

# Molecular motions of non-crystalline poly(aryl ether-ether-ketone) PEEK and influence of electron beam irradiation

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The dynamic mechanical relaxation of non-crystalline poly(aryl ether-ether-ketone) PEEK and the one irradiated with electron beam were studied. The three distinct  $\gamma$ ,  $\beta$ ,  $\alpha'$  relaxation maxima were observed in unirradiated PEEK from low to high temperature. It was revealed from the study on the irradiation effects that three different molecular processes are overlapped in  $\gamma$  relaxation peak, i.e., molecular motion of water bound to main chain (peak temperature; at  $-100^\circ\text{C}$ ), local motion of main chain (at  $-80^\circ\text{C}$ ), and local mode of the aligned and/or oriented moiety (at  $-40^\circ\text{C}$ ). The  $\beta$  relaxation connected with the glass transition occurred at  $150^\circ\text{C}$  and it shifted to higher temperature by irradiation. The  $\alpha'$  relaxation which can be attributed to rearrangement of molecular chain due to crystallization was observed in unirradiated PEEK  $\sim 180^\circ\text{C}$  and its magnitude decreased with the increase in irradiation dose. This effect indicates the formation of structures inhibiting crystallization such as crosslinking and/or short branching during irradiation. A new relaxation,  $\beta'$ , appeared in the temperature range of  $40^\circ$  to  $100^\circ\text{C}$  by irradiation and its magnitude increased with dose. This relaxation was attributed to rearrangement of molecular chain from loosened packing around chain ends, which were introduced into the non-crystalline region by chain scission under irradiation, to more rigid molecular packing. From these observations, we proposed that deterioration in mechanical properties of non-crystalline PEEK by high energy electron beam was brought about not only by chain scission but structural changes such as crosslinking and/or branching in the main chain.

(Keywords: PEEK; viscoelastic properties; effect of irradiation; electron beam)

## INTRODUCTION

Recently, attention has been paid to polymers composed of aromatic rings in the skeleton (aromatic polymers) as high performance thermoresistant engineering plastics. These polymers would be introduced into instruments used in nuclear fields because of their excellent performance, but are lacking in systematic studies of radiation effects<sup>1-4</sup>. We have begun a study on radiation damage of the aromatic polymers in various radiation environments and reported, as a first step, the relative radiation resistivity of several aromatic polymers in terms of changes in tensile properties by irradiation of high energy electron beam<sup>5</sup>. It is revealed through the study that poly(aryl ether-ether-ketone) PEEK has an excellent resistivity and the aryl ether and ketone linkages have excellent stability against electron beam. Macroscopic damage such as in tensile property is an important matter in practice and microscopic damage is also important in understanding its mechanism.

PEEK enters the non-crystalline state by quenching from the melt ( $\sim 330^\circ\text{C}$ ) and turns to semi-crystalline polymer by heat treatment above the glass transition temperature ( $\sim 150^\circ\text{C}$ )<sup>6</sup>. Structural information such as crystal lattice parameters<sup>7</sup> and morphology<sup>8</sup> has been reported recently. Microscopic damage and its mechanisms would be guessed from the studies on changes in crystallinity and crystallization process for the irradiated PEEK. A recent study about non-crystalline PEEK by X-

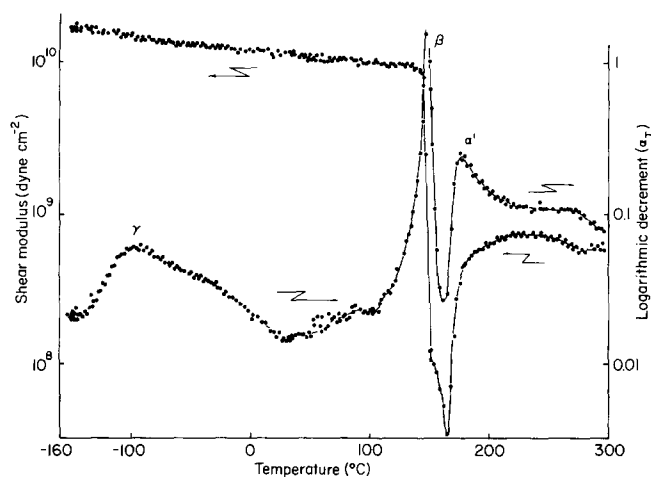
ray diffraction and thermal analysis showed that the crystallization was inhibited by irradiation of the electron beam<sup>9</sup>. In this paper we present the mechanical relaxation behaviour of non-crystalline PEEK and the one irradiated with electron beam and then discuss its microscopic damage revealed by the change in molecular mobility.

The mechanical relaxation of poly(aryl ether) has been studied extensively<sup>10-12</sup>, but some assignments of molecular motion are still not understood. It would be expected to obtain new information about the molecular process from the study on irradiated polymers.

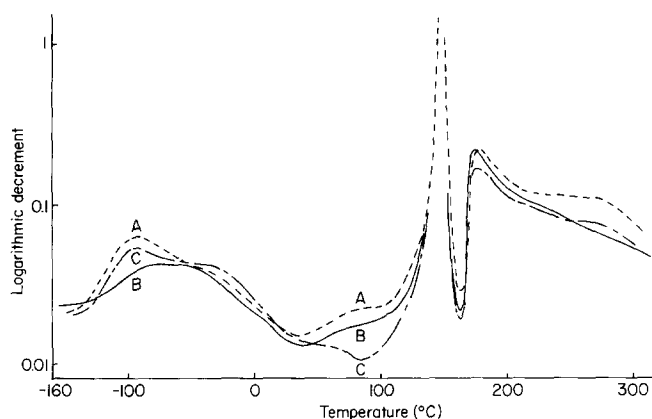
## EXPERIMENTAL

A semi-crystalline PEEK sheet with 1 mm thickness was kindly supplied from Sumitomo Kagaku Kogyo Co., Ltd. This sheet was quenched from  $360^\circ\text{C}$  to room temperature after reformation into a sheet with 0.5 mm thickness sheet in a hot press. By this treatment the specimen became transparent and non-crystalline.

For the study of quenched non-irradiated PEEK, the following specimens were used: (A) without further treatment after the quenching; (B) dried *in vacuo* at room temperature for 7 days; and (C) annealed at  $100^\circ\text{C}$  *in vacuo* for 1 h then conditioned in normal humidity ( $\sim 70\%$  R.H.) for more than 7 days. For the study on radiation effects, the specimen (C) was used.



**Figure 1** Dynamic viscoelastic properties of non-crystalline PEEK (A); quenched from 360°C



**Figure 2** Temperature dependence of logarithmic decrement of non-crystalline PEEK, (A); no treatment after quenching, (B); dried *in vacuo* at room temperature for 7 days, (C); annealed at 100°C *in vacuo* for 1 h, then conditioned in normal humidity

Irradiation was performed by electron beam with a dose rate of  $5 \times 10^3 \text{ Gy s}^{-1}$  (2 MeV, 1.5 mA) on a stainless steel plate with cooling water jacket to prevent a rise in the temperature of the specimen during irradiation. The dynamic viscoelastic properties were measured for  $100 \times 10 \times 0.5 \text{ mm}$  strips in the temperature range of  $-160^\circ$  to  $320^\circ\text{C}$  by a torsion pendulum type apparatus (RHESCA RD 1100AD) with the frequency range of 0.2 to 1 Hz.

## RESULTS AND DISCUSSION

### Non-irradiated PEEK

Figure 1 shows the mechanical relaxation spectrum of non-crystalline PEEK (A). Three distinct loss maxima are observed; named as  $\gamma$ ,  $\beta$  and  $\alpha'$  relaxation peaks from low to high temperature. The  $\gamma$  relaxation in rigid aromatic polymers such as poly(aryl ether), poly(aryl sulphone), and polyarylate was called mechanical secondary relaxation or low temperature mechanical relaxation<sup>10-12</sup>. The  $\gamma$  relaxation of flexible polymers composed of aliphatic chain was attributed to a rotation of short branching and/or local motion of non-crystalline molecules on the surface of crystals at low temperature. On the other hand, the low temperature mechanical relaxation in rigid polymers is attributed to a local motion of phenylene units in the main chain.

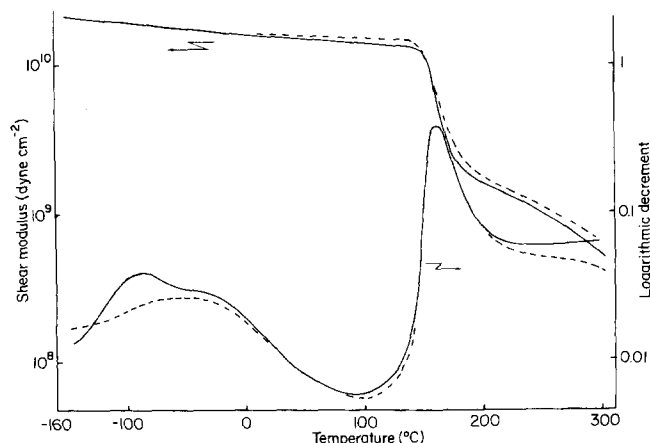
A very large loss peak is observed at 150°C ( $\beta$  relaxation). The  $\beta$  relaxation can be attributed to the molecular motion reflecting the transition from glassy to elastic state, because the shear modulus decreases sharply at the same temperature range.

Above 160°C both mechanical loss and shear modulus increase again and the loss becomes maximum at 180°C ( $\alpha'$  relaxation). This relaxation should be attributed to the molecular motion on rearrangement from non-crystalline to crystalline state, because the shear modulus increases at the same time. The observed crystallization temperature accords well with the one obtained by X-ray analysis<sup>6,9</sup>. In addition to the above three peaks, a shoulder is observed at the foot (40°–100°C) of the  $\beta$  relaxation.

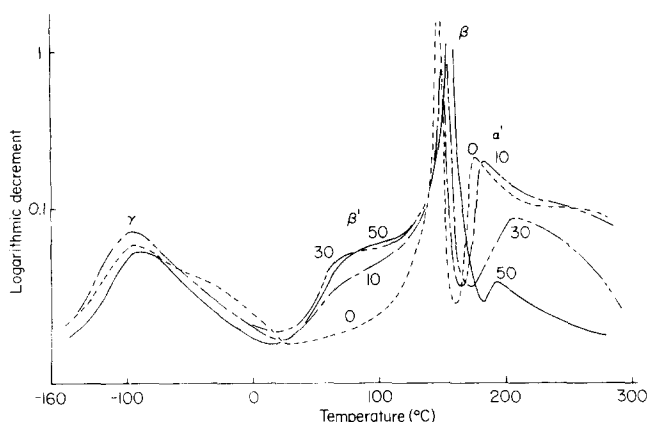
Figure 2 shows the temperature dependence of the loss factor (logarithmic decrement) for the specimens treated in three different ways. The quenched specimen (A) and annealed specimen (C) contain slight water and the content is about 0.1 wt%. The specimens (A) and (C) are named 'wet' and (B) as 'dry' specimen.

Figure 3 shows the relaxation spectra in the second run measured after measuring up to 320°C (first run).

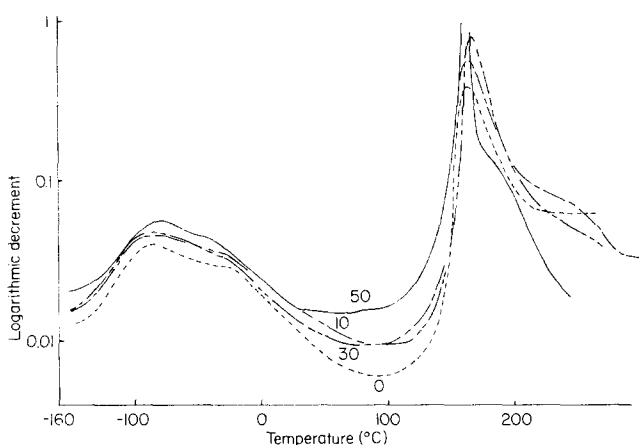
Comparing the Figures 2 and 3, it is clear that the profiles of  $\gamma$  relaxation peak are changed by drying treatment; i.e. the peak at  $-100^\circ\text{C}$  for 'wet' specimen disappears in the 'dry' one. Similar phenomena have been reported for the arylene polymers, such as polysulphones. Various polysulphones containing small amounts of water show large  $\gamma$  relaxation at about  $-120^\circ\text{C}$ , but its magnitude is decreased by drying<sup>10-12</sup>. Baccardda *et al.* concluded that the  $\gamma$  relaxation of polysulphone is due to rotational movements of absorbed water molecules bound to polar groups along polymer chains<sup>10</sup>. Kurz *et al.* described that the  $\gamma$  relaxation of polysulphone arises from the molecular process directly involving the  $-\text{SO}_2-$  group and its magnitude is enhanced by water absorption<sup>11</sup>. However, Robeson *et al.* pointed out that the  $\gamma$  relaxation of 'dry' polysulphone containing ether groups as well is due to a relaxation arising from the aryl ether group, and the one for 'wet' polysulphone is due to a complex of water with  $-\text{SO}_2-$  moiety and overlapped by the aryl ether relaxation<sup>12</sup>. Although detailed assignment differs from each other, the  $\gamma$  relaxation at the low temperature side may be concerned closely with molecular motion of water bound to the main chain, especially for polysulphone the one bound to  $-\text{SO}_2-$ .



**Figure 3** Temperature dependence of logarithmic decrement of unirradiated PEEK in the second run, (—) 'wet', (---) 'dry'



**Figure 4** Temperature dependence of logarithmic decrement of irradiated PEEK in the first run, doses are illustrated in the Figure in MGy



**Figure 5** Temperature dependence of logarithmic decrement of irradiated PEEK in the second run, doses are illustrated in the Figure in MGy

As shown in Figures 2 and 3, the  $\gamma$  relaxation peak at  $-100^\circ\text{C}$  shifted to  $-80^\circ\text{C}$  after drying. This means that the peak at  $-100^\circ\text{C}$ , overlapping with the  $-80^\circ\text{C}$  peak, disappears upon drying and that the  $-80^\circ\text{C}$  peak remains, since the peak at  $-100^\circ\text{C}$  is attributed to water molecules bound to the main chain by analogy with polysulphone. Robeson *et al.* studied the low temperature mechanical relaxation of several poly(aryl ether)s, but they did not report any effects of 'wet' or 'dry'. In the case of PEEK, the water absorbed moiety is probably phenyl ketone.

The magnitude of logarithmic decrement in the temperature range from  $40^\circ\text{C}$  to  $100^\circ\text{C}$  (named as  $\beta'$  relaxation region) is decreased by annealing and becomes very small in the second run. The mechanical loss in the  $\beta'$  relaxation region for the quenched specimen (A) is considered due to rearrangement of the main chain toward more rigid chain packing in non-crystalline region from a loosened packing introduced by rapid quenching, because this loss is decreased by annealing and becomes very small in the second run.

The  $\beta$  relaxation shifts to higher temperature and the peak is broadened in the second run. This can be interpreted as resulting from occurrence of restriction in a three dimensional molecular motion by the crystallites introduced during heating up to  $320^\circ\text{C}$  in the first run. The  $\alpha'$  relaxation disappears in the second run, indicating that

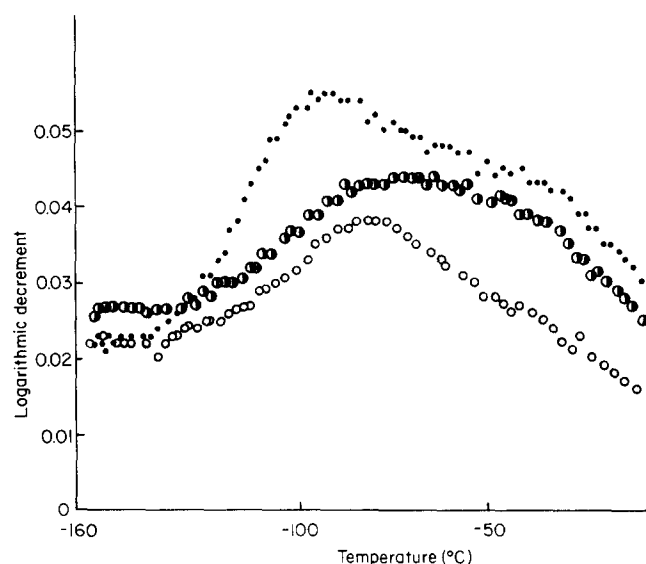
crystallization no longer occurs in the heating condition during the second run.

#### Irradiated PEEK

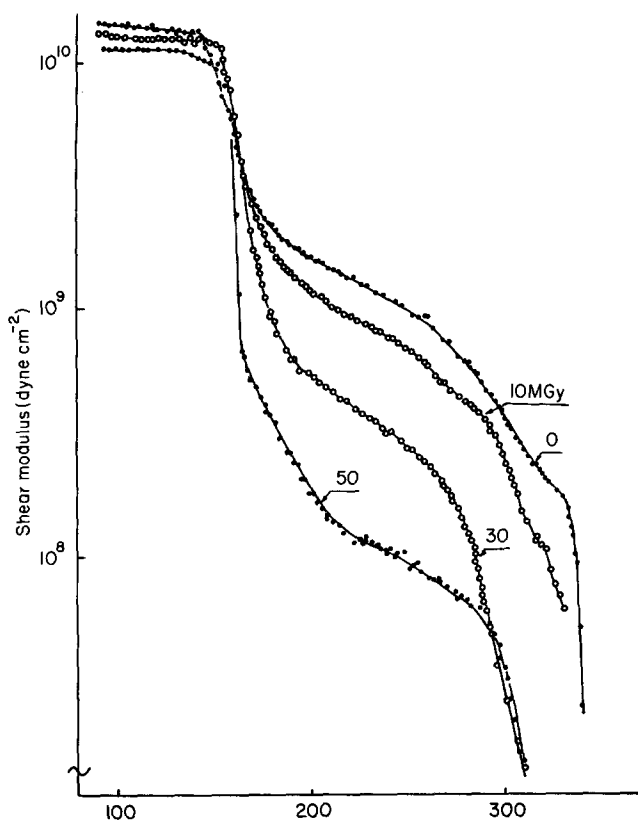
The results of unirradiated PEEK shows that the molecular packing in non-crystalline region is improved by annealing at  $100^\circ\text{C}$ , but that the crystallization process above the glass transition temperature is hardly affected by this annealing. In the present work, the specimens annealed at  $100^\circ\text{C}$  were used for the study on effects of irradiation, since changes in molecular packing by irradiation can be well detected. Measurements of viscoelastic properties were performed for the specimens conditioned in normal humidity after irradiation except the case in Figure 6. Thus, the relaxation spectra except those in Figure 6 are for 'wet' state containing small amounts of absorbed water.

Figures 4 and 5 show the loss factor as a function of temperature for the irradiated specimens with 0, 10, 30 and 50 MGy. Figure 4 is the result in the first run and Figure 5 is the result in the second run. In the first run, the  $\gamma$  relaxation peak becomes sharp and the shoulder at  $-40^\circ\text{C}$  disappears by irradiation. However, the shoulder appears again in the second run (Figure 5). The mechanical loss of the specimen irradiated with 30 MGy was measured after drying *in vacuo* for 7 days, and the spectrum in the  $\gamma$  relaxation region is shown together with those of 'wet' and 'dry' unirradiated specimens in Figure 6. The shoulder at  $-40^\circ\text{C}$  is extinguished by irradiation and the relaxation spectrum becomes simple in profile to have a peak temperature at  $-80^\circ\text{C}$ . This result means that different molecular processes are overlapped in the  $\gamma$  relaxation of unirradiated PEEK even in 'dry' state and one of them is extinguished by irradiation.

The disappearance of the shoulder at  $-40^\circ\text{C}$  (Figure 4) and the simplification of  $\gamma$  relaxation peak (Figure 6) by irradiation seem to indicate destruction of an inherent chemical structure. However, it might be better to consider that the shoulder is concerned with a molecular motion of the moiety in an inherent chain conformation, because the shoulder appears again in the second run after



**Figure 6** Temperature dependence of logarithmic decrement of irradiated and unirradiated PEEK in the relaxation region, (○) 30 MGy irradiated then drying, (○) unirradiated 'dry', (●) unirradiated 'wet'



**Figure 7** Temperature dependence of shear modulus of irradiated PEEK in the second run, doses are illustrated in the Figure in MGy

the first run up to 320°C. It can be considered that the original conformation disappears once by irradiation and reappears after melting then recrystallizing. PEEK consists of planar aromatic rings and the bond angle between aromatic rings is about 120°. Therefore, it can be said that the freedom of chain conformation is less compared with aliphatic polymer such as polyethylene. The entropy of fusion  $S_f$  of PEEK is obtained as 0.33 kJ kg<sup>-1</sup> deg<sup>-1</sup> by Blundell *et al.*<sup>8</sup> This value is smaller than that of polyethylene (0.67 kJ kg<sup>-1</sup> deg<sup>-1</sup>)<sup>13</sup>. The low value of  $S_f$  means that the conformational change by melting is less in PEEK compared with polyethylene. This indicates a probability that the molecular chains in PEEK are aligned and orientated partially even in a non-crystalline phase. Disappearance of the shoulder at -40°C may arise from destruction of such conformation.

The  $\beta'$  relaxation in the temperature range from 40°C to 100°C appears by irradiation and its magnitude increases with dose (Figure 4). As described above, the quenched unirradiated specimen (A) shows a similar relaxation behaviour in this temperature range and we assigned this relaxation to molecular motion of the main chain during rearrangement to a more rigid molecular packing. When main chain scission takes place during irradiation, the chain ends introduced by the scission could loosen the molecular packing and create similar packing to that obtained by quenching. Therefore, the  $\beta'$  relaxation in the irradiated specimen may be the molecular rearrangement from the loosened packing created by the irradiation to more rigid packing. The disappearance of  $\beta'$  relaxation in the second run supports the above discussions.

The  $\beta$  relaxation peak concerned with glass transition shifts to slightly higher temperature (Figures 4 and 5). The

glass transition temperature of polysulphone and polyarylate is lowered by irradiation as reported elsewhere<sup>14</sup>. The lowering of the glass transition of these polymers may be interpreted by lowering of the cohesive energy density by chain scission. Whereas, in the case of PEEK the glass transition temperature is increased by irradiation. This suggests that bulky structures to increase glass transition temperature are formed by irradiation.

The most marked change by irradiation appears in the  $\alpha'$  relaxation (Figure 4). The magnitude decreases with the increase of dose and the peak shifts to higher temperature with the irradiation of 10 and 30 MGy. However, with 50 MGy, the relaxation peak becomes very small and the peak temperature becomes lower. X-ray diffraction studies on the electron bombarded non-crystalline PEEK showed that the crystallization temperature became higher with increasing dose but that the crystallization was no longer observed even at 300°C, when irradiation was carried out up to 50 MGy<sup>9</sup>. These results indicate that structures inhibiting crystallization are formed by irradiation. Though not yet conclusive, the structure inhibiting crystallization may be crosslinking and/or branching. The increase of glass transition temperature as mentioned above supports such changes in the molecular structure. The  $\beta$  relaxation peak profile becomes sharp and its magnitude increases with increasing dose in the second run (Figure 5), and the profile for the specimen irradiated up to 50 MGy resembles that of unirradiated non-crystalline PEEK. The latter fact indicates that crystallization of highly irradiated PEEK is inhibited in the thermal history during the first run.

The magnitude of loss in the temperature range of 40°C to 120°C in the second run increase with dose. This indicates that a new relaxation mode is introduced by the formation of crosslinking and/or branching.

Figure 7 shows temperature dependence of dynamic shear modulus in the second run. The decrement of shear modulus just above the glass transition temperature becomes larger with dose, indicating also that crystallization during thermal history in the first run is inhibited with increasing dose. The sharp decrease in shear modulus for the unirradiated specimen at 320°C is due to melting of crystals. Similar decrease is observed in the irradiated specimens and the temperature giving the sharp change is lowered with dose. This also shows that structures inhibiting crystallization are formed by irradiation, since lowering of the temperature in this range corresponds to depression of crystallinity.

## CONCLUSION

Three different molecular processes are overlapped in the  $\gamma$  relaxation of 'wet' unirradiated non-crystalline PEEK, i.e. the relaxation at -100°C is due to molecular motion of water bound to main chain, the one at -80°C is due to local motion of phenyl ether and ketone, and the one at -40°C arises from molecular motion of an aligned and orientated moiety having near conformation to crystal.

The  $\beta'$  relaxation is appeared in the temperature range of 40°C to 100°C by quenching and irradiation. This relaxation is assigned to movement of main chain during rearrangement to more rigid molecular packing in non-crystalline region from the loosened packing brought about by quenching and radiation-induced chain ends.

The  $\beta$  relaxation concerned with glass transition occurs

at 150°C for unirradiated PEEK and the  $\beta$  relaxation peak slightly increased by irradiation.

The logarithmic decrement and shear modulus of unirradiated PEEK increases simultaneously above 160°C, then the loss reaches a maximum at 180°C ( $\alpha'$  relaxation). The  $\alpha'$  relaxation is assigned to molecular rearrangement during crystallization. The magnitude of  $\alpha'$  relaxation decreases with increasing dose. From the change in the behaviour of  $\beta$  and  $\alpha'$  relaxation structures inhibiting crystallization, for example crosslinking and/or branching, are formed by irradiation. Consequently, it is concluded that chain scission and three dimensional structure changes occur simultaneously in non-crystalline PEEK under irradiation of high energy electron beam.

#### REFERENCES

- 1 Gillham, J. K., Pezdirtz, G. F. and Epps, L. *J. Macromol. Sci.-Chem. A3* 1969, **6**, 1183
- 2 Brown, J. R. and O'Donnel, J. H. *J. Appl. Polym. Sci.* 1975, **19**, 405
- 3 Brown, J. R. and O'Donnel, J. H. *J. Appl. Polym. Sci.* 1979, **23**, 2763
- 4 Hinkeley, J. H. and Campbell, F. J. *J. Mater. Sci. Lett.* 1983, 276
- 5 Sasuga, T. and Hagiwara, M. *Polymer* (submitted)
- 6 Dawson, P. C. and Blundell, D. J. *Polymer* 1980, **21**, 577
- 7 Rueda, D. R., Ania, F., Richardson, A., Ward, I. M. and Calleja, F. *J. Polymer* 1983, **24** (Commun.), 258
- 8 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953
- 9 Yoda, O. *Polymer* 1984, **25** (Commun.), 238
- 10 Baccaredda, M., Butta, E., Forosini, V. and de Petris, S. *J. Polym. Sci. A-2* 1967, **5**, 1296
- 11 Kurz, J. E., Woodbrey, J. C. and Ohta, M. *J. Polym. Sci., A-2* 1970, **8**, 1169
- 12 Robeson, L. M., Farnham, A. G. and McGrath, J. E. *J. Appl. Polym. Symp.* 1975, **26**, 373
- 13 Quinn, Jr., F. A. and Mandelkern, L. *J. Am. Chem. Soc.* 1958, **80**, 3178
- 14 Sasuga, T., Hayakawa, N. and Yoshida, K. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 529