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On radiation effects in oriented poly(ether ether ketone)

A. S. Vaughan* and S. J. Sutton†
Polymer Science Centre, J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 2AF, UK
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The response of oriented poly(ether ether ketone) fibres to high energy electron radiation has been investigated by differential scanning calorimetry and wide angle X-ray scattering (WAXS). Absorbed radiation doses within the range 0–400 MGy have been considered. As the radiation dose increases, both the melting temperature and enthalpy of fusion decrease, and above 260 MGy no melting endotherm has been observed. However, the X-ray scattering behaviour indicates that these observations are not simply associated with radiation-induced crystallite destruction. Although the intensities of the crystalline reflections diminish with increasing dose, at 260 MGy the scattering curves appear only slightly changed from those of the unirradiated material. At higher doses, extensive modification of the scattering pattern does occur, but even at 400 MGy substantial remnants of the crystalline scattering peaks are evident. These results are interpreted in terms of the formation of crosslinks during irradiation which subsequently serve to modify the melting behaviour of the polymer extensively, but which do not disrupt molecular correlations (as sampled by WAXS) to the same extent.

(Keywords: poly(ether ether ketone); X-ray diffraction; electron irradiation)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high performance semicrystalline polymer. As a result of its excellent physical properties, PEEK has been proposed for use in many demanding situations and has been studied extensively in connection with potential applications. In addition to such applied investigations, PEEK has also been the subject of much fundamental study and, for example, its morphology[1–3], crystallography[4–6] and thermal behaviour[7–10] have all attracted much attention. However, in view of the potential of PEEK as a polymer for use in nuclear environments, it is surprising that the effects of ionizing radiation have received little attention.

In 1985, some preliminary results were reported by Yoda[11] in which he demonstrated the remarkable radiation resistance of PEEK crystals. From this study it was concluded that irradiation of oriented PEEK to 50 MGy only results in a reduction in the crystal thickness of ~15%. However, this is not to say that PEEK is unaffected by high energy ionizing radiation; indeed, in 1984 Yoda had previously demonstrated that a dose of 50 MGy was sufficient to prevent completely crystallization of PEEK samples that had been irradiated in the glassy state[12]. Taken together, these results imply that radiation damage occurs preferentially within the amorphous regions of the material, a conclusion strongly supported by more detailed study[13].

In this communication, the effects of electron radiation on oriented PEEK are considered up to very high absorbed doses (400 MGy). X-Ray diffraction and thermal analysis data are presented. No detailed analysis of radiation effects in PEEK is presented here, the intention being to compare the apparent radiation responses as revealed by two techniques.

EXPERIMENTAL

The material used in this study was supplied by ICI in the form of a length of oriented PEEK fibre ~330 μm in diameter. A single sample was used for all the X-ray and irradiation experiments described; this was prepared by clamping lengths of the fibre parallel to one another in a mount that could be accurately located and relocated within the X-ray scattering apparatus. A flat plate, wide angle diffraction pattern was first recorded (using monochromatic CuKα radiation), together with equatorial and meridional diffractometer scans. The sample was then irradiated for 1 h before being returned to the X-ray scattering apparatus. This procedure was repeated many times using the same sample, the total radiation does being built up in a number of steps between which the X-ray scattering data were recorded. Raw data are presented throughout; no corrections have been made to account for polarization, absorption, scattering effects, diffractometer geometry, etc. The X-ray data are intended solely for internal comparison and, for the above reasons, quantitative analysis is inappropriate.

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* To whom correspondence should be addressed

† Present address: Department of Physics, Kyoto University, Kyoto 606, Japan

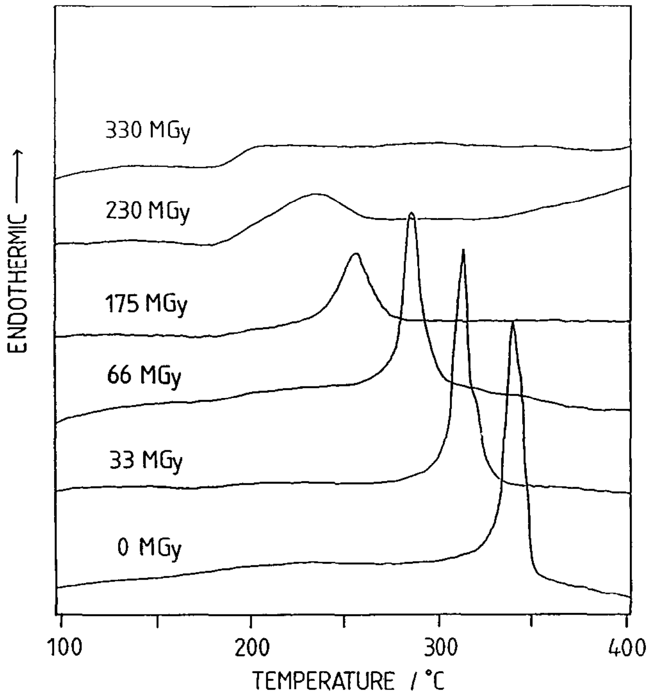

Figure 1 D.s.c. melting behaviour of oriented PEEK fibres as a function of radiation dose

Additional samples were irradiated in aluminium sample cans for subsequent thermal analysis. This was carried out using a Perkin–Elmer DSC-2C differential scanning calorimeter operating in conjunction with an IBM AT personal computer running MC^2 Thermal Systems data analysis software. Temperature calibration of the instrument was performed using indium and lead as standards, and sapphire was used for enthalpy calibration purposes. Differential scanning calorimetry (d.s.c.) samples were prepared for irradiation by first cutting the PEEK fibre into approximately 1 mm lengths. These were then loaded into d.s.c. cans to give samples which, in total, were ~5 mg in mass.

Throughout this study, electron irradiation was performed at room temperature in a van de Graaff accelerator producing a beam of 1 MeV electrons. The operating conditions[13] of the accelerator were chosen such that the beam diameter at the sample plane resulted in uniform sample irradiation (dose rate ~550 kGy min^{-1}) over an area of the order of 1 cm^2.

RESULTS AND DISCUSSION

Figure 1 shows d.s.c. traces of PEEK fibres following irradiation to the dose levels indicated. Exposure of PEEK to high energy ionizing radiation results in the formation of crosslinks[13,14], and in analysing these data two effects must be considered. Despite being formed preferentially in the more disordered regions, radiation-induced defects do result in a degree of crystallite destruction. Therefore, as the absorbed dose increases, the crystallinity and lamellar thickness should both decrease. However, the primary changes induced by the radiation may be masked by secondary effects that are related to the nature of the d.s.c. experiment itself. The detailed interpretation of the melting behaviour of PEEK, as revealed by d.s.c., has been debated at some length in the literature[7–9] in terms of possible annealing and recrystallization processes that occur during the course of the d.s.c. scan. Therefore, the appearance of the d.s.c. trace may vary with dose not because of crystallite damage, but simply in response to modified reorganization kinetics caused by intermolecular and intramolecular crosslinking. Extensive analysis of many amorphous, annealed and melt-crystallized samples of PEEK has clearly demonstrated that the effects of ionizing radiation are subtle and that a detailed interpretation of changes in peak shape, peak shifts, etc. is not possible on the basis of only a few experiments[13]. Nevertheless, in simple terms, it is clear from *Figure 1* and the derived data shown in *Figure 2* that as the absorbed dose increases, both the peak melting temperature and the enthalpy of fusion decrease. It would therefore appear that electron irradiation progressively disrupts the initial crystal population such that above an absorbed dose of 260 MGy no melting peak is observed.

On the basis of the above d.s.c. data alone, the qualitative response of PEEK to prolonged electron irradiation would appear to be quite straightforward, although quantitatively the material is clearly very highly resistant to ionizing radiation. However, complementary X-ray scattering data demonstrate that, in reality, the situation is rather more complicated. *Figure 3* shows the flat plate diffraction pattern obtained from an unirradiated specimen. Both the general form of this diffraction pattern and the positions of the {110}, {200}, {020} and {002} reflections are consistent with previously published data[4–6].

The effect of irradiation on the scattering behaviour can be seen in *Figures 4–7*. *Figure 4* shows two flat plate photographs, *Figure 4a* recorded at a dose of 66 MGy and *Figure 4b* after irradiation to 260 MGy, i.e. the dose above which no melting endotherm is evident by d.s.c. Comparison of the X-ray diffraction patterns shown in *Figure 4* with that for the unirradiated specimen (*Figure 3*) clearly reveals that although changes are induced by irradiation, these are, in contrast to the d.s.c. results, of a relatively minor nature. This general conclusion is confirmed by the series of equatorial and meridional diffractometer scans shown in *Figures 5* and *6* respectively. Since the data are intended for internal comparison only, they are presented as collected; all the scans were recorded from the same sample under identical conditions and they can, therefore, be compared directly. No quantitative analysis of these diffractometer data has been attempted owing to complications caused by the clamping arrangements that were necessary for the irradiation steps; these lead to a non-ideal geometry whereby the sample is displaced from the rotation axis of the diffractometer by ~5 mm. Nevertheless, internal comparison of the diffractometer data shows that any variation in the positions of the {110}, {200}, {020} and {00*n*} (where $n = 2$, 6 or 8) reflections with absorbed dose (0–260 MGy) is less than the resolution of the diffractometer.

Comparison of *Figures 2* and *5*, for example, would suggest very different radiation responses. Whereas *Figure 2* would seem to indicate that little crystallinity remains above 260 MGy, the X-ray data demonstrate very clearly that this is not the case. How can this

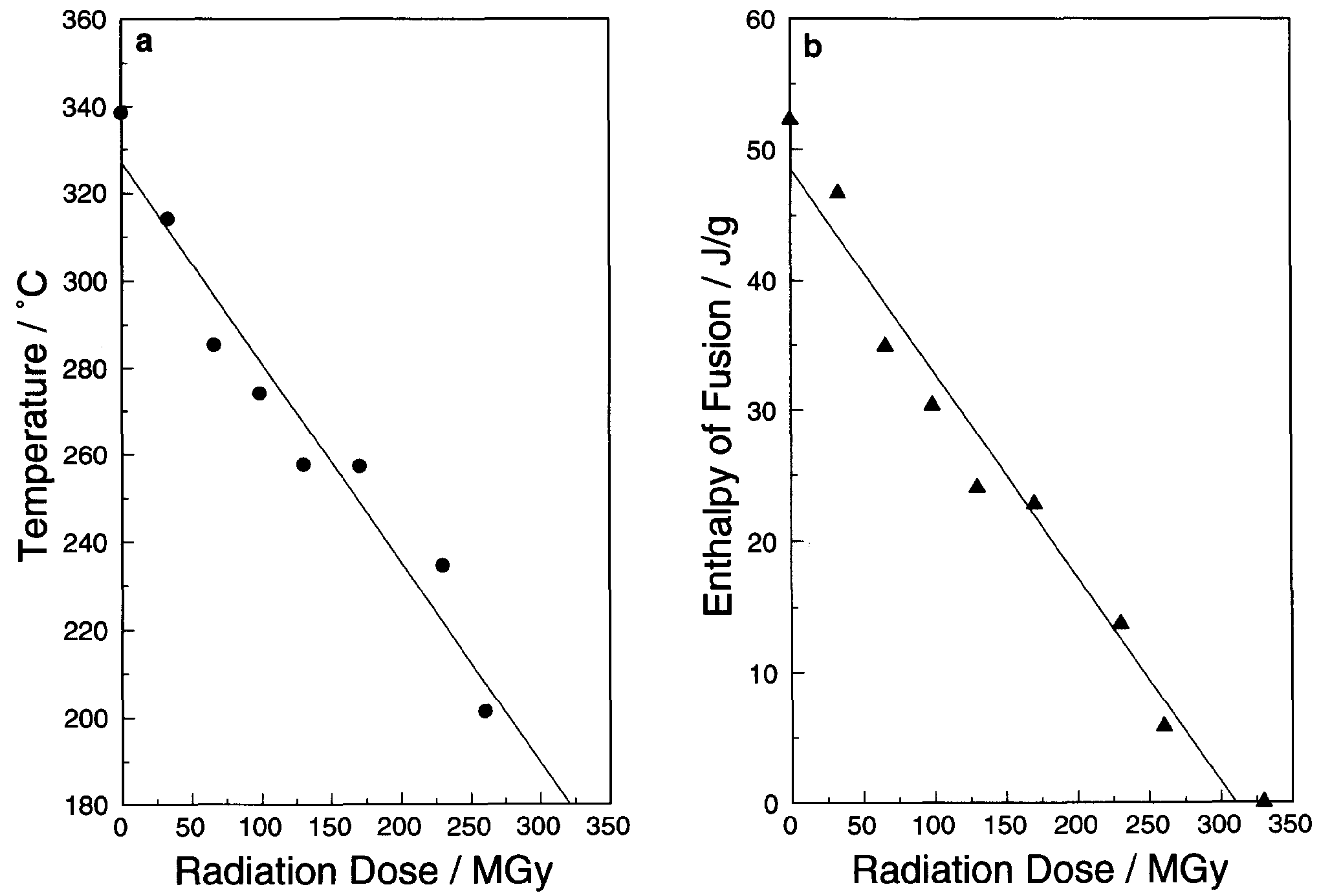

Figure 2 Variation of (a) melting temperature and (b) enthalpy of fusion with radiation dose for PEEK fibres

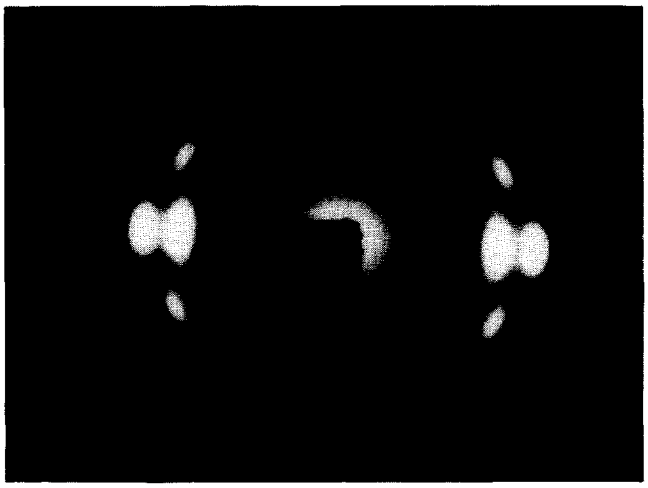

Figure 3 Flat plate, wide angle X-ray diffraction pattern from the PEEK fibre sample prior to irradiation

apparent contradiction be reconciled? A number of explanations can be proposed.

On irradiation, crosslinks are formed which are located primarily at or near lamellar surfaces[14]. As the absorbed radiation dose increases, the crosslink density increases, thereby limiting the extent to which changes in molecular conformation may occur on heating. In the case of amorphous PEEK, this general behaviour manifests itself at relatively low doses as a reduction in the extent to which the irradiated material can subsequently crystallize. Above ~50 MGy no crystallization whatsoever is observed in the d.s.c. analysis[12,13]. Similarly, for semicrystalline materials it is possible that at some dose the concept of crystal melting becomes obsolete; despite localized remnants of pseudo-crystalline ordering, the constituent molecular stems are so highly crosslinked that the 'crystal' is unable to melt. In this explanation nothing should occur on heating the sample to moderate temperatures; the molecules, which themselves are inherently stiff, are sufficiently highly crosslinked within thin[7,15] lamellar structures that they are unable to relax on heating. However, attempts to investigate molecular relaxation processes by dynamic mechanical thermal analysis demonstrated that this is not the case; few data were obtained, since the irradiated fibres snapped immediately the sample temperature exceeded T_g. Similarly, morphological studies[13] of bulk crystallized specimens which exhibit only a vestigal d.s.c. melting transition have revealed that dramatic changes do occur on heating. A specimen crystallized at 320°C, irradiated to 260 MGy and then examined revealed a well-defined lamellar texture which subsequently disappeared on heating to 370°C.

It would therefore appear that even in materials in which no transition is evident in the d.s.c. analysis,

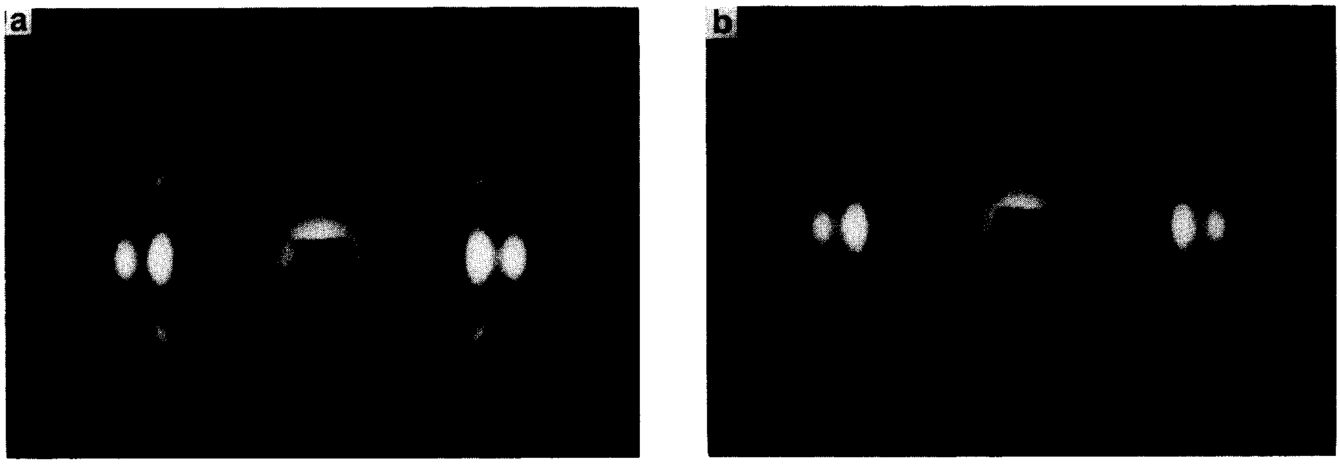

Figure 4 Flat plate, wide angle X-ray diffraction patterns from the PEEK fibre sample after irradiation to (a) 66 MGy and (b) 260 MGy

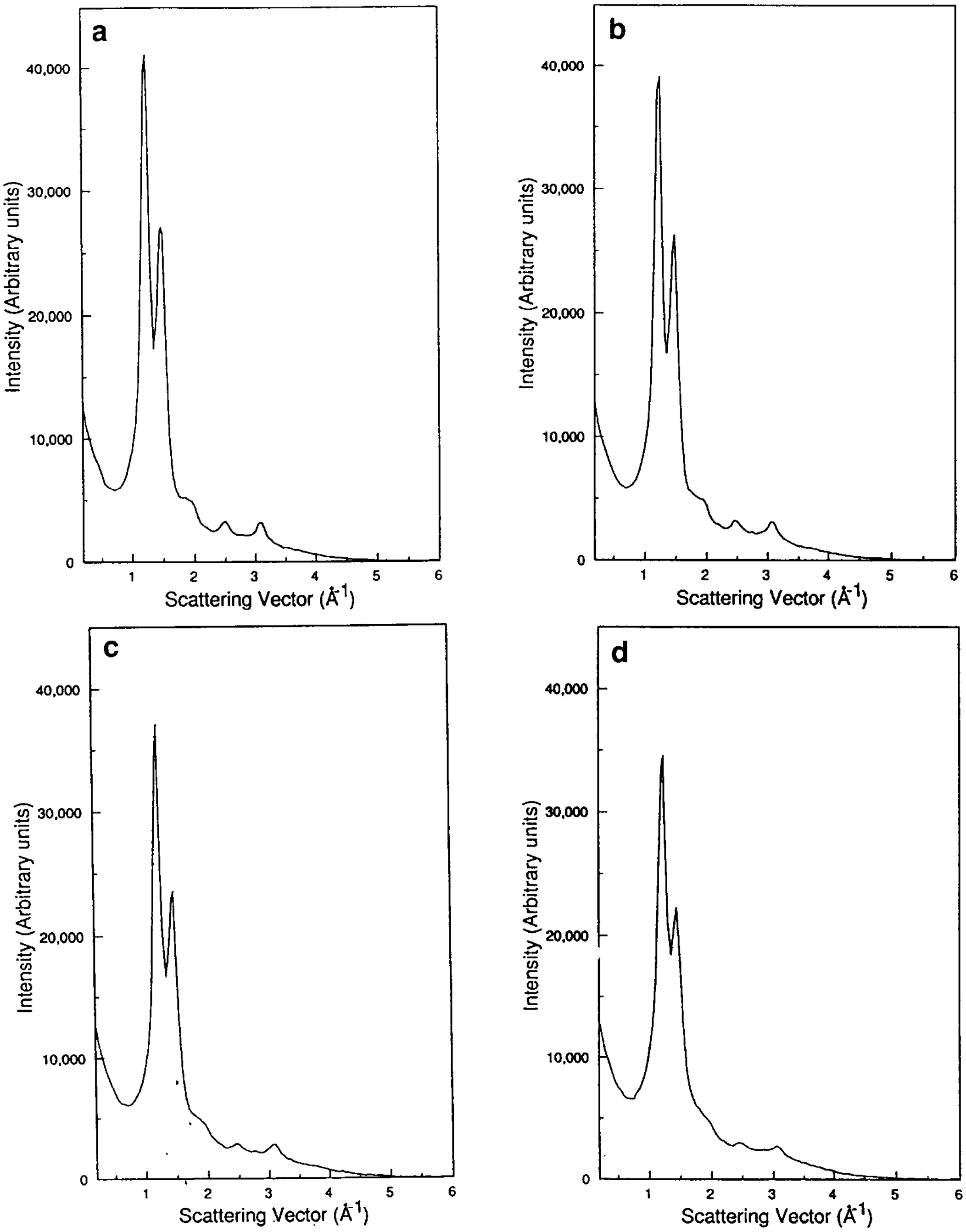

Figure 5 Equatorial diffractometer scans from the PEEK fibre sample after (a) 0 MGy, (b) 66 MGy, (c) 130 MGy and (d) 260 MGy

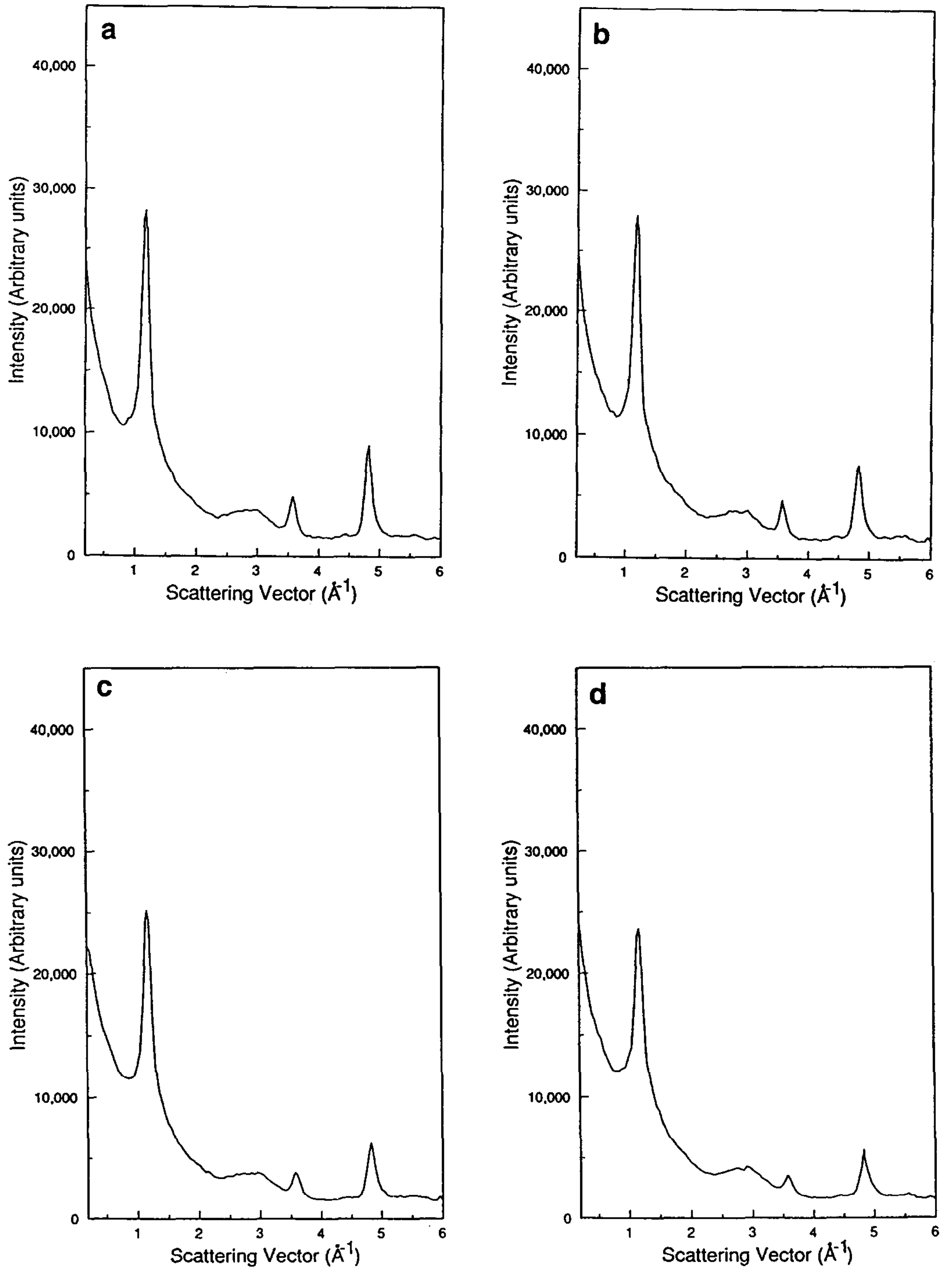

Figure 6 Meridional diffractometer scans from the PEEK fibre sample after (a) 0 MGy, (b) 66 MGy, (c) 130 MGy and (d) 260 MGy

conformational changes do occur on heating. In this explanation, the observed d.s.c. behaviour stems from thermodynamic effects; that is, the absence of a clear endotherm does not indicate the absence of any conformational changes, but rather implies that such changes are not readily detectable by d.s.c. Although extensive speculation concerning the origin and significance of such transitions in highly crosslinked, rigid molecular systems is not warranted at this time, some comment is necessary. By simply considering

$$\Delta G = \Delta H - T\Delta S$$

and assuming that at the melting temperature (T_m) $\Delta G = 0$, it is difficult to envisage why a transition should occur in which $\Delta H = 0$. Although it is possible to construct a free energy diagram in which the free energy lines for the crystal and melt phases form common tangents at T_m, it is unclear why such a precise condition should come about as a result of irradiation. From *Figure 2* it is evident that as the radiation dose increases, the melting endotherm is displaced to lower temperatures until eventually it coalesces with the glass transition. As this occurs $\Delta H \rightarrow 0$. Setting $\Delta G = 0$ at T_m gives

$$\Delta H = T_m \Delta S$$

and since the change in entropy ΔS on melting a highly

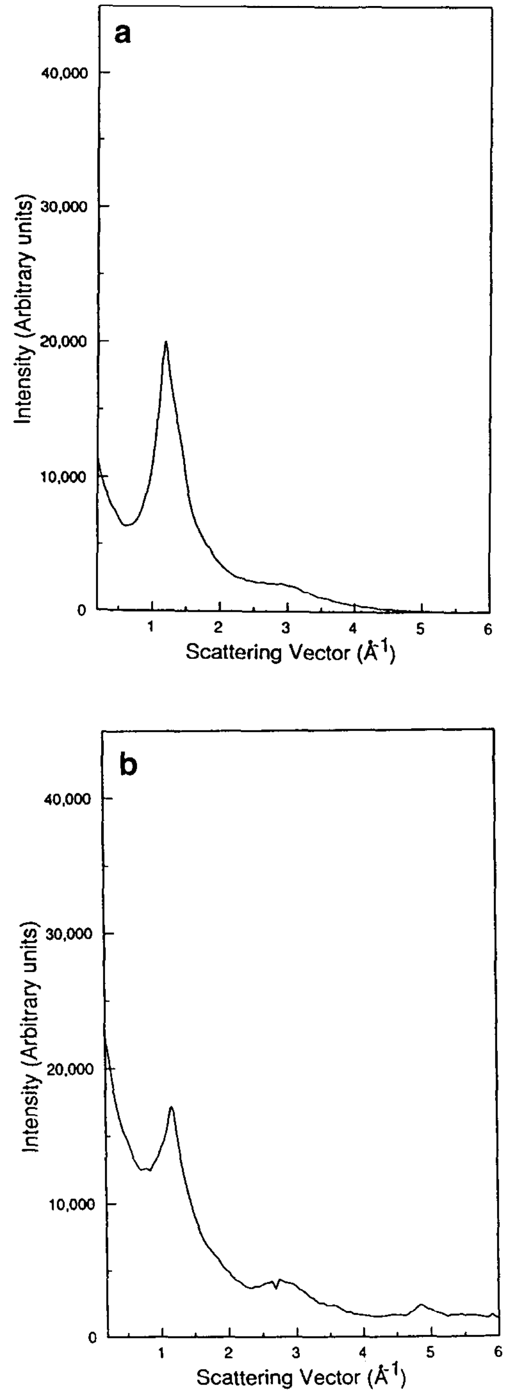

Figure 7 Wide angle X-ray scattering data obtained from the PEEK fibre sample after irradiation to 400 MGy: (a) equatorial diffractometer scan; (b) meridional diffractometer scan

crosslinked, rigid molecular system should be small, it is evident how a small but non-zero ΔH value may occur in such a situation (when highly crosslinked, the entropy of the melt may be similar to that of the crystal). That a corresponding transition is not observed may be because of instrumental insensitivity, or, since $T_m \approx T_g$, it may simply be that the small enthalpy of fusion is distributed in the form of a broad peak near a relatively large glass transition. If this were the case, then it would be reasonable to expect that at high scan rates an apparent enthalpy recovery peak[16] should be observed. No such effect has been seen and the nature of 'melting' in highly irradiated PEEK samples is quantitatively something of a mystery. Further experiments are therefore underway and results from these will be reported in due course.

CONCLUSIONS

The destruction of crystallinity during the irradiation of polymers is a process that has been well documented for many systems, for example through the direct observation of electron diffraction patterns in the transmission electron microscope. However, it would appear that in PEEK the formation of intermolecular crosslinks can occur in such a way as to affect its melting behaviour dramatically (no endotherm being visible by d.s.c.) but without completely destroying local ordering within the lamellae. Thus, as in the preceding papers, it can be concluded that the radiation response of PEEK is highly unusual.

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