BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 8, pp. 1541–1547, 1995

0032-3861/95/$10.00+0.00

On radiation effects in poly(ethylene terephthalate): a comparison with poly(ether ether ketone)

A. S. Vaughan*
Polymer Science Centre, J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 2AF, UK

and G. C. Stevens
National Power Research and Engineering, Windmill Hill Business Park, Whitehill Way, Swindon SN5 6PB, UK
(Received 27 May 1994)

The effects of irradiation on poly(ethylene terephthalate) have been investigated by differential scanning calorimetry. On irradiation, defect structures are formed which serve to reduce or prevent molecular reorganization. Irradiation of amorphous specimens shows that no crystallization occurs above an absorbed dose of ~30 MGy. The response of semicrystalline samples is dominated by radiation-induced crystal destruction; the lamellae have been extensively modified by 30 MGy and little crystallinity remains above 66 MGy. As a consequence of these factors, controlled irradiation does not constitute a viable means of investigating the melting behaviour of this polymer in the absence of reorganization effects. Comparison with the behaviour of poly(ether ether ketone) (PEEK) leads to the conclusion that the radiation resistance of crystalline conformations in PEEK is indeed highly unusual.

(Keywords: poly(ethylene terephthalate); radiation; d.s.c.)

INTRODUCTION

In the preceding paper[1], the effects of high energy electron radiation on poly(ether ether ketone) (PEEK) were considered. It was shown that during irradiation, crosslinks are formed and these serve to modify the crystallization, annealing and melting behaviour of the polymer in a very specific way: up to ~60 MGy, the radiation-induced changes are largely confined to amorphous regions, and only at higher absorbed doses does apparent crystal destruction tend to dominate the behaviour, as revealed by differential scanning calorimetry (d.s.c.). As a result of this characteristic radiation response, irradiation can be used to modify this polymer such that the melting behaviour of largely undamaged lamellar structures can be studied by d.s.c. in the absence of dynamic reorganization effects.

Poly(ethylene terephthalate) (PET) is a polymer which has some similarities to PEEK. Like PEEK, the PET backbone contains aromatic groups together with ether and ketone linkages, but in addition it has some aliphatic character. Both PET and PEEK can be prepared readily in the form of amorphous or semicrystalline specimens and both crystallize to only a relatively low level (typical crystallinity values for these systems are 20–40% for PEEK[2,3] and 30–50% for PET[4,5]). However, in the context of this general study, the most important feature of PET concerns its melting behaviour.

Crystallization and melting processes in PET have been studied extensively[4–16] and, like PEEK, early investigations led to a number of contradictory interpretations for the commonly observed multiple melting transitions. In early d.s.c. studies, two peaks were often reported and this behaviour was explained in terms of two distinct components[6–9]. However, subsequent studies[10–16] questioned this interpretation, suggesting instead that the high temperature melting transition (termed peak A′ below) comes about as a result of reorganization of material from the lower peek (A) during the courst of the d.s.c. scan. More recent studies of isothermally prepared PET have demonstrated that the melting endotherm may contain one, two or three features[16], depending upon the precise thermal history of the specimen. Nevertheless, in general the d.s.c. melting behaviour of PET is best considered in terms of three elements: a small transition ~10°C above the isothermal crystallization or annealing temperature (peak B), together with a much larger double peak (elements A and A′) which falls within the temperature range 230–260°C. The relative magnitudes and positions of these features will vary, and they may also overlap with one another. In this way, traces containing one, two or three peaks may be observed.

Whilst the origin of peaks A and A′ is now generally accepted, the nature of peak B is not so clear. Where reported, it is usually suggested that this feature is associated with some secondary crystallization process[15,16]. This explanation is very much in line with the upper peak hypothesis (U)[17–19] described for PEEK in the previous

---

* To whom correspondence should be addressed

paper[1], where it is similarly proposed that both endotherms are associated with the initial crystal populations and where the dominant lamellae result in the higher melting transition. This is in contrast to what we have termed the lower peak hypothesis (L)[1], in which the lower temperature endotherm is associated with the initial population and the higher temperature features result from reorganization during the course of the d.s.c. experiment[20,21]. Thus, in summary, both polymers exhibit multiple-peak melting behaviour, both possibly contain a number of lamellar populations and both are thought by some authors to reorganize during a d.s.c. experiment.

As a consequence of the various factors discussed briefly above, irradiation of PET seems a natural extension of the work on PEEK, particularly since there is evidence to suggest that PET can undergo crosslinking reactions when irradiated[22]. The work described below was therefore undertaken with two specific objectives in mind. As in PEEK, prior irradiation of PET may constitute a useful experimental expedient, enabling additional information to be obtained concerning the crystallization, reorganization and melting behaviour and morphology of this polymer. However, the primary aim of this study was to investigate whether the effects seen in PEEK are confined to that particular system, or whether they are a more general characteristic of low crystallinity polymers with aromatic character. The principle purpose was, therefore, to provide some reference point from which to judge the radiation response of PEEK that is described in the accompanying papers[1,23].

EXPERIMENTAL

The PET used in this study was manufactured by ICI and was supplied in the form of amorphous sheet ~0.25 mm in thickness. From this starting material, three different sets of specimens were prepared. One group was irradiated directly, without any prior thermal treatment, whilst another two sets were irradiated after annealing (heating from the glass). These semicrystalline samples were prepared under isothermal conditions (200°C for 15 min; 245°C for 17 h) in a Mettler FP5 hot stage. Reference to the various samples will be made using the same notation developed in the previous paper[1]: G/*d* samples were irradiated in the form of glassy (G) sheets, whereas the 200A/*d* and 245A/*d* samples were irradiated after annealing (A) at 200°C and 245°C, respectively. In all cases, *d* specifies the absorbed radiation dose in megagrays. All samples were irradiated in a van de Graaff accelerator under ambient conditions using 1 MeV electrons at a dose rate of ~0.55 MGy min^{-1} (see the preceding paper[1] for a detailed discussion of the irradiation conditions). Samples prepared as above were subsequently investigated by d.s.c. (Perkin–Elmer DSC-2C). All the traces shown were acquired at a heating rate of 10 K min^{-1}, following both temperature and enthalpy calibration of the system; indium, lead and sapphire were used as calibrants. The data were digitized, baseline corrected and processed using an MC^2 Thermal Systems thermal analysis package running on an IBM AT personal computer.

RESULTS AND DISCUSSION

Amorphous samples

The effect of irradiation on the crystallization and subsequent melting behaviour of PET irradiated in the form of amorphous sheets is shown in *Figure 1*. In general, the behaviour is very similar to that described previously for PEEK[1]: as the absorbed dose increases, crystallization is progressively inhibited such that the crystallization exotherm is displaced to higher temperatures. In parallel with these changes, the melting temperature is depressed to lower temperatures (see *Figure 2a*) such that the crystallization and melting transitions converge. The variation in melting temperature shown in *Figure 2a* is consistent with the limited data that are available elsewhere[24]. The effect of irradiation on the transition enthalpies is shown in *Figure 2b*. This shows that irradiation leads to a general reduction in the magnitude of both the enthalpy of crystallization and the enthalpy of fusion. At low doses (below ~10 MGy), the enthalpy of melting exceeds that of crystallization by typically ~20%. This figure is too great to be accounted for by the temperature dependence of the transition enthalpy, and therefore these data imply that additional crystallization (molecular reorganization) occurs during the course of the d.s.c. scan[25]. At higher doses, the data sets derived from crystallization and melting are indistinguishable, implying that post-crystallization annealing effects are insignificant. Finally, above 22 MGy no transitions are seen.

Thus, on the basis of the data shown in *Figures 1* and *2*, it would seem that three regimes of behaviour exist. At low doses (0–10 MGy), crystallization is followed by annealing, which gives rise to an increase in the overall crystallinity. Between ~10 MGy and 30 MGy, some crystallinity develops but this does not increase in

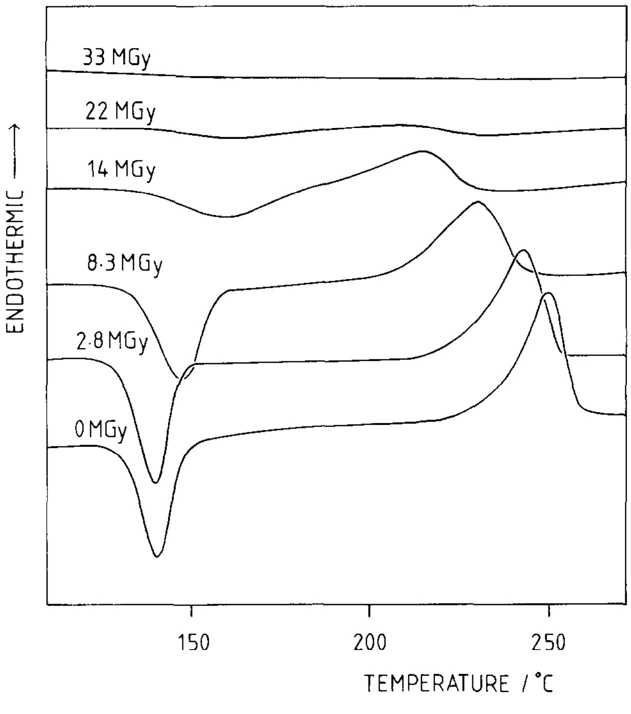

Figure 1 D.s.c. traces from PET samples irradiated in the form of amorphous sheets (G/*d*)

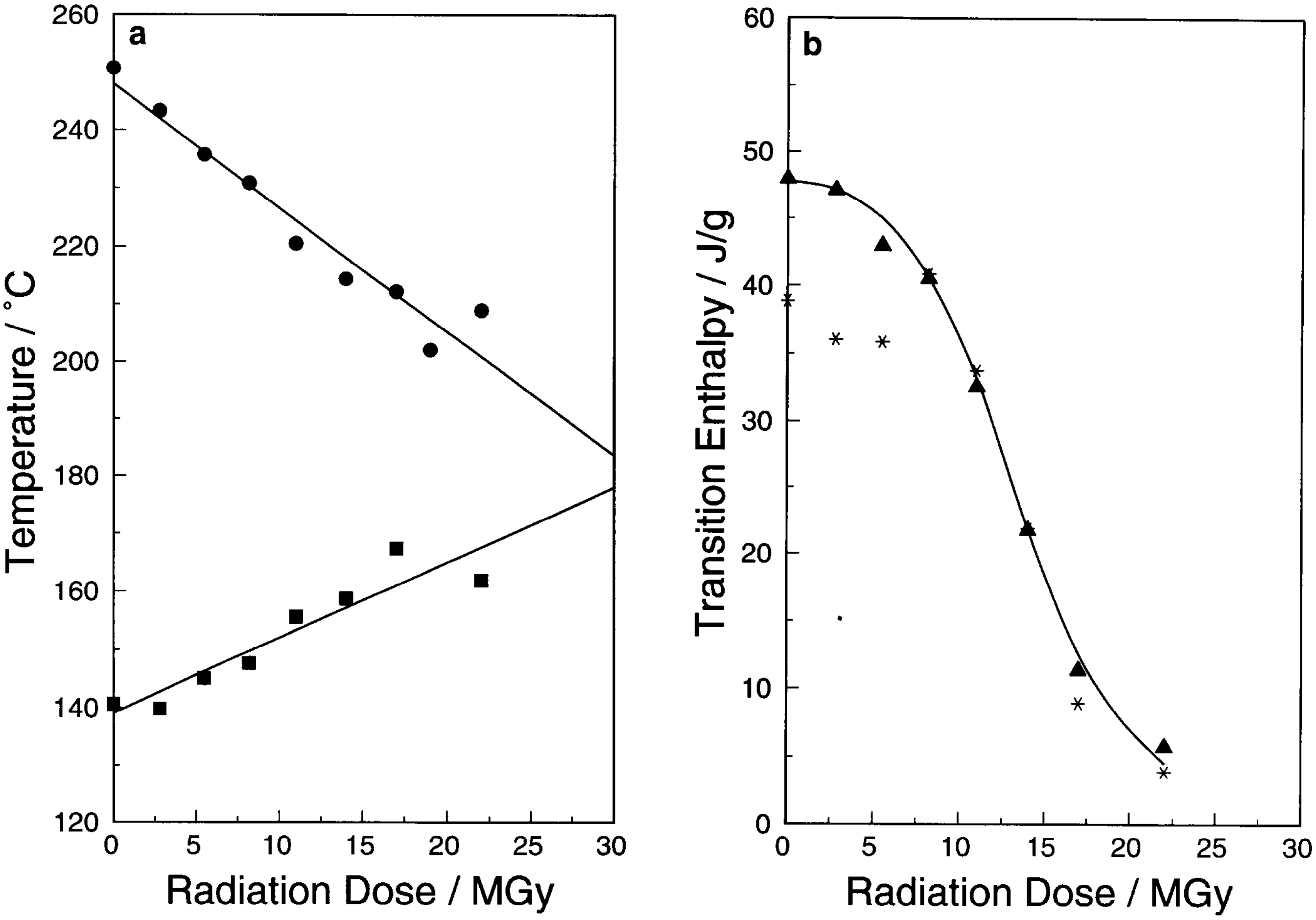

Figure 2 (a) Peak temperatures for the crystallization exotherm (■) and melting endotherm (●) as a function of radiation dose for amorphous samples (G/*d*). (b) Corresponding enthalpy data from the crystallization exotherm (*) and melting endotherm (▲)

the time-scale of the d.s.c. experiment. Finally, above ~30 MGy crystallization does not occur. In PEEK, an absorbed dose of the order of 60 MGy is required to prevent crystallization completely[1,26,27], but, with the exception of this quantitative difference, the radiation responses of the two amorphous systems are very similar.

In the case of PEEK[1], the general behaviour described above was interpreted in terms of crosslink formation, which increasingly restricts the rate of crystallization and annealing and the extent to which they can occur. Eventually, at a sufficiently high dose, the crosslink density is so high that no crystallization whatsoever is possible. This analysis was supported by solvent extraction experiments. Attempts to obtain similar quantitative measurements of gel content as a function of radiation dose in PET were unsuccessful. Exposure of unirradiated PET to trichloroacetic acid led to complete dissolution of the specimen within 1 h. Samples of G/8 and G/17 behaved in a similar manner. At 33 MGy and above, a gel phase could be observed, but this always broke up during recovery, possibly as a result of chemical interactions with the solvent. As a consequence, no quantitative data could be obtained. Nevertheless, in view of the literature[22], the d.s.c. data described above and these visual observations, it would seem that crosslinking reactions do occur in PET.

Samples annealed at 200°C

Figure 3 shows the d.s.c. traces obtained from samples irradiated after annealing at 200°C. The unirradiated material exhibits a melting endotherm that is made up of three elements: a small but distinct transition at 207°C (peak B) and two overlapping transitions (peak A at 240°C and A′ at 251°C) which span the temperature range 220–260°C. As such, this trace is typical of PET. However, irradiation to even very low levels (up to 5.5 MGy) results in a substantial modification of the observed endotherm; the most significant changes in the overall form of the melting behaviour concern peak B. Comparison of 200A/0 and 200A/2.2 reveals that the magnitude of peak B has been dramatically reduced by the irradiation, and by 5.5 MGy no trace of this feature can be seen. It is, however, difficult to quantify such changes; irradiation clearly causes some peak broadening and this, together with the difficulties associated with baseline estimation, makes the quantification of small endotherms highly problematical.

Examination of the trace obtained from 200A/5.5 reveals that both the A and A′ peaks are still well resolved, although both have been broadened somewhat by the radiation treatment and both have been displaced by about 10°C to lower temperatures. However, from *Figure 4b* it can be seen that the overall enthalpy of fusion has not been affected by the irradiation, implying that little net crystal destruction has occurred. The fact that the relative magnitudes of A and A′ in 200A/5.5 are comparable to those in the unirradiated material implies that molecular reorganization has not been extensively

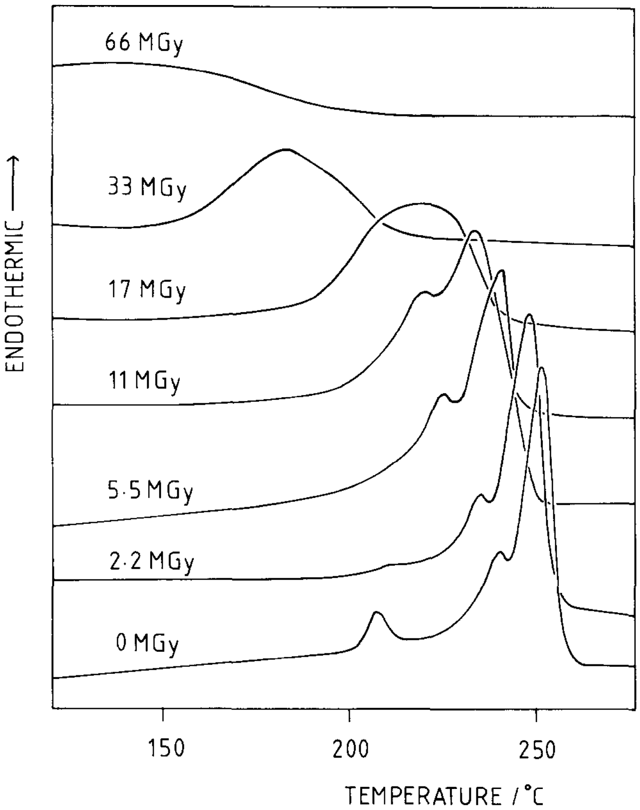

Figure 3 D.s.c. traces from PET samples irradiated after annealing at 200°C for 15 min (200A/*d*)

affected by irradiation to this level, and therefore it would appear that since A′ is a consequence of reorganization, at low doses any radiation damage is largely offset by subsequent annealing processes which become operative during heating in the d.s.c. experiment.

Additional irradiation results in a further depression of the melting transition (see *Figures 3* and *4a*) and a gradual reduction in both the overall enthalpy of fusion (A plus A′; see *Figure 4b*) and the relative magnitude of peak A′. At radiation doses above 11 MGy A and A′ merge, and above 17 MGy it is no longer possible to distinguish clearly between these two features, although there is some evidence of a high temperature shoulder on the remnants of peak A. This convergence of the A and A′ peaks can be seen clearly in *Figure 4a*. Above about 17 MGy, the enthalpy of fusion drops sharply, indicating that the absorbed dose has caused extensive destruction of crystallinity which is no longer offset by annealing in the d.s.c. scan. Comparison of the data sets obtained from the G/*d* and 200/*d* samples reveals a remarkably consistent picture. In both cases there is evidence of crystallite annealing during d.s.c. at low doses, whereas at higher doses the consequences of the radiation-induced changes are such that transition enthalpies drop dramatically.

On the basis of the above results, a number of conclusions can be drawn for the 200A/*d* sample set. The structural features associated with peak B and peak A respond very differently to irradiation. The variation in

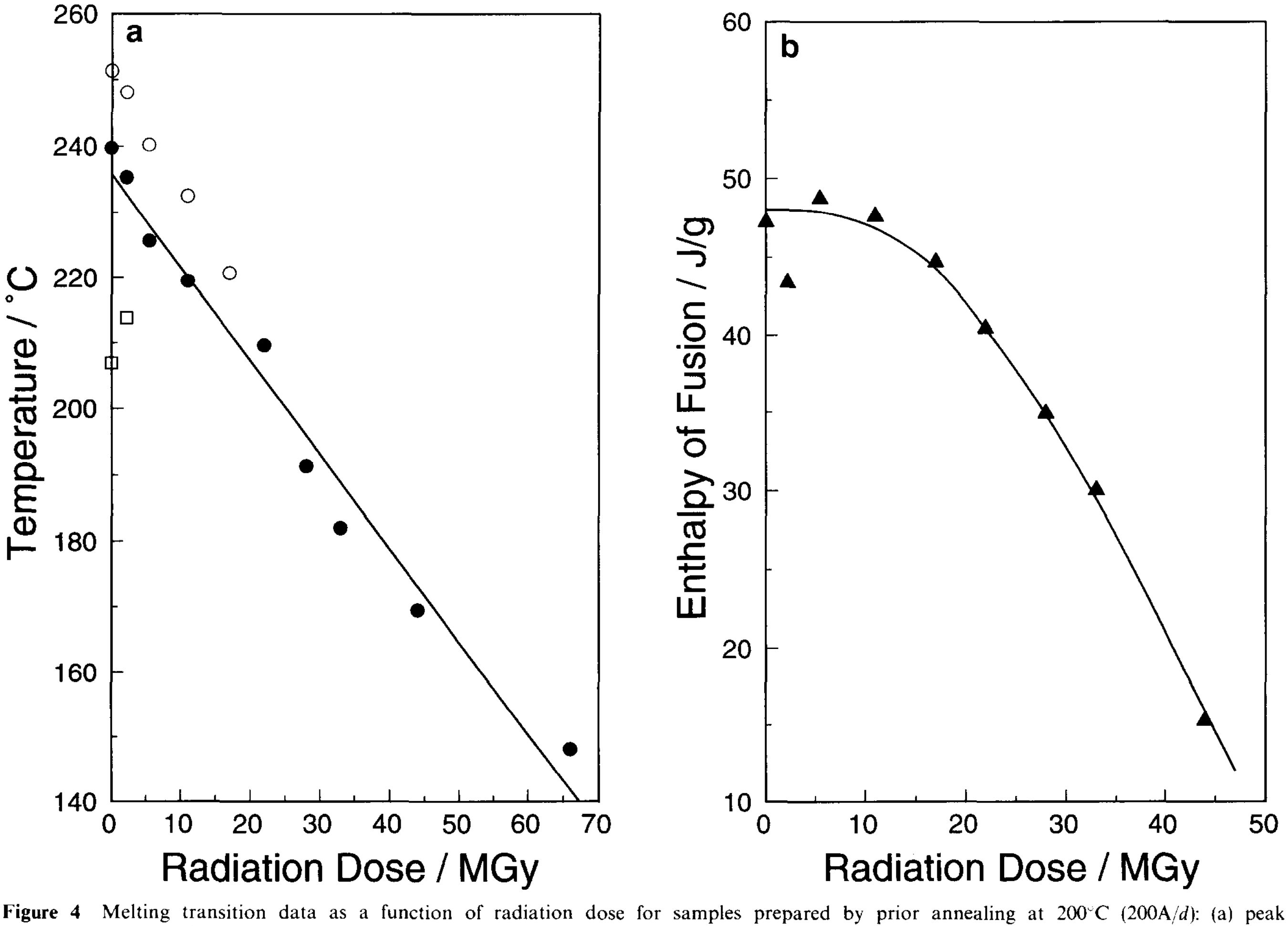

Figure 4 Melting transition data as a function of radiation dose for samples prepared by prior annealing at 200°C (200A/*d*): (a) peak temperatures (B, □; A, ●; A′, ○); (b) enthalpy of fusion

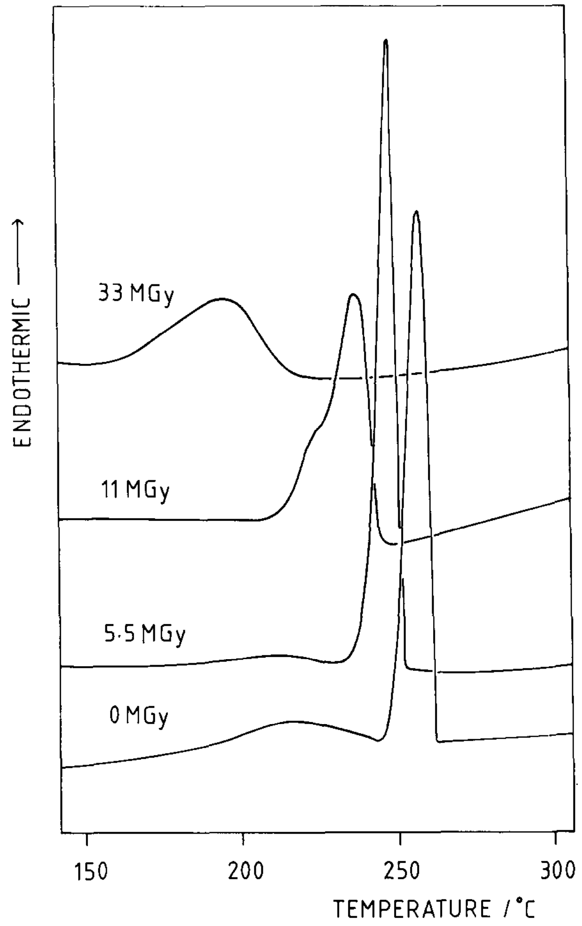

Figure 5 D.s.c. traces from PET samples irradiated after annealing at 245°C for 17 h (245A/*d*)

the relative magnitudes and positions of peaks A and A′ is consistent with the assertion that A′ develops as a consequence of reorganization of material from peak A during the course of the d.s.c. experiment; such annealing effects are restricted by irradiation. Finally, the dramatic difference between the traces obtained from specimens 200A/0 and 200A/33 means that direct comparison of particular constituent features is of very limited value.

Samples annealed at 245°C

Prolonged annealing at the relatively high temperature of 245°C was chosen in an attempt to prepare a well-crystallized, thermally stable material in which reorganization during the d.s.c. scan itself would play a relatively small role in influencing the observed d.s.c. behaviour. Before discussing the effect of irradiation on these samples, it is necessary to consider to what extent this objective was met. The chosen procedure resulted in a material which exhibits two distinct melting transitions and which, in total, is 49% crystalline[25]. This value is near the upper limit of the crystallinity range reported for PET[4,5,25]. Transition A occurs at 258°C, a temperature indicative of well-crystallized material; from *Figure 4a*, crystallization at 200°C and subsequent dynamic lamellar thickening in the d.s.c. experiment only leads to an A′ peak temperature of 251°C. Since no A′ peak is present in 245A/0, it would indeed appear that as far as this lamellar fraction is concerned, little reorganization occurs during heating in the d.s.c. experiment. In addition to peak A, a broad transition is also evident in the d.s.c. trace of this material. This spans the temperature range 170–240°C and, as such, is not associated with the isothermal treatment but is rather a consequence of a fraction which only crystallized on quenching. Thus, the lamellar population associated with this transition should not be associated with peak B, and this transition will therefore be referred to as peak Q. The fundamentally different origins of these two low temperature transitions explain their very different radiation responses, as described below.

Limiting the initial discussion to peak A, the absence of reorganization during d.s.c. means that any changes in melting behaviour observed following irradiation can be attributed to crystal damage alone. Examination of the d.s.c. traces shown in *Figure 5* and the derived data from these and other traces presented in *Figure 6* reveals that as for the 200A/*d* sample set, irradiation to even relatively low levels results in substantial changes in the melting behaviour of the isothermally crystallized material. The peak becomes broadened and the melting temperature falls with increasing radiation dose. The variation of the enthalpy of fusion with radiation dose is shown in *Figure 6b*. Initially, the total enthalpy of fusion (A plus Q) remains approximately constant (up to ~3 MGy), and then falls with increasing dose. This behaviour parallels that seen in the less thermally stable specimens (200A/*d*), and the origin of the initial plateau is probably the same: radiation-induced crystal disruption is offset, to some degree, by annealing effects, which in this case are associated with the thermally unstable quenched fraction in peak Q. This assertion is supported by the overall form of the d.s.c. traces shown in *Figure 5*, where the peak position of Q does not appear to vary greatly with radiation dose up to 11 MGy, beyond which point convergence of A and Q makes further analysis impossible.

By 33 MGy, the dose necessary to prevent crystallization of amorphous specimens, changes in the melting behaviour of this material are, once again, so extensive that the observed peak bears no resemblance whatsoever to that of the starting material. Indeed, reference to *Figures 3* and *5* demonstrates that the d.s.c. trace obtained from 245A/33 is almost identical to that from 200A/33, despite their very different thermal histories and initial crystallinity levels.

Comparison of irradiated PET and PEEK

It is clear from the above discussion and that contained within the preceding paper[1] that PET and PEEK have very different radiation responses. When irradiated prior to crystallization, both polymers behave in a qualitatively similar way: in the case of PEEK, a dose of ~60 MGy is required to prevent crystallization, while for PET the same effect can be achieved with a radiation dose of only ~30 MGy. These doses therefore constitute the critical level necessary in each polymer to prevent extensive molecular reorganization, and act to define what in the previous paper was termed the 'low dose' radiation regime. However, whereas in semicrystalline PEEK irradiation to ~60 MGy appears to result in little crystal destruction, as gauged by the d.s.c. examination of a thermally stable starting material (this point is reinforced in the following paper in which wide angle X-ray results are discussed[23]), the same cannot be said of PET that

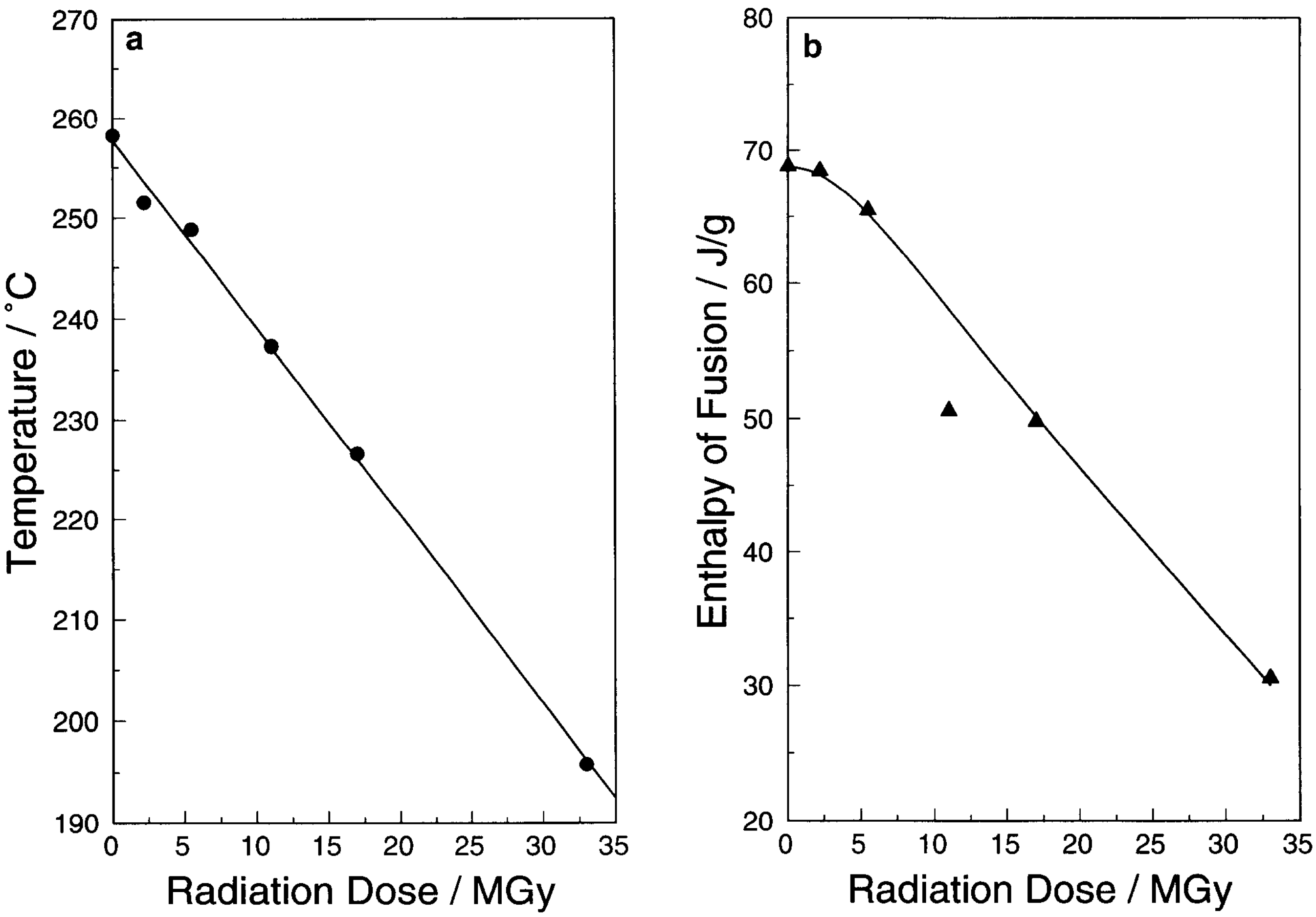

Figure 6 Melting transition data as a function of radiation dose for samples prepared by prior annealing at 245°C (245A/*d*): (a) peak melting temperature; (b) total enthalpy of fusion (A plus Q)

has been irradiated to ~30 MGy. Indeed, in the semicrystalline PET samples considered here, the effect of such an absorbed dose is so significant that the irradiation procedure has effectively erased any memory of the prior thermal history of the polymer; the observed behaviour is then determined by radiation effects alone. Thus, summarizing the low dose radiation response of each polymer, for PEEK (0–60 MGy) crosslinking reactions appear to occur preferentially at interlamellar sites or at fold surfaces with relatively little crystal disruption, whereas for PET (0–30 MGy) defect formation results in extensive crystal disruption. As a consequence, controlled irradiation does not constitute a viable aid to the study of morphology or crystallization, annealing and melting effects in PET, as it does in PEEK.

CONCLUSIONS

Exposure of PET to high energy electrons results in the formation of defect structures which serve to limit molecular motion and give rise to crystal disruption. Irradiation of amorphous samples indicates that a dose of the order of 30 MGy is required to prevent molecular reorganization (crystallization) completely in the glass. On irradiation, semicrystalline materials reveal evidence of extensive radiation damage and irradiation to even the modest levels required to prevent molecular reorganization results in such marked changes in the melting behaviour that the resulting endotherms cannot be compared with those obtained from equivalent unirradiated materials. Indeed, the crystal destruction that results from irradiation to 33 MGy is so significant that any 'memory' of the prior thermal history of the material is effectively erased by the procedure. The observed behaviour is then dominated by radiation effects alone. As a consequence, it is not possible to use irradiation as a means of studying the melting behaviour of PET in the absence of reorganization effects. The radiation response of PEEK described in the preceding paper would therefore appear to be highly unusual.

ACKNOWLEDGEMENT

The authors wish to thank National Power for giving permission to publish the work described.

REFERENCES

1 Vaughan, A. S. and Stevens, G. C. *Polymer* 1995, **36**, 1531
2 Kumar, S., Anderson, D. P. and Adams, W. W. *Polymer* 1986, **27**, 329
3 Hay, J. N., Langford, J. I. and Lloyd, J. R. *Polymer* 1989, **30**, 489
4 Elenga, R., Seguela, R. and Rietsch, F. *Polymer* 1991, **32**, 1975
5 Groeninckx, G., Reynaers, H., Berghmans, H. and Smets, G. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 1311
6 Mitsuishi, Y. and Ikeda, M. *J. Polym. Sci. A-2* 1966, **4**, 283
7 Roberts, R. C. *Polymer* 1969, **10**, 117
8 Bell, J. P. and Murayama, T. *J. Polym. Sci. A-2* 1969, **7**, 1059

9 Nealy, D. L., Davis, T. G. and Kibler, C. J. *J. Polym. Sci. A-2* 1970, **8**, 2141

10 Sweet, G. E. and Bell, J. P. *J. Polym. Sci. A-2* 1972, **10**, 1273

11 Roberts, R. C. *J. Polym. Sci., Polym. Lett. Edn* 1970, **8**, 381

12 Holdsworth, P. J. and Turner-Jones, A. *Polymer* 1971, **12**, 195

13 Coppola, G., Fabbri, P., Pallesi, B., Alfonso, G. C., Dondero, G. and Pedemonte, E. *Makromol. Chem.* 1975, **176**, 767

14 Groeninckx, G. and Reynaers, H. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 1325

15 Zhou, C. and Clough, S. B. *Polym. Eng. Sci.* 1988, **28**, 65

16 Cotton, C. MPhil Thesis, University of Reading, 1987

17 Cheng, S. Z. D., Cao, M.-Y. and Wunderlich, B. *Macromolecules* 1986, **19**, 1868

18 Bassett, D. C., Olley, R. H. and Al Raheil, I. A. M. *Polymer* 1988, **29**, 1745

19 Cebe, P. *Soc. Plast. Eng. Tech. Pap.* 1989, **35**, 1413

20 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953

21 Blundell, D. J. *Polymer* 1987, **28**, 2248

22 Charlesby, A. 'Atomic Radiation and Polymers', Pergamon Press, Oxford, 1960

23 Vaughan, A. S. and Sutton, S. J. *Polymer* 1995, **36**, 1549

24 Kusy, R. P. and Turner, D. T. *Macromolecules* 1971, **4**, 337

25 Séguéla, R. *Polym. Commun.* 1993, **34**, 1761

26 Yoda, O. *Polym. Commun.* 1984, **25**, 238

27 Vaughan, A. S. and Stevens, G. C. in 'Crystallization of Polymers' (Ed. M. Dosière), Kluwer, Dordrecht, 1993, p. 449