On the interpretation of multiple melting peaks in poly(ether ether ketone)

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The double-peak differential scanning calorimetry melting endotherms from isothermally crystallized poly(ether ether ketone) have been scrutinized in terms of two hypotheses: (i) they are due to two separate crystal morphologies; (ii) they are attributable to recrystallization effects. Supplementary data from density, wide-angle X-ray scattering and small-angle X-ray scattering suggest that (ii) is the most appropriate.

(Keywords: PEEK; d.s.c.; multiple melting endotherms; lamellar morphology)

INTRODUCTION

Multiple melting peaks have been observed in many semicrystalline homopolymers. The origin of the phenomenon was the subject of intense activity in the early days of thermal analysis of polymers. The effect is most vividly demonstrated on samples of polymers such as poly(ethylene terephthalate) (PET), which have been previously crystallized isothermally. In such a case, two endothermic melting peaks are observed in subsequent d.s.c. scans; a minor low-temperature peak a few degrees above the prior crystallization temperature and a major high-temperature peak (~250°C for PET). The explanations that have been proposed for these two peaks can be grouped into two main hypotheses:

(i) The peaks are associated with two distinct crystals or morphologies[1,2].

(ii) The peaks are related to a melting and recrystallization phenomenon of one initial crystal morphology which is characteristic of the prior crystallization history[3,4]. Accordingly it has been proposed that the lower peak is indicative of the onset of melting of the characteristic crystals. In the interval between the peaks, all the molecules experience a continuous melting and recrystallization process. The upper peak indicates the point at which the net difference between melting and recrystallization passes through a maximum.

Hypothesis (ii) has tended to be the explanation favoured by most workers. In 1983 we published a paper on the morphology of ICI's new high-performance polymer 'Victrex PEEK' (poly(ether ether ketone)) and showed that the crystallization behaviour is closely analogous to PET[5]. In particular PEEK also exhibits multiple melting peaks and we concluded they were also consistent with hypothesis (ii). More recently two papers have appeared on PEEK which challenge this interpretation. Both Cebe and Hong[6] and Cheng, Cao and Wunderlich[7] ascribe the larger upper peak to the melting of the main crystal population grown during the isothermal crystallization and the smaller lower peak to the less stable, secondary population formed in intermediate spaces.

Following the approaches of various workers on PET[3,4], we have therefore carried out further experiments to check the above hypothesis for the case of PEEK. We feel the results still substantiate our original conclusions.

The experimental approach has been to obtain structural information that is representative of a sample as it is being heated in a d.s.c., in particular in the region between the two melting peaks. If hypothesis (i) is correct there should be no substantial change until the main upper peak is reached. If hypothesis (ii) is correct, one would expect a continuous change as a result of the recrystallization process. Samples were prepared that were large enough to allow other structural tools to be brought to bear. The starting material was an isothermally crystallized sheet of PEEK which exhibited two endotherms. Parts of the sheet were post-annealed for short times at temperatures between the peaks in an attempt to simulate the morphology during a scan.

Supplementary experiments in a d.s.c. on samples whose initial scan is interrupted and then cooled show reheat scans that are almost identical to those of the post-annealed samples.

SPECIMEN PREPARATION

Specimens were prepared from reasonable-sized 250 μm thick films so that data could be obtained from the supplementary techniques of wide-angle and small-angle X-ray diffraction (WAXS and SAXS) and from density measurements.

The main starting specimen was isothermally crystallized by clamping amorphous PEEK film for 30 min in a hot press, maintained at 210°C. After 30 min, the film was quenched to room temperature.

The control film was then cut into smaller pieces which were then post-annealed at various temperatures between 210°C and the melting temperature 335°C. The object was to subject the control sample to thermal histories that were representative of that experienced during a d.s.c. heating scan. This was achieved by clamping pieces of film for 2 min in a press held successively at 250, 275 and 300°C. A time of 2 min was chosen since it was judged to be long enough to allow the whole sample to equilibrate to the annealing temperature and yet short enough to be

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representative of the transient conditions occurring during a 20°C min^{-1} d.s.c. scan. We wished to avoid excessively long times, especially at high temperatures (>300°C), to avoid complications from isothermal thickening of crystals. It is felt that some of the effects observed by Cheng *et al.* by crystallizing at 310°C for times up to 2 h (figure 18 in ref. 7) can be attributed to isothermal thickening of the crystals after formation, increasing the crystal stability and strengthening the prominence of their *lower* melting peak.

EXPERIMENTAL

All specimens (the 210°C isothermally crystallized film and the three post-annealed films) were examined by the following techniques.

Differential scanning calorimetry

10 mg specimens were heated at 20°C min^{-1} and 2 mg specimens at 80°C min^{-1} using a Perkin–Elmer DSC-7.

Wide-angle X-ray scattering

The films were examined with a Philips vertical diffractometer in the transmission mode.

Small-angle X-ray scattering

The films were examined in a Kratky camera using a position-sensitive detector. After background subtraction, the intensity profile was desmeared and Lorentz corrected by multiplying by the factor $16\pi\sin^2\theta/\lambda$.

Density

This was measured in a density gradient column.

RESULTS

D.s.c. scans at 20°C min^{-1} and 80°C min^{-1} are shown in *Figures 1* and *2* respectively. Both sets clearly show the two peaks in question for the control sample. The effect of the short post-annealing treatment is to shift the smaller, lower peak upwards to a temperature that is typically 20 to 30°C above the post-annealing temperature. In fact the appearance of the d.s.c. traces is very similar to that expected by isothermally crystallizing at the annealing temperatures. In both figures, it should be noted that the shape of the main upper peak remains unchanged as a result of the post-annealing treatment. The lower peak appears as a movable superimposed feature on the side of the main peak.

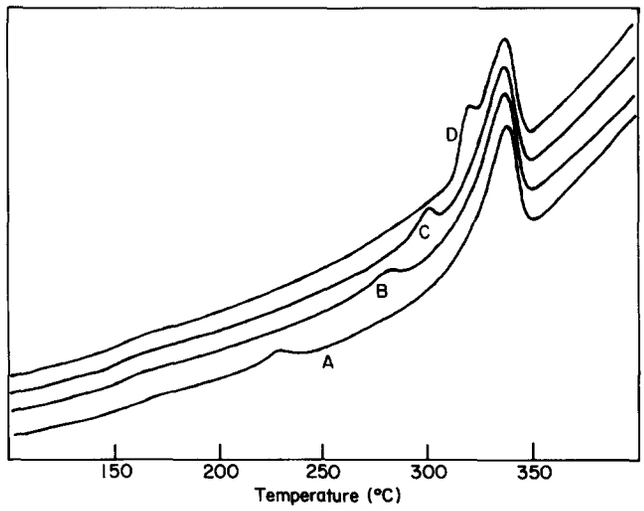

Figure 1 D.s.c. melting scans at 20°C min^{-1}: A, control sample; B, C and D, post-annealed at 250°C, 275°C and 300°C, respectively

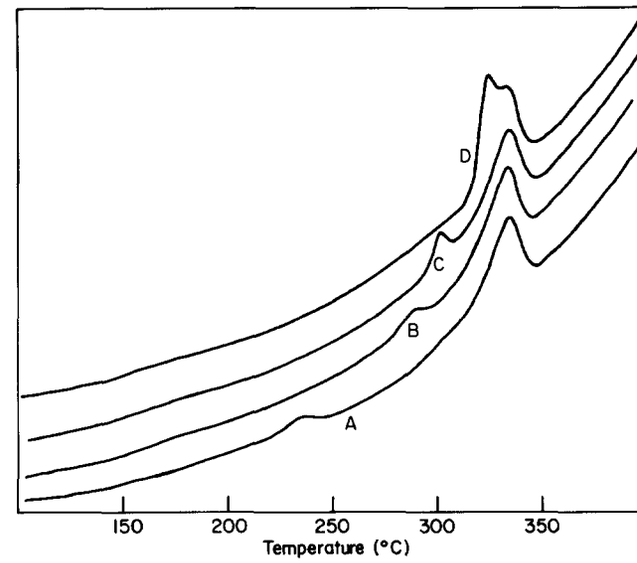

Figure 2 D.s.c. scans at 80°C min^{-1}: A, control sample; B, C and D, post-annealed at 250°C, 275°C and 300°C, respectively

Table 1 D.s.c. peak positions

	20°C min^{-1}		80°C min^{-1}	
Sample	Lower (°C)	Upper (°C)	Lower (°C)	Upper (°C)
Control: crystallized 210°C	228	337	234	334
Annealed 250°C	283	337	287	334
Annealed 275°C	300	337	302	334
Annealed 300°C	320	337	325	334

The positions of the two peaks are listed in *Table 1*. The effect of increasing the heating rate is to shift the positions of the two peaks in opposite directions. The lower endotherm position increases by a few degrees, whereas the main upper is moved downwards by about the same amount.

Table 2 shows the density measurements and the crystallinities that are deduced using the two-phase model with crystalline density $\rho_C = 1.400\,\text{g ml}^{-1}$ and an amorphous density $\rho_A = 1.263\,\text{g ml}^{-1}$. There is a systematic increase in crystallinity with increasing annealing temperature.

The WAXS scans are shown in *Figure 3*. A diffraction profile from an amorphous sample has been scaled to fit these profiles following the method used in our previous papers. The estimated crystallinities obtained from the integrated intensity above and below the fitted profile are listed in *Table 2*. They agree well with the density estimates and again show the systematic increase of crystallinity with annealing. One should also note that this crystallinity increase is accompanied by a steady sharpening of the crystalline diffraction peaks, implying that the crystallinity increase is also associated with an overall improvement in the quality and perfection of the crystals.

Table 2 Crystallinity data

Sample	Density (g cm^{-3})	Crystallinity (%)		SAXS	
		From density	From WAXS	Long period (Å)	Invariant η^2 ((mol elect)^2 cm^{-3})
Control: crystallized 210°C	1.2945	24.9	26.7	112	1.21×10^{-3}
Post-anneal 250°C	1.2968	26.6	28.5	119	1.24×10^{-3}
Post-anneal 275°C	1.2980	27.6	30.7	126	1.39×10^{-3}
Post-anneal 300°C	1.3020	30.6	32.2	135	1.44×10^{-3}

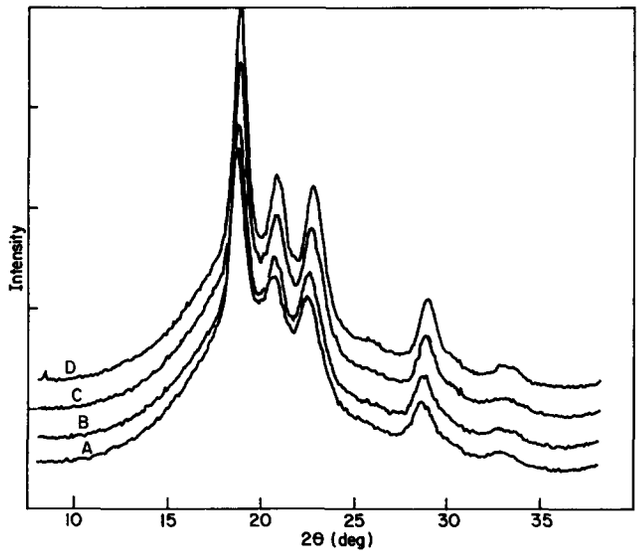

Figure 3 WAXS diffractograms: A, control sample; B, C and D, post-annealed at 250°C, 275°C and 300°C, respectively

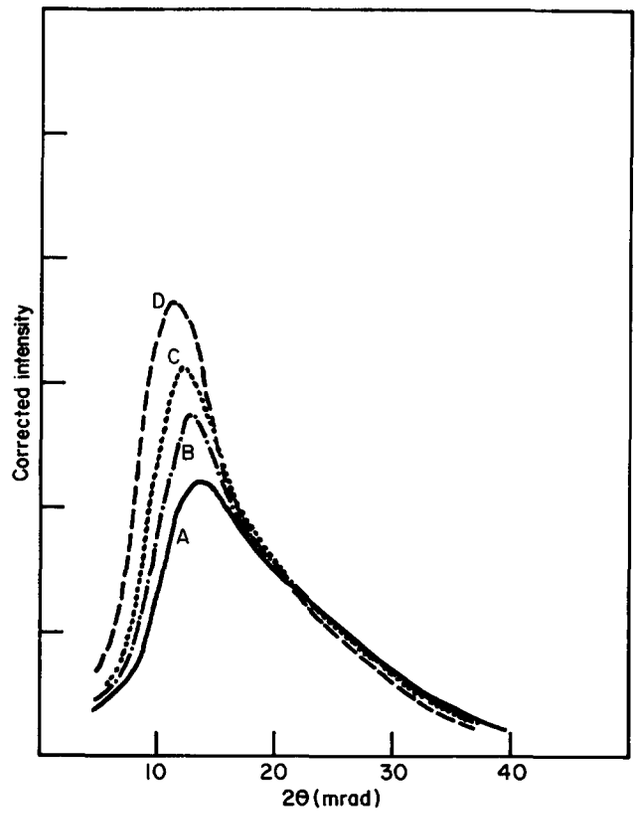

Figure 4 Corrected, desmeared SAXS intensity profiles: A, control sample; B, C and D, post-annealed at 250°C, 275°C and 300°C, respectively

The corrected SAXS curves are shown in *Figure 4* and show a steady movement in the peak maximum to lower angles, together with an increase in the intensity of the peak. The Bragg long periods obtained from the peak positions are listed in *Table 2* and indicate a significant increase in the periodicity of stacking of the crystalline lamellar structure as a result of the short annealing. The integrated slit smeared intensity (η^2) (i.e. invariant integral) has been estimated and is expressed in absolute units in the table. This also increases with annealing. The variation of the invariant integral is in agreement with a two-phase crystal/amorphous structure whose crystallinity is given by the experimental estimates in *Table 1* and whose crystal and amorphous densities have the values quoted above. Thus as far as crystallinity and overall lamellar structure are concerned, there is a self-consistency between all the structural data and a two-phase crystal/amorphous lamellar model, in which the crystallinity is increasing with the post-annealing treatment.

DISCUSSION

The three post-annealed samples were prepared in the belief that they would consist of a crystalline morphology that is representative of the instantaneous morphology inside a d.s.c. sample at various stages during a heating scan.

If we accept that the data from the post-annealed samples is meaningful in this context, then the explanation of the double melting peaks must be consistent with the following facts:

(1) The lower melting process is essentially the only feature that changes as a result of post-annealing; the profile of the main upper peak remains unchanged.

(2) Increasing the d.s.c. heating rate raises the position of the lower peak and lowers that of the upper peak.

(3) Crystallinity and overall crystal perfection systematically increase as the temperature is raised above the original isothermal crystallization temperature.

(4) The lamellar superstructure as revealed by SAXS systematically changes with temperature to give greater long periods.

These facts can be reconciled readily to the second of the two hypotheses involving the continuous recrystallization hypothesis of just one type of morphology. The continuous recrystallization hypothesis is clearly consistent with the changes in density, WAXS and SAXS data. The lower minor d.s.c. peak accordingly marks the point where the original isothermally formed

crystals become unstable and where the onset of melting and recrystallization occurs. If the heating is interrupted one will be left with a crystal population of greater stability than the originals. During subsequent reheating, the melting and recrystallization process will recommence and will be marked by another small peak at a corresponding higher temperature as seen in the post-annealed samples. The raising of the position of the lower peak with increasing heating rate reflects the superheating effect for the onset of the melting process. According to the second hypothesis, the main upper peak represents the point where the sum of the rate of melting and the rate of recrystallization goes through a maximum. The fact that the profile of this peak is unaffected by the prior history in the present samples suggests that the recrystallization process is mainly governed by the molecular characteristics and little affected by the starting crystal population. The decrease in the position of the main peak with increasing heating rate can be seen to be a consequence of the dynamics of the recrystallization process. At faster rates there is less time for recrystallization so that the maximum in the net melting will occur at a lower temperature.

It is more difficult to construe an explanation for the first hypothesis that is consistent with all the data. The explanation of the bare d.s.c. data by themselves is fairly straightforward. The upper peak represents the melting of the majority structure. As long as the temperature remains below this peak there will not be any melting of the structure. By inference the majority structure will have remained unchanged during the post-annealing process. The lower peak represents a minor proportion of material which is associated with a different structure or morphology. The upward shift of the lower peak after post-annealing would need to be ascribed to some recrystallization or reformation of the minor morphology during the preparation of the samples. One still needs an explanation of why the upper peak shifts downwards at faster heating rates. However the real difficulties with hypothesis (i) arise when considering the evidence from the other techniques. If one assumes that the main peak represents the true melting profile of the majority crystal morphology, then an explanation is needed as to why this peak remains unchanged when there is such a clear improvement in overall crystal perfection as shown by WAXS and why there was such a significant change in the size and relative arrangement of crystallites as revealed by SAXS. The only feature in the d.s.c. scan to change as a result of the post-annealing is the small lower peak, which only accounts for about 10% of the total endotherm. An explanation is needed of how the 10% minority crystal population can be arranged in the structure so that changes in it during post-annealing can cause the increases in both overall crystallinity and long period of crystallites as revealed by SAXS.

We believe the above evidence is strongly in favour of the recrystallization explanation as in hypothesis (ii). However, to obtain incontrovertible evidence we would agree that there is a need for direct information from high-resolution microscopy. To avoid ambiguity from isothermal thickening it would be important to study samples such as those used here which have been isothermally crystallized well below the melting point.

There is, however, further circumstantial evidence in favour of hypothesis (ii) from the relationship between crystal thickness and melting point which we discuss in ref. 5. According to the Thomson–Gibbs equation the melting point of a lamellar crystal with a finite thickness l_c is depressed from the equilibrium melting point T_m^* by an amount:

$$\frac{2T_m^*\sigma_e}{\Delta H_F \rho_c l_c}$$

where σ_e is the planar surface energy of the lamellae. By relating the depressed crystal melting point to the lower d.s.c. melting peak we were able to deduce that $\sigma_e \sim 50$ erg cm^{-2}. This value is comparable in magnitude to that found in other crystallizing polymers, although somewhat smaller than expected. However if we follow the dictates of hypothesis (i) and relate the same crystal thickness data to the upper d.s.c. melting peak then we would deduce a σ_e value closer to 5 erg cm^{-2}. This is considerably lower than would be anticipated and surely must cast further doubt on hypothesis (i).

A final comment is appropriate on the observations of Cheng *et al.* (figure 18 of ref. 7) which are used to substantiate hypothesis (i). In their experiments they interrupt isothermal crystallization at 310°C after various times and immediately scan the d.s.c. Their melting scans show the second upper peak appears first; this is interpreted as being associated with the melting distribution of the main crystal population. The lower peak only becomes more prominent as the crystallization proceeds and is attributed to a separate lower-melting crystal species. We would venture to suggest that hypothesis (ii) still adequately explains this observation and that in this case the lower peak is again associated with the onset of melting and recrystallization. Our experience with PEEK leads us to believe that significant isothermal thickening can occur during crystallization processes >300°C. We would suggest that as crystallization proceeds the previously formed crystals isothermally thicken to become more stable entities, so that the onset of melting/recrystallization at the first d.s.c. peak will occur at higher temperature and will become more pronounced. At the early stages, just after crystallization has started, the crystals are less stable and the recrystallization occurs immediately after the heating scan occurs, thus giving a melting endotherm with only the final peak observable.

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