On the origin of the multiple endotherms in PEEK

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Two models have been proposed to explain the two melting endotherms commonly observed in polyethers: (1) the crystals with the lower melting temperature may transform into a higher melting form during heating; (2) the two melting peaks come from separate populations of crystals. Our TEM studies of thin films of PEEK have shown two crystal populations, with widely differing lamellar thicknesses, which can occur in quite separate areas of the samples. These results strongly support the second model.

(Keywords: PEEK; TEM; separate crystal populations)

Introduction

There is considerable controversy in the literature concerning the origin of the two melting endotherms commonly observed in polyethers. The two melting peaks observed by d.s.c. are often separated by as much as 100°C. In PEEK the higher melting peak always occurs at a temperature of 330–340°C while the lower temperature peak may be seen at any temperature from ~200 to 330°C depending on the crystallization conditions.

Two opposing models have been proposed to explain this behaviour. In the first of these[1,2] it is supposed that the crystals with the low melting temperature form first and then transform into a higher melting form during annealing or heating. The cause of the increase in the melting temperature is suggested to be either the increasing perfection of the crystals or the thickening of the lamellae. The second model[3–5] suggests that the two melting peaks come from separate populations of crystals, the higher melting peak coming from the primary crystals and the lower melting peak coming from secondary crystals which may grow between the original crystals. The question of whether these secondary crystals form from parts of molecules which are also involved in the primary crystals or from another, separate population of molecules is left open.

In this communication some results obtained by combined d.s.c. and transmission electron microscopy (TEM) of PEEK are presented, which, we believe, permit us to distinguish between the two models. We shall argue that our results strongly support the second model and are not consistent with the first. We have used direct TEM on specially prepared thin films of PEEK. In this way, we have been able to observe the actual crystals giving rise to each of the melting peaks. We shall show that the two populations, which have widely differing lamellar thicknesses, can occur in separate areas of the samples. We take this to indicate that at least some of the molecules in the crystals with the lower melting temperature do not have any part in crystals with higher melting temperatures. Further, by performing TEM at high temperatures, we can observe the separate melting of the two sets of lamellae.

Experimental

Sample preparation. The polymer used was supplied by ICI in the form of an amorphous sheet. Samples (10 mg) for d.s.c. studies were cut from this sheet and prepared by suitable thermal treatment (see below). Thin film samples, suitable for direct TEM, were prepared from solution. PEEK was dissolved in benzophenone, and single crystals grown on slow cooling. The benzophenone was exchanged with acetone, and drops of solution placed on electron microscope grids; carbon support film was not used since carbon could cause crystal nucleation. The crystals were melted to form a thin film and subsequently subjected to various heat treatments, as detailed below.

All the d.s.c. experiments were carried out using a Perkin Elmer DSC2 and TEM work employed a Philips 301 microscope operating at 80 kV.

Results and discussion

D.s.c. experiments. Figure 1A shows a d.s.c. trace from a PEEK sample on heating from the glassy state (the sample was initially melted at 397°C for 10 min before quenching to room temperature). This trace, which shows the glass transition at ~140°C, the crystallization of the polymer during heating at ~170°C and its melting at ~340°C, is characteristic of PEEK. Similar results have been reported by many other workers.

It has also been shown by many authors that if a sample is cooled from the melt to a temperature, T_c, between the glass transition temperature (T_g) and the melting temperature (T_m) and held there, then a second melting endotherm appears at a temperature just above T_c. A similar effect occurs if a sample is rapidly heated from the glassy state and held at a temperature above T_g for some time before continuing to heat; an example of a d.s.c. trace obtained following such an experiment is shown in *Figure 1B*.

It has been argued from such results that on heating from the glass only one population of crystals is formed, while, on annealing, a second population grows. We were not convinced by this simplistic argument and performed a further experiment to test whether there are actually two populations in both cases. If the polymer is cooled from the melt as fast as the d.s.c. permits to a temperature

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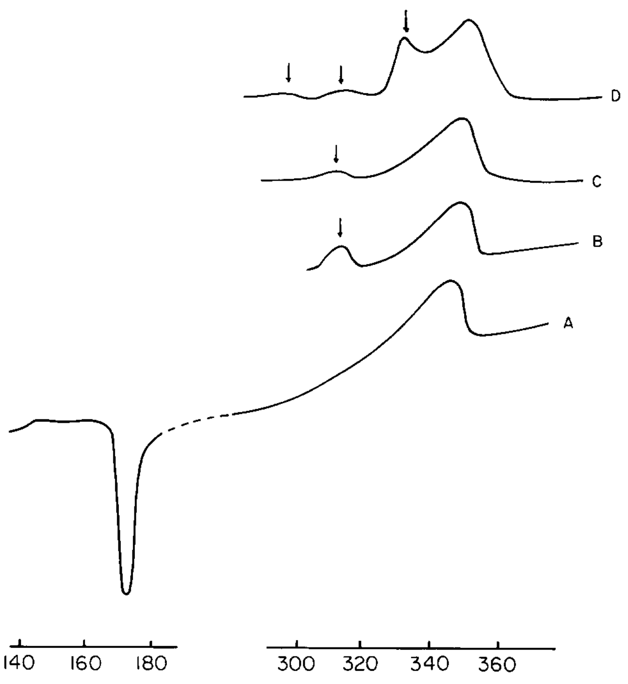

Figure 1 D.s.c. traces obtained on heating various PEEK samples at 10°C min^{-1}. Sample preparation as follows: (A) sample heated from the glass. Glass obtained by melting at 397°C for 10 min before quenching to room temperature; (B) sample heated from the glass to 237°C, held for 10 min before further heating; (C) sample quenched to a glass, heated at 10°C min^{-1} to 307°C, quenched to 237°C and then reheated (only the latter part of the trace is shown); (D) sample quenched to a glass, heated at 10°C min^{-1} to 307°C and held for 30 min; quenched again to 237°C, then reheated to 287°C and held for a further 30 min. After further storage for 30 min at both 267 and 237°C the sample was heated to melting point, obtaining the trace shown

T_q, between T_g and T_m, and then immediately reheated at 10°C min^{-1}, then only a single melting peak is seen. However, if the polymer, after quenching, is heated at 10°C min^{-1} to an intermediate temperature, T_c, immediately quenched back to T_q and then again heated at 10°C min^{-1}, two melting endotherms are found, one just above T_c and the other at 340°C. This is shown in *Figure 1C*, where T_q was 237°C and T_c was 307°C.

As far as we are aware, this type of behaviour has not been reported previously. We suggest that the result indicates that on the original heating from 237 to 307°C some crystals were formed which annealed during the heating process, on cooling and reheating these all melted at a temperature just above 307°C. This behaviour indicates that the crystals which give rise to the low temperature endotherm can easily become more perfect in some way and hence increase their melting temperature. In practice they will display an endotherm at a temperature just above the highest temperature they have been heated to. In a continuous heating experiment there can be no such peak as there is no large population of crystals all of which have previously been heated to the same temperature. This suggests that there may be cases in the literature where it has been supposed that samples possess only one melting peak, and hence only one crystal population, when in fact there were two populations. This may help to resolve some of the apparent contradictions in the results from various groups.

We have thus established, in accordance with previous workers, that at least some of the material which crystallizes at low temperatures is able to rearrange itself so as to increase its melting temperature. We next tried to establish whether all the material was capable of behaving in this manner and whether it was possible to crystallize all the material at any temperature. A series of experiments was performed in which the sample was held at a series of progressively lower temperatures allowing it to crystallize as far as it was able at each temperature. The subsequent melting behaviour was then observed. The result of a typical experiment is shown in *Figure 1D*. It was found in every experiment that there was a melting endotherm at a temperature just above each of the temperatures at which the sample was held. A very long storage time at any higher crystallization temperature did not suppress crystallization at the lower temperatures. We were able to generate as many as five distinct endotherms in this way; similar results have been obtained previously[6].

We contend, from these results, that there is a range of molecules present; within this range there are some that cannot crystallize above any given temperature. Thus on holding a sample at some high temperature all those molecules, or parts of molecules, that can crystallize do so and the rest remain molten. Then, when the temperature is reduced again, further molecules, or parts of molecules, become able to crystallize and do so, and so on. In this way, we are assured that at each crystallization temperature we have grown crystals which possess the maximum possible stability. In other words, the crystals should melt just above the formation temperature as they will be unable to make themselves more perfect. If this is the case then we are led to suspect that there are two distinct populations of molecules, one which forms the crystals which melt at the highest temperature ($\sim$340°C) and one which gives crystals with broad distribution of lesser stability.

Electron microscopy. The arguments presented above suggest that there are two distinct populations of crystals; if we are correct it should be possible to observe both in the electron microscope. We prepared thin film samples of the PEEK in ways which, from our d.s.c. experiments, should have resulted in films giving only one melting peak and others which should have displayed two well separated peaks. Amorphous samples of PEEK appear featureless. *Figure 2a* shows a sample crystallized by cooling at 10°C from the melt (a procedure which gives a single peak in the d.s.c.), and *Figure 2b* shows a sample cooled from the melt as fast as possible to 237°C, then heated at 10°C min^{-1} to 307°C, held for 30 min and finally cooled rapidly to room temperature (a procedure which gives two distinct d.s.c. peaks).

It is clear from micrographs such as *Figure 2a* that in samples prepared in such a way as to give one melting peak, there are some large regions in which no crystals have grown and only glassy PEEK is visible. Where there are crystals they are of a uniform, lamellar nature with a lamellar thickness of $\sim$25 nm. In *Figure 2b*, however, we can see that there are two populations of crystals with differing lamellar thicknesses. The thicker crystals correspond to those in *Figure 2a* while the thinner ones have a thickness of $\sim$13 nm and are much smaller in lateral dimensions. These smaller crystals appear both between the thick lamellae and in the regions between spherulites, in some cases much more extensive regions than that

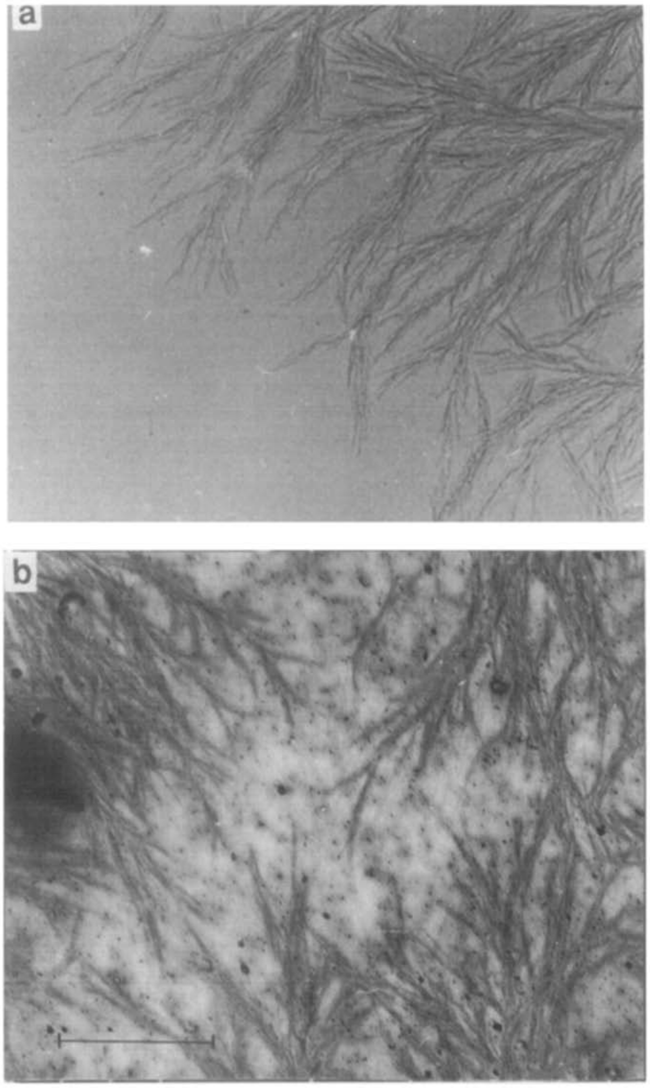

Figure 2 Transmission electron micrographs of thin films of PEEK. Details of sample preparation are given in the main text: (a) sample crystallized using a procedure which gives a single d.s.c. peak; only one crystal type is seen in the micrograph, together with regions of apparently amorphous polymer; (b) sample crystallized using a procedure which gives two d.s.c. peaks; two crystal types are clearly visible in the original micrograph; thicker crystals, as observed in (a), together with much thinner crystals which are rather difficult to reproduce photographically. Scale bar = 1 μm. Both prints are at the same magnification

shown in *Figure 2b*. The smaller crystals are more difficult to observe in photographic prints due to the lower contrast.

The fact that we can observe a single crystal population in the sample with a single melting endotherm and two populations in the sample with two endotherms is satisfactory but perhaps not surprising. However, the fact that many crystals belonging to the second population, present in *Figure 2b* and absent in *Figure 2a*, have clearly formed in quite extensive regions where no thick lamellae grew is important. It indicates a clear distinction in the molecular make-up of the two populations. It appears that there is some material which cannot form thick lamellae but can form the less stable thinner ones.

In order to test this hypothesis further, some experiments were carried out using a hot stage in the electron microscope. We hoped to observe the polymer at a temperature between the two melting peaks and see whether the thin lamellae melted to leave large areas of amorphous material or whether they transformed to leave the sample entirely made up of thick lamellae. In fact we found that on heating samples with two lamellar populations to any temperature between the melting temperatures of the two crystal types, the thinner crystals were first seen to melt. But then, within ~30 s, new populations of thin crystals began to grow, in the regions where the melting had taken place. The thicker crystals were unaffected by this process. This experiment clearly shows that the thin lamellae actually melt and do not transform into thick ones. We believe that the second population of thin crystals, growing at the melting temperature of the first group, are those appropriate to that crystallization temperature.

We also crystallized the polymer in the electron microscope. The sample was held at 307°C for 30 min. The development of the crystals after 6 min and after 30 min was observed. In both cases two populations of lamellae were present. The sample was then heated to 327°C and the thinner lamellae disappeared. Thus we have seen that during isothermal crystallization at 307°C both types of lamellae are formed at the same time.

Conclusions

We have shown that the two melting endotherms commonly observed in PEEK come from the melting of two distinct crystal populations. We have further shown that these populations can exist in widely separated areas of the sample. Thus we conclude that there are two populations of molecules in the sample which give rise to the two types of crystal. We may further conclude that the two populations of molecules can phase separate in the melt, since there are distinct regions where no thick lamellae grow. The difference between the two populations remains open—they may differ in molecular weight, in molecular perfection or in branch content.

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