there appears to be a definite jump in value from about 35 Å at 200 and 230°C to above 50 Å for 260°C and above.

Daresbury SAXS temperature scans

Figures 8 and *9* show the change in SAXS patterns taken at 10 s intervals while two of the samples were being heated at 10°C min^{-1}. To help follow the changes, each figure shows four sequences of frames covering approximately successive 50°C ranges.

The results for the 260°C crystallized sample in *Figure 8* show a uniform, gradual increase in peak height and a very gradual shift in position while being heated between 150 and 250°C. Assuming that this diffraction peak is being caused by a stack of lamellar crystals, then these shifts are reasonably consistent with thermal expansion caused mainly by the dilation of the amorphous material between the crystals. Beyond 260°C, there is a change in the rate of shift in height and position of the diffraction peak. This behaviour coincides with the lowest endotherm peak in the d.s.c. scan (*Figure 1d*) and is consistent with the onset of instability of the original crystals and the beginning of a continuous melting/recrystallization process. The last few frames in *Figure 8* above 300°C show the eventual melting of all the crystals and takes the form of a rapid disappearance of the diffraction peak as it moves to lower angle to become a shoulder, which then reduces to a monotonically falling curve.

The data for the 200°C crystallized sample in *Figure 9* show a similar gradual change in diffraction peak up to 200°C, consistent with thermal expansion. Beyond 200°C there is a change in the movement of the peak coinciding with the first d.s.c. endotherm and the onset of instability in the original crystals. After this there is a region of larger change in the peak consistent with a continuous melting/recrystallization process. At about 250°C, there is a sudden change in behaviour where the peak shows the characteristics of melting in which it tends to a shoulder at a lower angle. This is immediately

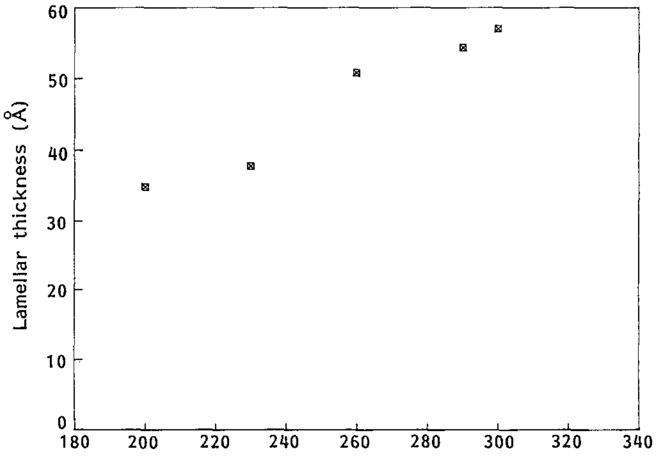

Figure 7 Deduced lamellar thickness as a function of temperature of crystallization or post-annealing

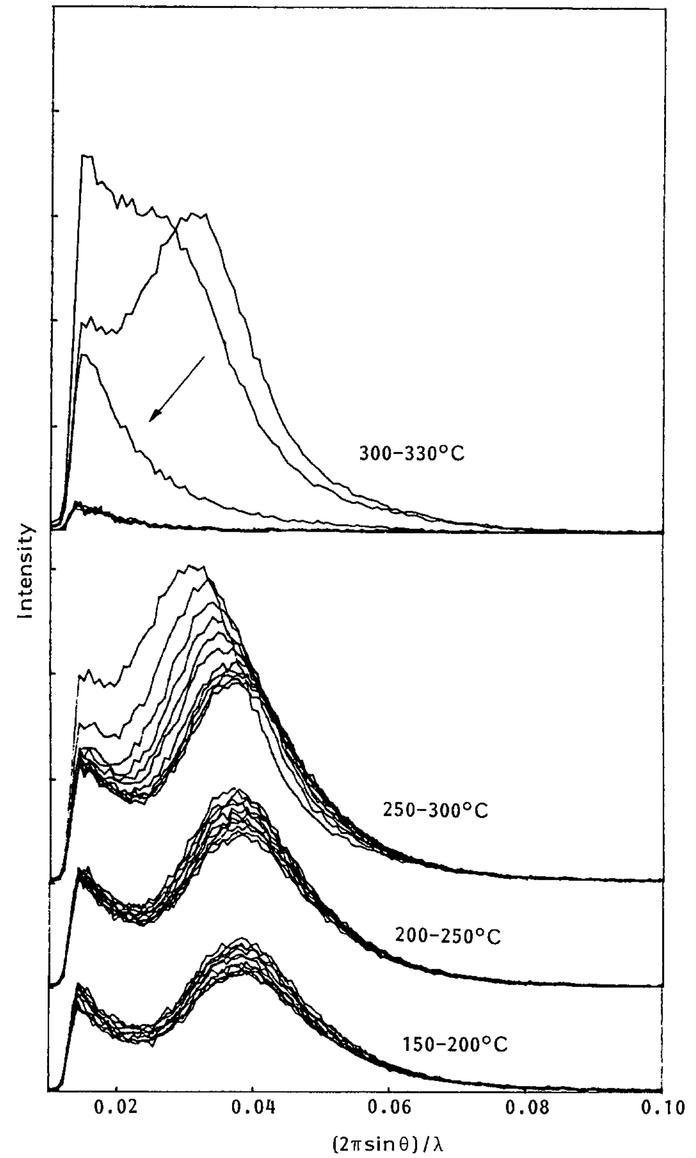

Figure 8 Temperature scan of SAXS from the Darebury synchrotron for sample crystallized at 260°C while scanning at 10°C min^{-1}

followed by the creation of a new, much larger peak. This series of events is consistent with the d.s.c. curve in *Figure 1b* in that it indicates the destruction of the original crystal morphology and its replacement by another crystal set of different character. The remainder of the data beyond 260°C closely follow the behaviour in *Figure 8* for the 260°C sample.

DISCUSSION

Interpretation of d.s.c. transitions

The melting/recrystallization process at around 260°C is a novel feature, and we are not aware of its occurrence in other polymers. For isothermally crystallized samples, experience with PEEK would lead one to expect just two melting processes similar to that shown in *Figure 1d* for the sample crystallized at 260°C, i.e. a smaller process about 15°C above the crystallization temperature and a larger final melting peak[8]. One favoured interpretation of this familiar effect is that the first peak represents the onset of instability of the crystals that formed during the previous isothermal crystallization process[7]. At this point the crystals begin to melt, but almost immediately start to recrystallize and anneal to a more stable crystal configuration so that the observed process only occurs as a small peak. In the region between the two peaks, the interpretation would be that there is a continuous melting and recrystallization that balance each other, so that no net process is seen in the d.s.c. trace. The final melting peak is then regarded as the region where the recrystallization process becomes slower than the d.s.c. scanning rate, so that there is a net total melting of all crystals.

Seen from the viewpoint of this interpretation for the normal two-peak phenomenon, the additional melting process at 255°C in *Figures 1b* and *1c* together with the associated pronounced exotherm at 260°C can be seen as a special case of melting and recrystallization. The main distinction according to both the d.s.c. and the Daresbury SAXS is that there is an indication that the original crystals are eliminated before the formation of a new population of crystals. That this should happen indicates that the new crystals are structurally distinct from the old crystals and that there is no easy transformation between the two. From this viewpoint it

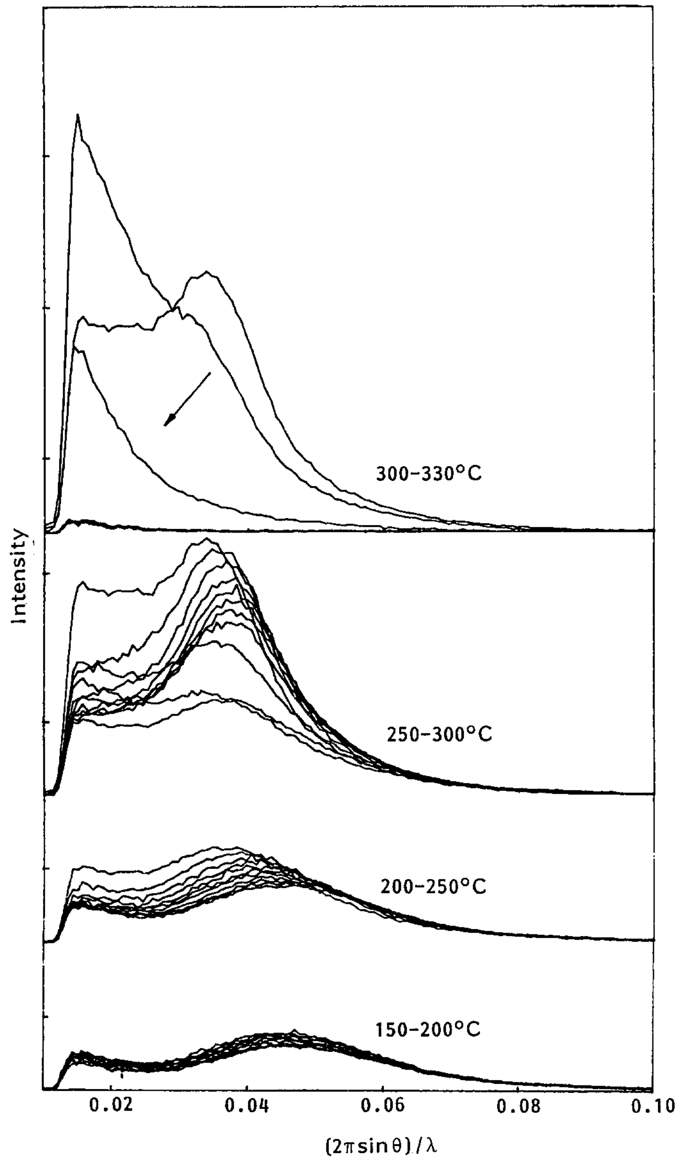

Figure 9 Temperature scan of SAXS from the Daresbury synchrotron for sample crystallized at 200°C while scanning at 10°C min^{-1}

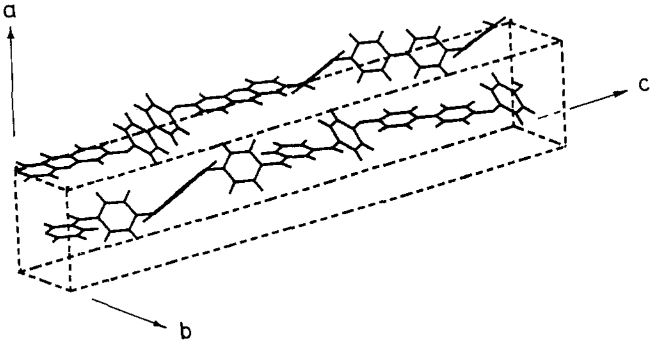

Figure 10 View of crystal unit cell

is surprising that the WAXS scans show no major change in the chain packing within the crystal structures. However, the long period and the crystallinity do show a slight step change in the crystal thickness. This is accompanied by improved crystal perfection as judged by the resolution of WAXS peaks and a small step change in the dimensions of the crystal cell. Thus from these data the dominant difference between the two sets of crytals is one of crystal size and perfection rather than the mode of chain packing. Such differences would account for a lower melting point for the first crystals. However, an explanation is still needed to account for why the old crystals appear to melt totally rather than smoothly recrystallize as in conventional behaviour. There must be a distinct difference in the crystal morphology that frustrates the easy transformation from one type of crystal to the other.

Link between crystal structure and lamellar morphology

At this point it is pertinent to introduce data on the crystal structure that has been gained from other experimental work, which will be reported elsewhere. The information was obtained by using diffraction modelling software to analyse and simulate X-ray fibre patterns diffracted from a uniaxially oriented sample of the PK99 polymer. From this study the crystal structure was determined to be orthorhombic with lattice parameters $a = 7.85$ Å, $b = 6.05$ Å and $c = 47.7$ Å; there was found to be two chains in the unit cell, giving a crystal density of 1.374 g ml^{-1}. The conformation of the chains in a crystal is shown in *Figure 10*. The salient points to note are that the *para*-phenyl links (including the all-planar biphenyl units) form a planar zigzag backbone, which is analogous to that in the crystals of all-*para* polymers such as PEEK and PEK. The planes of the neighbouring *para*-phenyl units are torsionally rotated in opposite directions on either side of the ether or ketone links relative to the zigzag plane. However, in the case of the *meta*-phenyl, the plane of the phenyl ring is aligned in the plane of the *para*-ring zigzag. Thus there is no torsional rotation of the *meta* ring relative to bordering ketone links. Semi-empirical molecular-orbital calculations have also been carried out on the energy associated with torsional rotation about the ketone link. These show that the 0° torsion does not represent the lowest energy conformation and infers that the adoption of this conformation around the *meta*-phenyl unit in the PK99 crystal structure imposes an energy penalty relative to that of an equivalent all *para*-phenyl unit cell.

If one compares the crystal conformation in *Figure 10* with the experimental results for the crystal thickness l_c, one finds that the l_c are comparable in magnitude to the crystal periodic repeat of 47.7 Å. In fact, for samples crystallized at low temperatures, l_c is significantly smaller. One is therefore dealing with a novel situation in which the lamellar crystals are not strictly 3D crystals, in that the full 3D lattice is not achieved in the *c*-axis chain direction because the lamella is not thick enough. However, the chains still pack laterally in the same way that they would do if the crystal had been infinitely thick and there are also enough atoms in the lamella to give a diffraction pattern with a typical crystalline character.

Given this situation, we can now proceed to propose an explanation for the unusual behaviour of this polymer. From the above crystal data one can see that for samples crystallized at low temperatures where l_c is small (~ 30 Å), there is more than one way of choosing the units along the chain that can be incorporated into a lamellar crystal. Various examples are shown in *Figure 11*. Example 2 incorporates one *meta* unit in the middle of the sequence, whereas in example 1 the only *meta* units are those confined to the borders.

Remembering the energy penalty associated with incorporating a *meta* group with zero torsion angle, one can now see how two distinct lamellar types can occur with quite different melting and crystallization characteristics. One can speculate that, for the samples crystallized at 200 and 230°C, lamellae are formed incorporating a sequence such as in example 1, where there are no centrally placed *meta* units that are able to impose an energy penalty from the zero-torsion-angle conformation. Accordingly, such lamellae will have a maximum thickness to which they can grow without fully incorporating a *meta* unit. This maximum thickness is ~ 30 Å and agrees very reasonably with the estimated l_c deduced for the samples crystallized at 200 and 230°C. A crystal of this thickness will have a well defined melting point and we propose that this melting point is around 255°C, corresponding to the endotherm that immediately precedes the sharp 260°C crystallization exotherm. Thus for temperatures beyond 255°C, such lamellae will either have to melt or thicken so as to incorporate bordering *meta* groups. We suggest that it is easier for them to melt and for completely new lamellae to be nucleated comprising sequences as in example 2, with one *meta* unit in the middle. Samples crystallized above 260°C would also adopt this second sequence at the time of formation. This second type of lamellae would be able to thicken up to about 50 Å while still incorporating only one *meta* unit. This maximum size would again have an associated melting point, which we would suggest

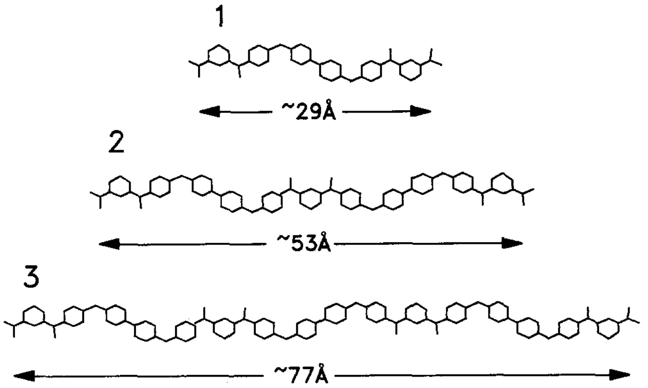

Figure 11 Possible chain sequences incorporated in crystal lamellae

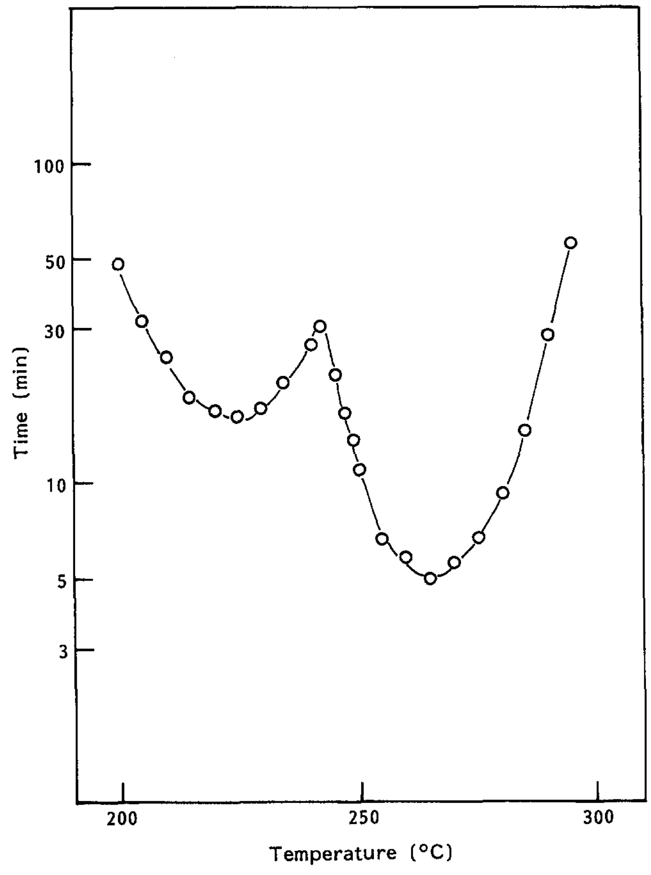

Figure 12 Times to the peak in the crystallization process when crystallized isothermally in a d.s.c.

corresponds to the normal upper d.s.c. melting peak at about 306°C. Beyond this temperature we would suggest, as in the previous case, that the second lamellar type will melt and, if the conditions are suitable (i.e. very slow heating rates or long annealing times), a third type of lamellae will grow incorporating a sequence as in example 3, with two central *meta* groups. We would suggest that the extra high melting process of the sample annealed at 310°C can be attributed to the melting of such lamellae. In principle, even thicker lamellar types incorporating more *meta*-phenyl groups could occur providing suitable conditions for their growth exist.

Upper melting point

According to the above discussion there are two explanations for the low melting point of PK99. First, on thermodynamic grounds the energy penalty associated with the incorporation of *meta*-phenyls in the crystal will reduce the enthalpy of fusion of the polymer and hence the thermodynamic melting point. This would account for why the deduced value of 125 J g^{-1} is lower than for PEEK. However, because of the way the lamellar thickness interacts with the chain sequences within the lamellae, there is also a kinetic explanation, which is associated with the inability of the polymer to reorganize while being heated. It would appear that it is difficult for one type of sequence to thicken to the next longest sequence without first undergoing a partial melting. We can therefore propose that a reason why a higher melting point is not observed at normal heating rates is that there is unsufficient time for thicker types of lamellae to nucleate and grow after the second type has melted.

Crystallization processes

With the above model for the different lamellar types, an explanation can now be proposed to explain the unusual variation of the crystallization rate. *Figure 12* shows the crystallization times described in our previous paper. Instead of the conventional U behaviour with a minimum (i.e. maximum in rate) approximately half-way between T_g and T_m, one observes two minima indicating the occurrence of two distinct crystallization processes. Interestingly they span the temperature regions that closely correspond to those associated with the types of lamellar crystals.

As pointed out in our previous paper, this behaviour bears a close resemblance to observations on long-chain paraffins by Keller and Ungar[10]. In the case of the paraffins, Keller and Ungar identified the lower process with crystals in which the molecules are once-folded and the upper process where the molecules are fully extended in the crystal. They deduced that if the crystallization temperature is decreased through the upper region, a point is reached where the once-folded configuration competes for the crystallization process on the growing crystal faces and begins to frustrate the growth of the chain-extended molecules. The overall growth rate is therefore reduced, but increases again when the temperature is low enough for the once-folded growth to become dominant. Interestingly, in this case, the chain packing within the crystals themselves is identical for both types of crystal. Similar observations of a growth-rate minimum have since been reported for poly(ethylene oxide) by Cheng and Chen[11].

One can make a direct analogy with the paraffins by relating the once-folded and extended crystals to the lamellar types in PK99. The region between the two minima in *Figure 12* corresponds to where the two crystal growth processes are competing and frustrating the overall growth rate. If this competition had not occurred, then we would have expected the crystallization rate of the type II crystals to have continued to increase on cooling and to have reached a minimum around 240°C rather than the frustrated maximum observed.

CONCLUSIONS

The X-ray data show that crystals grown above and below the unusual 250–260°C transition region have essentially the same chain packing. The main differences are in their degree of perfection and their lamellar thickness.

The lamellar thicknesses are comparable to and often smaller than the periodic repeat along a chain. This is a new situation not normally observed in other crystalline polymers. As a consequence, the crystal lamellae do not constitute a true three-dimensional lattice. Lamellae can differ in their character according to the particular sequence of chain that they incorporate. It is proposed that lamellae that form below 260°C are about 30 Å thick or less and are composed of sequences where the *meta*-phenyl groups are excluded from their centres. Above 260°C, the lamellae contain one *meta*-phenyl in the middle and can thicken up to about 50 Å. This second type of lamellae melt around 306°C and are associated with the normally observed melting point. Further, thicker types of lamellae can exist containing more than one *meta* sequence in their centre and exhibiting higher melting points. However, they will be unable to form unless there is suitable annealing with slow enough heating rates.

The two crystallization processes that have been identified in the growth-rate experiments are attributable to the first and second types of lamellae. The minimum in the growth rate is the result of a competition between the two processes frustrating the overall crystallization rate.

The abnormally low T_m of this polymer is partly due to the energy penalty of incorporating *meta*-phenyl sequences in the crystal lamellae. However, it is also due to the failure in the timescale of a d.s.c. scan for the polymer to recrystallize to form thicker types of lamellae once the second type of lamellae have been removed.

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