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On crystallization, morphology and radiation effects in poly(ether ether ketone)

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The effects of high energy electron radiation on poly(ether ether ketone) (PEEK) have been investigated by differential scanning calorimetry (d.s.c.), transmission electron microscopy (TEM) and solvent extraction. It has been shown by extraction that irradiation results in the formation of crosslinks which affect the crystallization and reorganization kinetics and disrupt crystal structures. The d.s.c. behaviour is described in terms of two regimes: up to ~66 MGy the observed effects principally result from changes in the amorphous regions, whereas at higher doses crystal destruction appears to become increasingly important such that by 260 MGy only a small residual melting peak is observed. This characteristic radiation response can be employed as an expedient to prevent molecular reorganization without extensively disrupting the lamellar population. In this way the d.s.c. behaviour of PEEK has been studied in the absence of complications caused by annealing. It is shown that although some reorganization does normally occur, the high temperature melting endotherm is not purely an artifact of the experimental procedure. TEM examination reveals well-defined lamellar morphologies, even in specimens that have been irradiated to such a level that little or no d.s.c. endotherm remains. Despite the absence of a distinct d.s.c. melting transition, the morphology of such samples changes dramatically on heating to above their nominal melting temperature.

(Keywords: poly(ether ether ketone); electron radiation; morphology)

INTRODUCTION

Poly(ether ether ketone) (PEEK) has found many applications as a result of its combination of highly desirable properties. These include good processability, high mechanical strength and excellent stability in many harsh environments. This last factor has led to PEEK being adopted for use in situations where other materials have proved unsatisfactory for reasons of thermal or radiation stability. However, whilst thermal processes have been studied extensively over the last decade[1–12], the effects of ionizing radiation have received less attention. One possible reason for this is that for most practical engineering purposes the properties of PEEK appear completely unaffected by exposure to radiation doses of the magnitude experienced in, for example, routine power generation applications. To put the extraordinary radiation stability of PEEK into perspective, it is enlightening to compare some results obtained from PEEK with those derived from an aliphatic system, such as polyethylene.

In the absence of oxygen or other mobile reactive molecules, exposure of polyethylene to ionizing radiation results in bond scission and the formation of crosslinks. These serve to disrupt the crystal lattice such that at absorbed radiation doses of the order of 30 MGy, the crystalline component of the material is largely destroyed[13,14]. Conversely, in PEEK, crystalline order has been shown to be stable against prolonged electron irradiation[15]. On the basis of wide angle X-ray scattering results, Yoda[16] concluded that irradiation to 50 MGy effects a reduction in the average crystal thickness of some 15% as a result of some radiation-induced degradation process (presumed to be crosslinking) that occurs near the lamellar surfaces. Similar conclusions were also reached by Sasuga and Hagiwara[17] on the basis of mechanical relaxation measurements.

In contrast, whilst the crystalline component of PEEK appears largely unaffected by irradiation to moderate levels (~50 MGy), this is not true of amorphous PEEK. Indeed, differential scanning calorimetry (d.s.c.) examination of glassy PEEK similarly irradiated to 50 MGy has shown it to be incapable of crystallization as a consequence of the formation of defect structures which serve to prevent molecular reorganization on heating[18]. Therefore, on the basis of the limited evidence available, it would seem that ionizing radiation introduces defects

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into PEEK, and that, in semicrystalline materials these chemical changes are located predominantly within amorphous regions.

Whilst radiation is widely used technologically as a means of modifying the properties of polymers, in the case of PEEK it would appear that controlled irradiation may also serve as a useful experimental expedient, enabling molecular reorganization kinetics to be modified without incurring large scale crystallite destruction. This paper reports upon the first part of an investigation in which controlled irradiation is exploited to provide new insight into the crystallization, annealing and melting behaviour and microstructure of this polymer. Here, some general aspects of the radiation response of PEEK are considered together with the thermal behaviour of this polymer, as revealed by differential scanning calorimetry. Particular aspects of radiation effects in PEEK will be considered in more detail in subsequent publications.

EXPERIMENTAL

Materials

The PEEK considered here was obtained (from ICI International Materials Centre, Wilton) in the form of a 250 μm thick amorphous sheet; analysis by gel permeation chromatography (g.p.c.) gave number and mass average molecular mass values of 1.3×10^4 and 4.1×10^4, respectively. From this, three sample types were prepared. Samples of the first type were annealed at 200°C for 15 min and then irradiated, samples of the second type were annealed at 320°C for 16 h prior to irradiation, and samples of the third type were irradiated directly without any initial thermal treatment. Each of these sample types were prepared with a particular objective in mind. The second and third types of samples were chosen to represent extremes of structural thermal stability; prolonged annealing at 320°C was employed to give a stable crystal phase (i.e. little reorganization on heating), whereas in the amorphous sample set a high degree of molecular reorganization (i.e. crystallization) was possible. Finally, the specimens prepared at 200°C represented an intermediate case.

The three sample types described above will subsequently be referred to as 200A/*d*, 320A/*d* and G/*d*, respectively, where 200 or 320 refers to the temperature of the initial thermal treatment, A or G refers to the type of sample (respectively annealed or glassy) and *d* specifies the radiation dose received. In addition, M is also used in place of A or G in the above scheme to define samples prepared by crystallization from the melt. Thus, a sample designated 320A/66 would have been annealed at 320°C and then irradiated to 66 MGy.

Irradiation conditions

All irradiations were conducted using a van de Graaff electron accelerator operating at 1 MeV with total beam current of the order of 40 μA. Beam current densities were routinely measured at the sample plane using a Faraday cup and were generally of the order of 9 μA cm^{-2}. Absorbed radiation doses were estimated by a number of different methods. First, dose rates were calculated[19] using the measured beam current densities and a figure for the average electron energy loss rate in a material of density ρ. This approach resulted in a calculated dose rate for PEEK ($\rho \approx 1.3$ g cm^{-3} according to Blundell and Osborn[20]) of ~ 1.5 MGy min^{-1} under the above conditions. However, this figure is likely to represent something of an overestimate, since the sample thickness employed in this study was somewhat less than that required for optimum energy transfer[19]. In addition, an attempt was made to measure the electron energy deposition rate directly using amber dosemeters (type 3042B). These devices are ideally suited to the measurement of low doses at low dose rates. This required alterations to be made to the operating conditions of the accelerator in order to obtain readings, and these results were translated to the actual operating conditions used in the PEEK irradiations. Consequently, the derived dose rate of 0.8 MGy min^{-1} is rather unreliable. Finally, PEEK dose rates were estimated using data obtained in a previous study of irradiation effects in polyethylene. This work[21] suggested that under operating conditions of 1 MeV and 9 μA cm^{-2}, the absorbed dose rate for linear polyethylene is ~ 0.8 MGy min^{-1}. Correcting this figure for differences in density gives a PEEK dose rate of ~ 1.0 MGy min^{-1}. From the above figures, a final value of ~ 1.1 MGy min^{-1} was adopted for PEEK under the irradiation conditions described. On the basis of this, the results reported here are consistent with other published data on PEEK.

In order that the required doses could be achieved within a reasonable time-scale, a high dose rate such as that discussed above was essential. However, high dose rates can introduce problems as a result of sample heating. To minimize such effects, all irradiations were conducted on a water-cooled block, in air, using an auxiliary fan to assist energy dissipation further. Despite irradiation being conducted in air, no detrimental effects were anticipated as a consequence of oxidation. The reasons for this are two-fold. Firstly, at very high dose rates, oxidized skin depths are very small[22,23]. Secondly, previous experience suggests that even if high dose rate irradiation is conducted in vacuum, the concentration of radicals present at the end of the irradiation period is such that post-irradiative oxidation can occur on exposure of the sample to the atmosphere[21]. Thus it was concluded that the additional complications necessary for the irradiations to be conducted under inert conditions were not justified.

Calorimetry, microscopy and gel content

After irradiation, various PEEK samples were characterized to provide information concerning gel content, thermal behaviour and morphology. Gel content values were estimated simply by immersing small samples (~ 15 mg) of irradiated polymer in 10 g of hot trichloroacetic acid for 24 h. At the end of this period any remaining gel was thoroughly washed in distilled water and methanol and left to dry under vacuum before finallly being reweighed. Thermal characterization was performed using a Perkin–Elmer DSC 7 differential scanning calorimeter operating at a heating rate of 10 K min^{-1}. All post-irradiation annealing and recrystallization experiments were also performed using this instrument. Baseline corrections were carried out and temperature and enthalpy calibrations were performed against indium and checked with a range of organic melting point standards.

Finally, the internal morphologies present within a cross-section of representative samples were examined

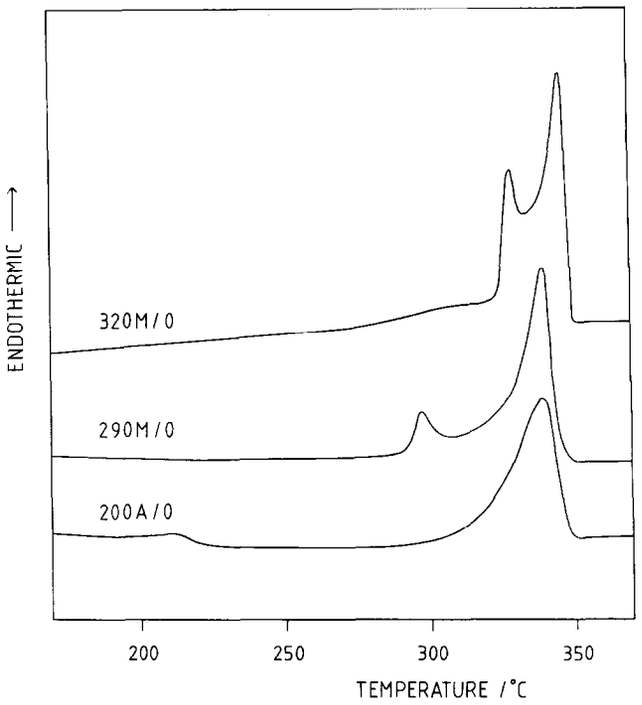

Figure 1 D.s.c. melting behaviour of unirradiated PEEK samples prepared isothermally at 200°C (200A/0), 290°C (290M/0) and 320°C (320M/0)

using an etching technique based on that first described by Bassett *et al.*[24]. Internal surfaces were first prepared by microtomy and were then etched with a 0.5% w/v solution of potassium permanganate in a 4/1 v/v mixture of orthophosphoric acid and water. After etching, the samples were thoroughly washed in distilled water and then methanol. Finally, the etched surfaces were replicated using a standard two-stage replication technique: an intermediate impression was first made in cellulose acetate, which was then shadowed and carbon coated; the acetate was finally dissolved to leave a clean replica ready for examination by TEM (Philips EM301).

RESULTS AND DISCUSSION

D.s.c. behaviour of unirradiated PEEK

Before considering the effect of electron radiation in modifying the thermal behaviour of PEEK, it is necessary to review briefly the behaviour of the unirradiated material. *Figure 1* contains three d.s.c. traces obtained from samples of PEEK prepared at different temperatures. Isothermal crystallization (from the melt) or annealing (from the glass) generally produces a material which, when heated in the d.s.c. experiment, gives a melting endotherm containing two distinct peaks: a relatively small feature 10–20°C above the crystallization or annealing temperature and another much larger peak at about 340°C. Although only three traces are shown here, the more detailed studies discussed below demonstrate the generality of this behaviour.

These general observations have been interpreted in a number of different ways. The d.s.c. melting behaviour of PEEK was first reported in 1983 by Blundell and Osborn[20]. In this and a subsequent paper[25], d.s.c. data of the type described above were interpreted, in conjunction with wide angle and small angle X-ray scattering results, in terms of a single initial crystal population, a proportion of which rapidly reorganizes during the course of the d.s.c. heating programme to give two peaks. In this analysis it was proposed that of the two endotherms, it is the small lower temperature one that is indicative of the onset of melting of the original lamellar population initially present in the sample prior to performing the scan; the upper peak results from reorganized lamellae that form during the course of heating in the d.s.c. scan. Alternatively, it has also been suggested by a number of independent groups[26–29] that the two peaks are, in truth, both representative of the original as-prepared material, being associated with two distinct lamellar populations. It is accepted that some reorganization does occur during the course of the d.s.c. heating scan, as in other polymers which exhibit a multiple-peak melting behaviour (e.g. isotactic polystyrene[30] or poly(ethylene terephthalate)[31]; see the following paper[32]), but in this analysis such effects are believed to be of secondary importance.

Whilst, in general, discussions concerning the interpretation of multiple melting peaks in PEEK have concentrated on comparing the two hypotheses outlined above, a third, somewhat intermediate analysis has also been proposed by Porter and coworkers[33,34]. These workers consider neither the upper nor lower peak melting temperature to be truly representative of the material as it exists prior to heating in the d.s.c. scan. In this interpretation, the lower temperature endotherm is believed to represent only a portion of the initial lamellar population, whilst the higher temperature endotherm is seen as resulting from a degree of reorganization. Thus, these workers envisage the initial lamellar population as being characterized, in the absence of any reorganization, by a single endotherm which peaks at a temperature between the two observed melting features and has a long tail extending down towards the sample crystallization temperature, i.e. to the small lower temperature transition.

Thus, summarizing the three hypotheses outlined above, in the first (hypothesis L) it is the small lower temperature endotherm that is believed to be more representative of the initial lamellar population; in the second (hypothesis U) it is the upper peak that is believed to define best the melting temperature of the initial morphology; and in the third (hypothesis I) the melting behaviour of the initial population, in the absence of reorganization, is believed to be characterized by an endotherm that peaks at some intermediate temperature. Although the above account contains the salient features of each hypothesis, simplifications have been made for the sake of brevity. Reference to the original publications is therefore recommended.

Radiation effects in PEEK

Figure 2 shows solvent extraction data obtained from the three specimen types examined in this study. Considering first the samples irradiated as amorphous sheets, it is clear from *Figure 2* that after an initial period ($\sim$6 MGy), the gel content increases with increasing dose until at $\sim$65 MGy the gel content levels off at about 75%. This behaviour indicates that during 1 MeV electron irradiation, the predominant process is cross-linking. These results are similar to those reported by Connell *et al.*[35], who studied the effects of 1 MeV

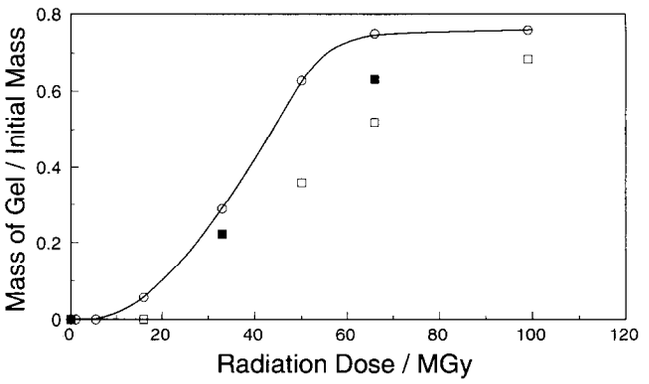

Figure 2 Gel content data for various PEEK samples obtained by solvent extraction with trichloroacetic acid: (○) G/*d* samples; (□) 200A/*d* samples; (■) 320A/*d* samples

electrons on a series of poly(arylene ethers) by g.p.c. and solvent extraction. Semicrystalline materials exhibit a similar response, although it is clear that more extended irradiation is required to produce the same gel content as in an amorphous sample. This behaviour can be explained in two ways: either crystalline molecular conformations are able to dissipate deposited energy in a manner that is less disruptive to the local molecular structure (cage effect[36]), or material that is more soluble may result simply because the network that is able to form is less uniform (the crosslinks are concentrated at certain sites) in semicrystalline materials than in similarly irradiated amorphous samples. Nevertheless, whatever the precise origins of the detailed effects revealed by *Figure 2*, it is sufficient to conclude that PEEK undergoes some crosslinking reaction on irradiation; no detailed chemical mechanisms are necessary and none are proposed.

D.s.c. behaviour of irradiated PEEK

Amorphous samples. *Figure 3* shows the d.s.c. crystallization and melting behaviour of PEEK samples irradiated in the glassy state to absorbed doses in the range 0–260 MGy. As the radiation dose increases, a number of effects become apparent, and in discussing these it is convenient to divide the samples into two groups on the basis of the radiation treatment received. Below 66 MGy, the induced changes are not of sufficient severity to prohibit crystallization of the material at appropriate temperatures. In the unirradiated case, crystallization occurs rapidly at ~20°C above T_g to give a narrow exotherm. However, as the absorbed dose increases, both the temperature of crystallization and the peak width increase, whilst the magnitude of the enthalpy of crystallization generally decreases. Concomitant with these changes are parallel reductions in both the peak melting temperature and enthalpy of fusion. These changes in behaviour, which are in good agreement with the limited data available elsewhere[18], are shown more quantitatively in *Figure 4*.

In *Figure 4b*, the upper line was derived by a linear regression analysis of all the melting data (first and second scans), whilst the lower line was similarly calculated from the crystallization transitions. Although in the case of PEEK the temperature interval between crystallization and subsequent melting is so large that the temperature dependence of the transition enthalpy is significant, this, in itself, cannot explain why the enthalpy of fusion repeatedly exceeds that of crystallization[37]. Rather, *Figure 4b* supports the notion that additional crystallization can occur between the initial exotherm and melting[37,38]. Whilst the crystallization and melting data are well separated at low doses, the situation becomes less clear above about 20 MGy: both the initial crystallization process and subsequent reorganization are being suppressed by irradiation.

Over the range 66–260 MGy, where no crystallization is observed, increasing the radiation dose results in a progressive increase in T_g. This effect is discussed more quantitatively later in this series of papers[39].

Samples annealed at 320°C. The d.s.c. melting behaviour of samples prepared at 320°C is shown in *Figure 5*. Although the melting endotherm obtained from the unirradiated sample is unusual for PEEK in that it does not contain two distinct peak (compare with the melting behaviour of 320M/0 shown in *Figure 1*), this trace is not believed to be anomalous; the result was entirely repeatable and similar traces have also been reported by other workers[5,40]. This distinction between melt crystallization and annealing from the glass will be discussed fully in a subsequent publication[41]. As in the case of the glassy samples, it is once again convenient to discuss these results in two groups.

Up to 66 MGy, the main effect of the radiation treatment is to cause slight shifts in the peak melting

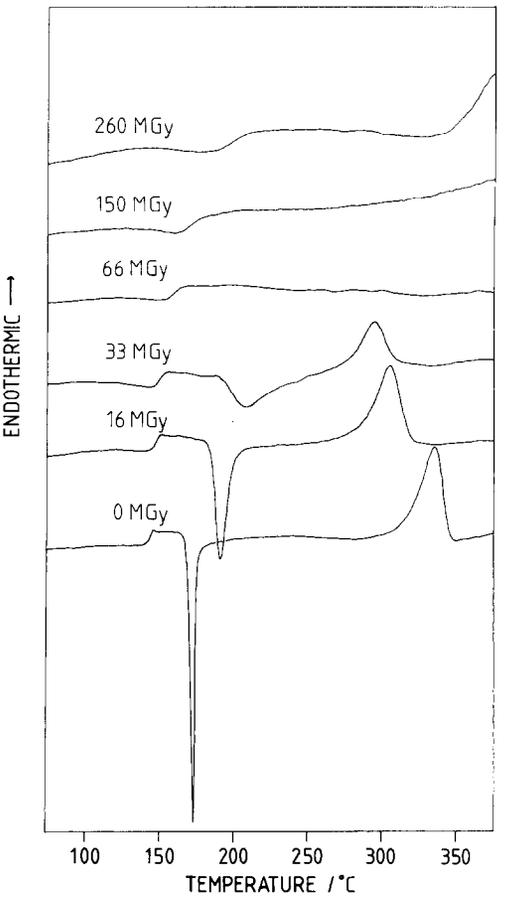

Figure 3 D.s.c. traces from PEEK samples irradiated in the form of amorphous sheets (G/*d*)

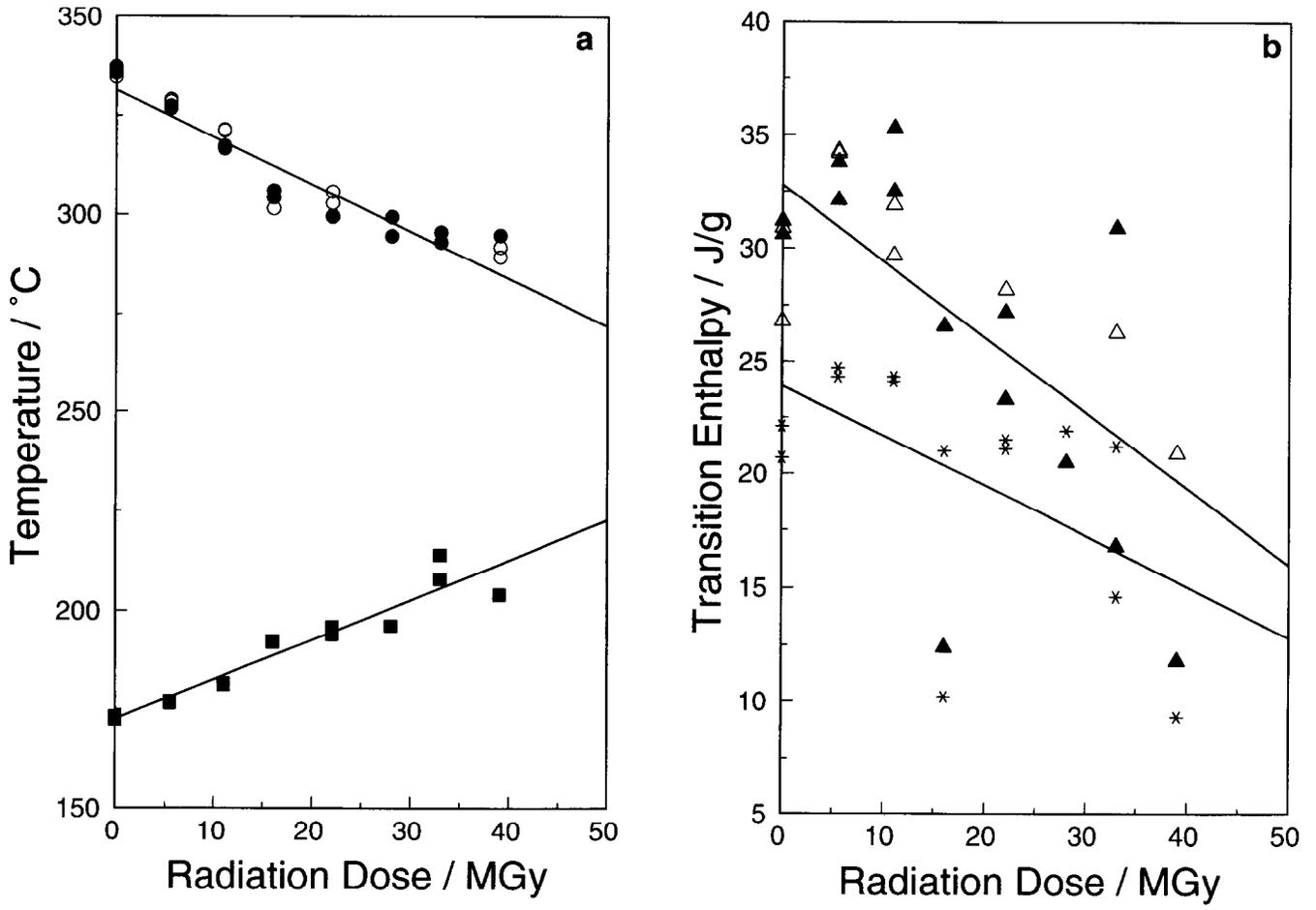

Figure 4 (a) Transition temperatures obtained from samples of PEEK irradiated as amorphous sheets (G/*d*): (●) first scan; (○) second scan (after melting and subsequent recrystallization at 200°C). (b) Transition enthalpies obtained following irradiation of amorphous PEEK (G/d). The lines shown were derived by linear regression analysis of the crystallization (lower, *) and melting (upper, first scan ▲ and second scan △) transition enthalpies

temperature, the peak shape remaining substantially unchanged. Initially, irradiation to low doses results in a displacement of the melting endotherm to higher temperatures. However, beyond about 30 MGy this trend is reversed, such that as the absorbed dose increases, the peak melting point decreases. This effect was explained by Flory[42] in terms of changes in the configurational entropy of the melt phase as a consequence of the formation of crosslinks. Similar radiation effects have previously been reported in well-crystallized polyethylene[14], and in a recent study it has been shown that thermally induced crosslinking reactions can also lead to a substantial increase in the observed melting temperature of PEEK[43]. The above is therefore a thermodynamic effect that is primarily associated with changes in the molecular configurations that are initially present within the amorphous phases and then, following melting, within the melt. However, what of the crystalline regions? On simple kinetic arguments, these samples, which were prepared by prolonged annealing at high temperatures, would not be expected to undergo substantial reorganization during the comparatively short time-scale involved in a d.s.c. scan. The annealing procedure used in their preparation is effectively analogous to a partial d.s.c. scan; the sample is heated to the temperature chosen for the isothermal preparation, held at that temperature and then cooled once again to room temperature. For the unirradiated sample shown in *Figure 5*, the time between reaching the annealing temperature and the completion of melting was only of the order of 2 min – too short a time for extensive lamellar thickening to occur at such temperatures, where crystallization kinetics will be relatively slow[44,45]. Thus, reorganization during the course of the d.s.c. experiments can be largely ignored as far as *Figure 5* is concerned, any changes in peak shape or position being attributable to radiation effects alone.

Figure 5 demonstrates that within the lower dose regime (up to 66 MGy), the effects of irradiation are not so significant as to cause major changes in either peak shape or peak melting temperature. However, at higher doses the endotherms do appear substantially different. These effects are quantified in *Figure 6*, which shows the variations of the peak melting temperature and enthalpy of fusion with radiation dose for the samples annealed at 320°C. In summary, the d.s.c. changes shown in *Figures 5* and *6* are consistent with radiation effects where at low doses, changes in the appearance of the d.s.c. trace are dominated by entropic considerations, i.e. changes in molecular configurations outside the crystals; however, at higher dose levels enthalpic terms become increasingly important, i.e. crystal modification.

It is useful at this point to contrast briefly the two sets of data so far considered. Whereas for samples irradiated in the non-crystalline state 66 MGy proved sufficient to

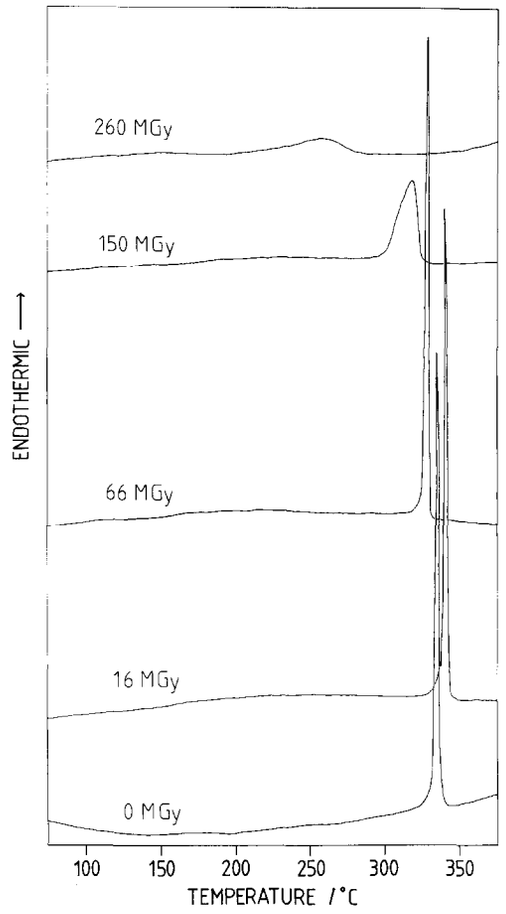

Figure 5 D.s.c. traces from PEEK samples irradiated after annealing at 320°C (320A/*d*)

suppress crystallization completely, *Figure 5* shows that for a well-crystallized material (the enthalpy of fusion of 320A/0 corresponds to a crystallinity level of 30%[37]) in which dynamic d.s.c. annealing effects are unimportant, irradiation to such a level manifests itself in only a slight depression of the melting endotherm and a reduction in the enthalpy of fusion of ~10%. Thus, to a first approximation it would appear that whilst a dose of 66 MGy is sufficient to prevent reorganization of non-crystalline regions, it does not constitute so severe a treatment as to result in the large scale destruction of crystallinity.

Samples annealed at 200°C. The two sample types considered thus far effectively represent extreme examples of PEEK as far as radiation and annealing effects are concerned. Glassy PEEK constitutes a material which reorganizes during the course of a d.s.c. experiment (in the absence of irradiation, crystallization occurs) and in which the effects of radiation on disordered molecular conformations can be studied. Conversely, the annealing procedure at 320°C was intended to give a material in which reorganization would not be significant, so enabling the effects of radiation on the crystalline melting behaviour to be studied in the absence of complications caused by reorganization during d.s.c.; the observed behaviour is entirely consistent with this hypothesis. Whilst both sets of samples are of some interest in their own right, of more consequence to the objectives of this study are materials that are initially semicrystalline but which, as a consequence of their thermal history, also possess the potential for reorganization.

Figure 7 shows a set of d.s.c. endotherms for PEEK samples initially prepared at 200°C. Examination of the trace of the unirradiated material reveals all the typical features, namely a glass transition at about 160°C, a small endotherm just above 200°C and a large peak at 336°C. Similar features can also be identified in sample 200A/16. However, whilst the radiation treatment does not appear to have substantially altered either the glass transition or the minor feature at 222°C, the temperature of the major endotherm has been substantially depressed. This behaviour is in marked contrast to that previously reported for 320A/16, in which an elevation of melting point was observed (compare *Figures 6a* and *8a*).

These observations may be explained in two ways. Firstly, the two thermal treatments will produce different crystal populations which respond very differently to the radiation treatment. Although the precise nature of the crystallites will undoubtedly influence their radiation resistance, the morphologies of 320A/0 and 200A/0 appear so similar (see the following section) that it is difficult to account for the markedly different behaviour entirely in this way. Alternatively, it is clear from the discussion of samples G/0–260 that even comparatively low radiation doses are sufficient to affect dramatically the crystallization (i.e. molecular reorganization) kinetics of PEEK. Thus, it would seem more reasonable that the observed reduction in the melting temperature of 200A/16 relative to that of 200A/0 is largely due to suppression of reorganization during the d.s.c. scan as a consequence of the radiation-induced changes. That is, the change in

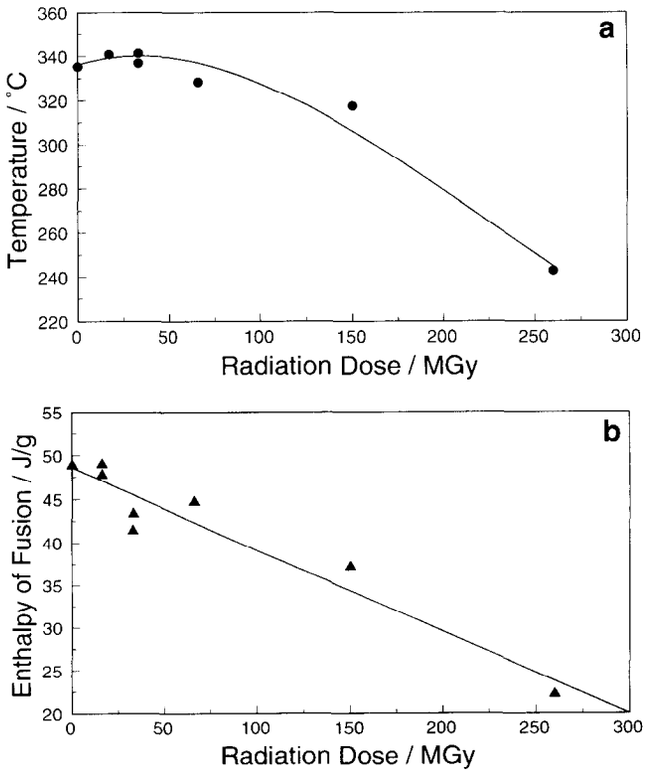

Figure 6 Melting transition data from samples prepared at 320°C (320A/*d*) as a function of radiation dose: (a) peak melting temperature; (b) enthalpy of fusion

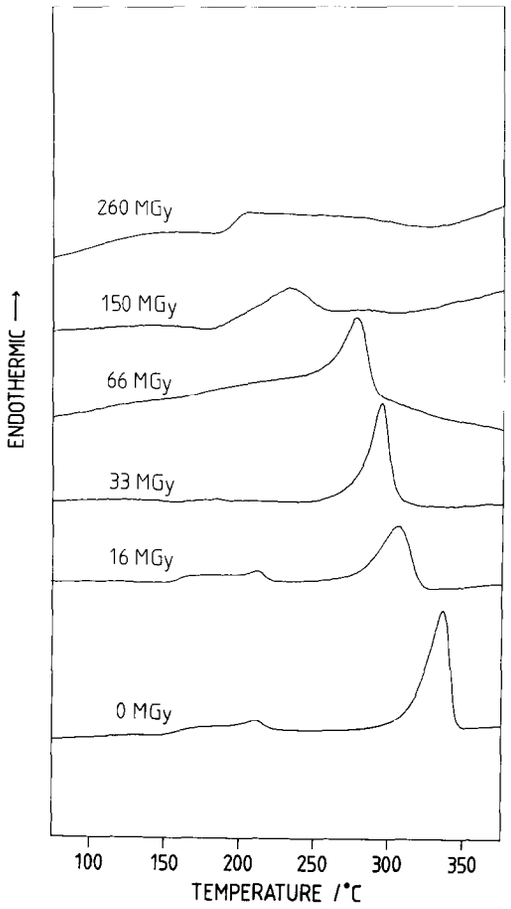

Figure 7 D.s.c. traces from PEEK samples irradiated after annealing at 200°C (200A/*d*)

the melting behaviour of the crystal population is an indirect effect resulting from changes in the molecular conformations present within the sample as a whole, rather than being a direct consequence of radiation damage within the lamellae themselves.

Further increases in absorbed dose lead to a progressive reduction in the peak temperature of the major endotherm and also, by 66 MGy, the development of a low temperature tail which extends down towards the glass transition to include the previously observable low temperature endotherm. It is useful at this point to compare in detail the d.s.c. behaviour of 200A/66 with that of 200A/0.

All the traces included in *Figures 1, 3, 5* and *7* are shown following background subtraction to remove, as far as possible, instrumental features such as baseline curvature. In 200A/0 the small peak at 222°C is followed by a reduction in heat flow into the sample between ~200°C and ~250°C compared with that between T_g and ~200°C. Such a change must either be associated with a reduction in the effective value of the specific heat capacity of the sample as a whole or must indicate combined partial melting and recrystallization in which the exothermic crystallization process dominates; this effect has previously been discussed by Cheng *et al.*[28]. However, in 200A/66 no similar change in power input is evident.

In view of the procedure used to prepare samples at 200°C, it is reasonable to assume that some reorganization will occur during a d.s.c. scan, although whether or not these changes are of a sufficient magnitude to affect the observed trace greatly has been the point of dispute in the literature. Nevertheless, in irradiated materials the kinetics of reorganization should depend upon the absorbed dose. Considering the data derived from traces such as those shown in *Figure 7*, typical values for the enthalpy of fusion (*Figure 8b*) indicate that the samples prepared at 200°C are initially ~26% crystalline[37], a figure that is reasonably typical of PEEK. If we assume that the amorphous phase in the semicrystalline materials behaves in a similar way to an entirely glassy sample, then when irradiated to 66 MGy the amorphous phase (~70%) will be incapable of reorganization during the d.s.c. scan. In this case it is unlikely that the crystalline regions (~30%) will alter markedly, particularly since crosslinking is believed to occur preferentially at lamellar surfaces[16,17] (this assumes that the amorphous and rigid amorphous fractions[28] respond to irradiation in a similar manner). Based on the data presented in *Figure 3*, it is clear that a dose of 66 MGy is sufficient to inhibit molecular reorganization completely in amorphous samples, and thus it is proposed that a dose of 66 MGy is sufficient to prevent reorganization in a semicrystalline material.

If radiation-induced changes were confined entirely to the amorphous component, then in the absence of dynamic kinetic effects the trace obtained from 200A/66 would be representative of the lamellar population formed by annealing at 200°C for 15 min, but displaced upwards in temperature relative to the equivalent

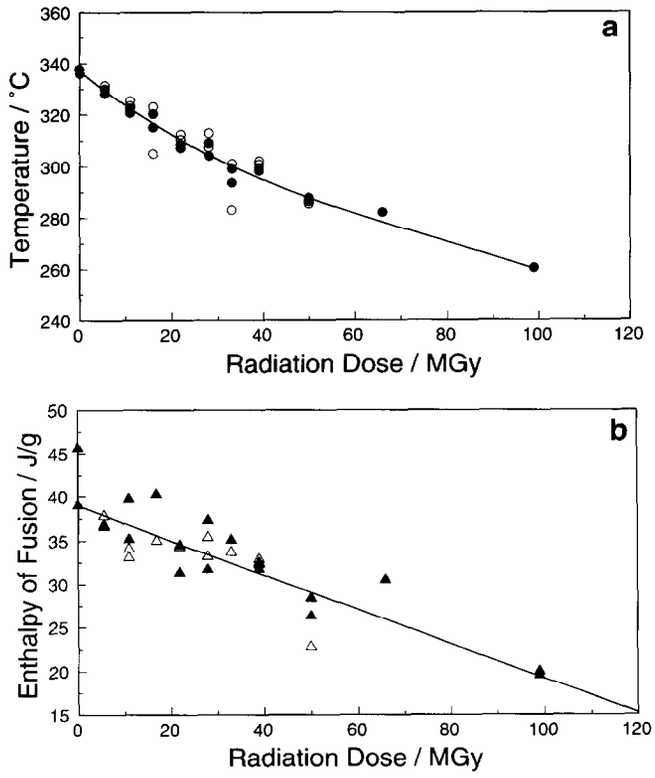

Figure 8 Melting transition data from samples prepared at 200°C (200A/*d*). The variation in the position of the main melting peak with absorbed dose is shown in (a), both as obtained directly following irradiation (first scan, ●) and after melting and subsequent recrystallization at 200°C (second scan, ○). Corresponding peak enthalpy data are shown in (b): (▲) first scan; (△) second scan

unirradiated material as a result of entropic changes in the melt. In practice, radiation-induced changes are not confined to the non-crystalline regions; some crystallite damage does occur, and this will tend to depress the melting temperature. The second of these two effects tends to dominate, except at low doses in well-crystallized samples (see *Figure 5*, 320A/66). Therefore, some reduction in melting point would be anticipated in a specimen prepared at 200°C and then irradiated to 66 MGy, although it is not possible to be quantitative concerning its magnitude. Nevertheless, the d.s.c. trace obtained from 200A/66 should give a reasonable indication of the lamellar population present in 200A/0 prior to performing a d.s.c. scan, and the observed peak melting temperature will, at worst, set a lower bound for the peak melting temperature of the initial, unirradiated material.

Implicit in the above analysis is the notion that PEEK responds to irradiation in a very specific way; at low doses ($< \sim 66$ MGy) the amorphous material is changed dramatically, whilst the crystalline component remains comparatively unaffected. This assertion is supported by the results of recrystallization experiments. *Figure 8* includes plots of peak melting temperature and enthalpy of fusion as a function of radiation dose for samples scanned directly after irradiation (first scan) and also for samples irradiated, melted, recrystallized for 15 min at 200°C and subsequently re-examined by d.s.c. (second scan). Whilst comparison of data from first and second scans reveals no substantial differences up to 50 MGy, at higher doses recrystallization proved to be impossible. Again these results are consistent with previous observations derived both from glassy samples and from the 320A/*d* specimens.

Thus far, consideration of *Figure 8* has been limited to the lower dose irradiations, up to 66 MGy, whereby an interpretation of the data has been proposed based upon correlations between the different sets of samples. At higher doses similarities are again evident. From *Figure 7* it would appear that progressive destruction of crystallinity occurs as the dose increases above 66 MGy, such that at 260 MGy the material appears, by d.s.c., to be completely non-crystalline. This behaviour is similar to that previously shown in *Figure 5* and will be considered further below.

Irradiation and morphology

Figure 9 shows the two semicrystalline materials considered in this study, prior to irradiation: *Figure 9a* shows 200A/0 whilst *Figure 9b* shows 320A/0. It is clear from these micrographs that the two materials have similar morphologies, although the lamellar texture is better defined in the material which has undergone prolonged annealing, as would be expected. Nevertheless, considerable lamellar detail can be seen in each micrograph and there is little evidence of lamellae being organized into large scale structures such as spherulites or axialites. Since the two materials appear very similar, only the samples initially prepared at 320°C will be considered further.

Figure 10 shows the effect of electron radiation on the morphology of PEEK, as revealed by TEM. The two micrographs shown appear very similar to one another. Indeed, comparison with *Figure 9b* would suggest that even irradiation to as high a dose as 260 MGy has little effect on the lamellar texture, a conclusion that would appear to be sharply at odds with the d.s.c. data included in *Figures 5* and *6*. More detailed discussion of this effect will be deferred to a later publication, where wide angle X-ray scattering results will be considered[46]. Although irradiation to 260 MGy does not, in itself, change the morphological appearance to any great degree, if the sample is irradiated, melted and then examined it is clear from the 'recrystallized' morphology that the radiation step has greatly modified the polymer, even though the changes were not initially visible at the lamellar level. *Figure 11* shows a sample of 320A/260 that has been heated to 370°C after irradiation and then quenched into liquid nitrogen. Although some structure is evident in this micrograph, it is clear that the irradiation step has largely prevented recrystallization following melting, a conclusion that is in line with expectations based upon the d.s.c. recrystallization results reported above.

CONCLUSIONS

The results presented above consider the effects of high energy radiation on the crystallization, reorganization

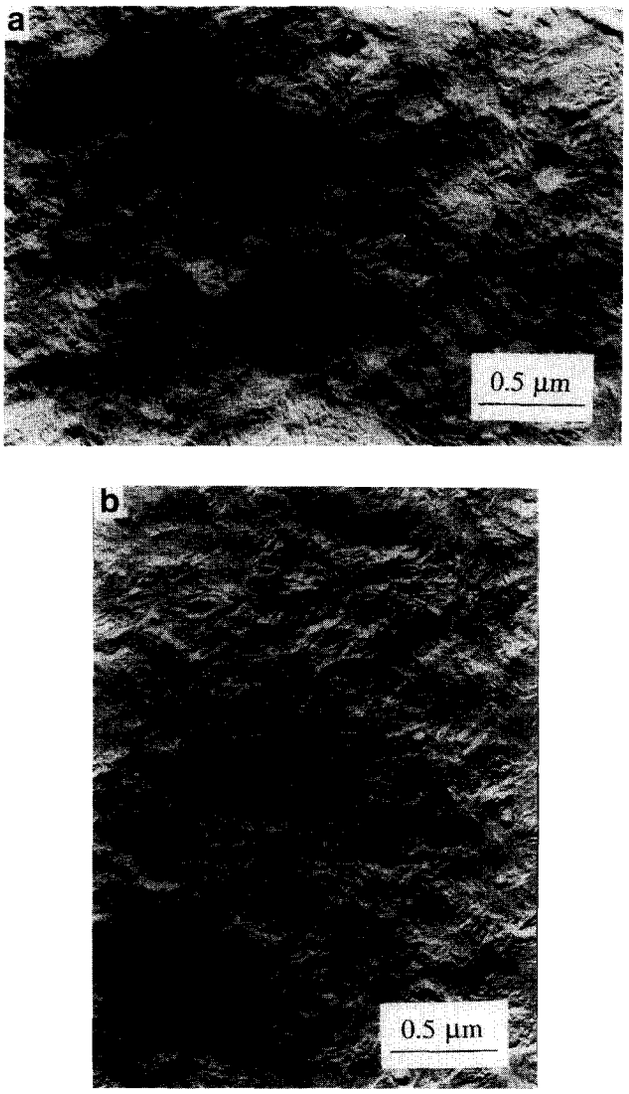

Figure 9 Transmission electron micrographs showing typical morphologies in (a) 200A/0 and (b) 320A/0

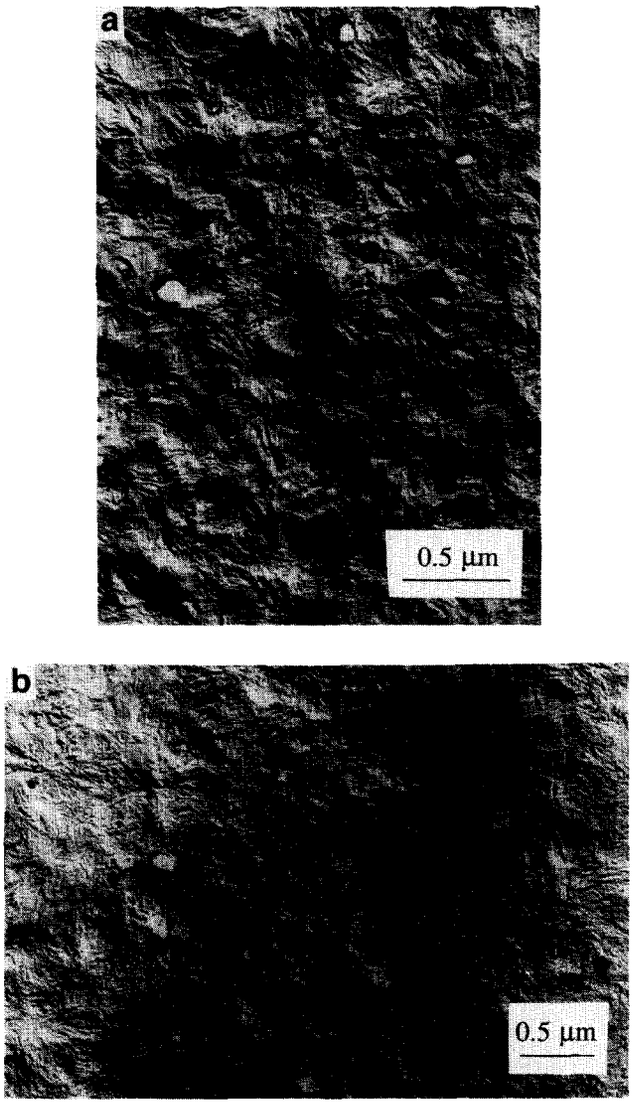

Figure 10 Transmission electron micrographs showing the effect of irradiation on the lamellar morphology in (a) 320A/150 and (b) 320A/260

and melting behaviour of a number of PEEK samples irradiated to a wide range of dose levels. In general, the effects of radiation may be summarized as follows. At low doses, up to ~66 MGy, the radiation-induced changes manifest themselves most clearly in reduced rates of crystallization and reorganization, in response to the formation of crosslinks within the amorphous regions. However, the precise mechanism of radiation-induced intermolecular and intramolecular bonding is unknown at this time. This is not to say, however, that the lamellae are unaffected by low dose radiation, but rather that such effects are of secondary importance as far as the observed d.s.c. behaviour is concerned.

At higher doses, the significance of the increased crosslink density decreases, since only a finite level is necessary to prevent molecular reorganization completely. Thus at high doses the appearance of the d.s.c. melting endotherm, when considered in isolation, suggests that extensive crystal destruction has occurred. Ultimately, at very high doses, no melting peaks are observed whatsoever. However, structural studies demonstrate that the morphologies appear little changed even by irradiation to very high doses. These observations are supported by X-ray scattering results. It would therefore appear that although prolonged irradiation does result in some loss of crystallinity, the 'disappearance' of the d.s.c. melting peak does not indicate the absence of a phase transition but rather reflects changes in the thermodynamics of the process[46].

Whilst the above summarizes the direct effects of radiation in PEEK, a major element of this study concerned using radiation as means of reducing reorganization during d.s.c., thereby obtaining endotherms that are representative of the lamellar population present in the sample prior to commencing the d.s.c. experiment itself. It is therefore appropriate to reconsider the three hypotheses (L, U and I) outlined above in the light of the data obtained from irradiated samples. In view of these results, it is clear that the lower melting endotherm cannot be representative of the lamellar population formed by annealing at 200°C for 15 min. Specimen 200A/0 exhibits a small feature in the d.s.c. trace at 222°C together with a large endotherm at 336°C, whereas the peak melting temperature of 200A/66 is 282°C; it is hard to see how irriadiation to 66 MGy could result in the peak melting temperature being elevated by some 60°C, particularly when the 320A/*d* samples respond to irradiation in such a conventional manner. However, in considering the other two propositions, the situation is not so clear since, effectively, these only differ in the extent to which the major peak is displaced along the temperature axis as a consequence of performing the d.s.c. scan. To differentiate between these two cases it is necessary to irradiate to such a level that reorganization is prevented and then to be able to estimate the melting point depression that has resulted. In irradiating to 66 MGy, the net depression in peak melting temperature of the 320A/*d* materials was 7°C. In going from 200A/0 to 200A/66 the peak melting temperature drops by some 54°C; it is difficult to reconcile these quantitative differences solely in terms of differences in the radiation response of the two crystal populations. In addition, hypothesis U involves the notion of two distinct lamellar populations giving rise to two melting endotherms, whereas hypothesis I is based upon a broad lamellar distribution and a single broad melting endotherm. Thus,

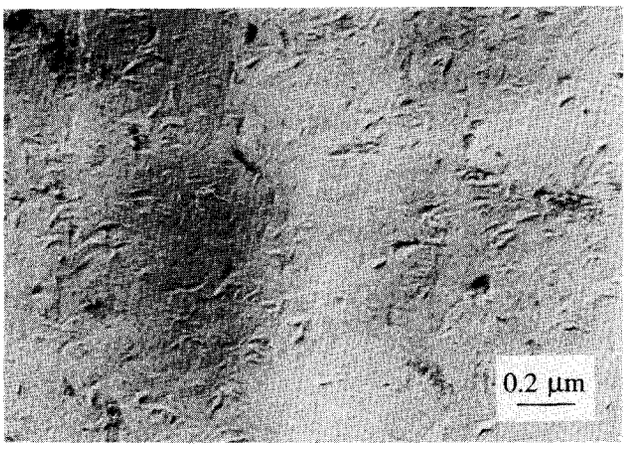

Figure 11 Transmission electron micrograph showing a sample of 320A/260 after melting at 370°C and quenching into liquid nitrogen

on the basis of the results considered so far, it would appear that in general the melting behaviour of the lamellar population present in a sample of PEEK prior to performing a d.s.c. scan is best represented by an endotherm peaking just below the high temperature feature obtained experimentally and having a tail extending down towards the crystallization temperature, very much in line with the interpretation proposed by Lee and Porter[33].

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