Electron beam irradiation effects on mechanical relaxation of aromatic polysulphones

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The effects of electron beam irradiation on the molecular motion of poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene oxy-1,4-phenyleneisopropylidene-1,4-phenylene) (U-PS) and poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene) (PES) were studied by measuring the dynamic viscoelastic properties. The γ relaxation peaks existing at low temperature (–100°C for U-PS, –110°C for PES) shifted to higher temperature and became narrower with increasing dose. A new relaxation (β' relaxation) appeared upon irradiation in the range from 40°C to just below the glass transition temperature. The magnitude of the β' relaxation was reduced by heat treatment and this relaxation disappeared in the second run. The β' relaxation was assigned as a molecular motion during rearrangement induced by chain scission from a loosened chain packing to a more rigid chain packing. The β relaxation peak responsible for the glass transition shifted to a lower temperature with increasing dose. It was concluded from these facts that polysulphones are mainly degraded by chain scission on the sulphone moiety.

(Keywords: polyarylsulphone; electron beam irradiation; viscoelastic properties; chain scission; chain packing)

INTRODUCTION

We have reported deterioration of mechanical properties with electron beam irradiation for ten kinds of aromatic polymers whose main chains are composed of aromatic rings[1]. Most aromatic polymers are more resistant to irradiation than aliphatic polymers, but the radiation resistances of poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene) (PES) and poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene oxy-1,4-phenyleneisopropylidene-1,4-phenylene) (U-PS) were of the same order as aliphatic polymers.

The ductility of glassy polymers such as polycarbonate[2,3] and polysulphone[4] was discussed in terms of the secondary or low-temperature relaxation, which relates to the local motion of the main chain in the glassy state. Deterioration in mechanical properties by irradiation would be related to changes in the low-temperature relaxation. Electron beam irradiation effects on mechanical relaxation of U-PS[5] and PES[6] have been reported. The changes in relaxation behaviour by irradiation of U-PS are summarized as follows: (1) the low-temperature relaxation (γ relaxation) shifts to a higher temperature and the peak profile becomes narrow; (2) the β relaxation, which is responsible for the glass transition, shifts to a lower temperature; and (3) a new relaxation appears in the range from 40°C to just below the glass transition temperature (β' relaxation). These findings were obtained by use of specimens conditioned in normal humidity, so that they contained a small amount of water molecules.

It is well known that the low-temperature relaxation of polysulphone observed about –100°C is affected by the absorption of a small amount of water[7–10]. To understand the actual radiation effects on mechanical relaxation, study of dried specimens is needed. Comparison of radiation effects on mechanical relaxation between dried and non-dried polysulphones was made in this paper.

The β' relaxation is often observed in the mechanical relaxation spectra of irradiated polymers with high glass transition temperature[11,12]. Another purpose of this work is to clarify the nature of the new relaxation that appears with irradiation.

EXPERIMENTAL

Poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene oxy-1,4-phenyleneisopropylidene-1,4-phenylene) (U-PS) (Union Carbide Corp.), poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene) (PES) (ICI Co. Ltd) and, for comparison, poly(oxy-1,4-phenyleneisopropylidene phthalate) (U-polymer, Unitika Co. Ltd) were used as samples. The specimens for viscoelastic properties were cut out from as-received sheets with about 0.5 mm thickness to strips of 100 × 10 × 0.5 mm dimension. Irradiation was performed with an electron beam with a dose rate of $5 \times 10^3\ \mathrm{Gy\,s^{-1}}$ (for CTA film dosimeter, 2 MeV, 1.5 mA) on a stainless-steel plate with a cooling water jacket to prevent a rise in the temperature of the specimen during irradiation. By this method an increase in specimen temperature during irradiation was avoided.

Drying of specimens was carried out in a vacuum over silica gel for 20 days after irradiation. In this paper, a specimen conditioned under normal humidity is called 'wet' and a specimen after drying is called 'dry'. The dynamic viscoelastic properties were measured in the

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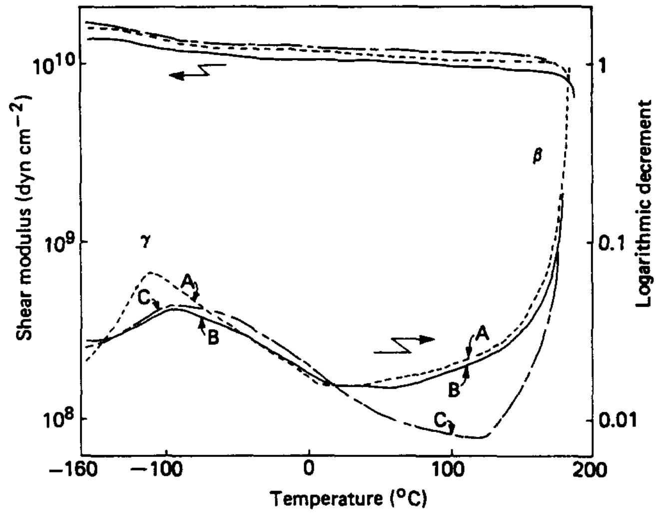

Figure 1 Mechanical relaxation spectra of unirradiated U-PS: A, 'wet'; B, 'dry'; C, second run of A

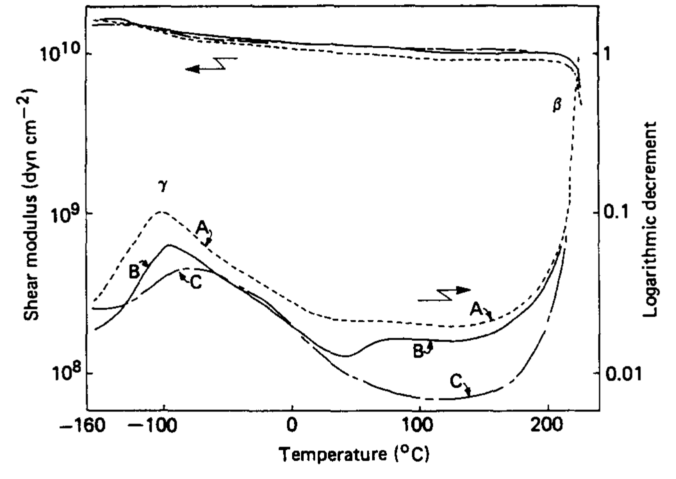

Figure 2 Mechanical relaxation spectra of unirradiated PES: A, 'wet'; B, 'dry'; C, second run of A

temperature range of −160 to 220°C by a torsion pendulum type apparatus (Rhesca RD-1100AD) with a frequency range of 0.2 to 1 Hz.

RESULTS

Figures 1 and *2* show the mechanical relaxation spectra of unirradiated U-PS and PES, respectively. Curve A represents the spectrum for a 'wet' specimen, curve B is for a 'dry' specimen, and curve C exhibits the result for the second run of a 'wet' specimen. Since the specimen used for the second run was kept in a vacuum after the first run, the spectra in the second run are in a 'dry' state. Two mechanical relaxations are observed in the logarithmic decrement vs. temperature curves. The loss peak observed at about −100°C is named the γ relaxation and the sharp increase in loss at higher temperatures is named the β relaxation.

By drying, the γ peak shifts to a higher temperature and the peak profile becomes broadened. The change in the γ relaxation behaviour for PES on drying is less than for U-PS. The weight loss of water on drying was 0.38% for U-PS and 1.07% for PES. The γ peak temperature and its profile for U-PS in the second run are similar to those of the 'dry' specimen, but in the case of PES the peak temperature and profile in the second run differ markedly from those in the first run.

Although the magnitude of the loss factor in the temperature range from 40°C to just below the β relaxation temperature for U-PS is scarcely affected by drying, it decreases markedly in the second run. In the case of PES, the magnitude of the mechanical loss in this range decreases on drying and a shoulder appears in the temperature range 40 to 100°C. This shoulder disappears and the magnitude of the loss factor decreases markedly in the second run.

Figures 3 and *4* show the relaxation spectra in the 'wet' state of U-PS and PES irradiated with various doses. In the case of U-PS, the γ relaxation peak becomes narrower and the peak shifts to a higher temperature with increasing dose. PES shows similar changes in the γ relaxation region, but the changes are less than those of U-PS. With irradiation a new mechanical relaxation appears in the temperature range of 40°C to just below the β relaxation temperature, and its magnitude increases with increased dose for both polymers. This relaxation is named the β′ relaxation. The β′ relaxation shifts to a lower temperature with increasing dose.

Figures 5 and *6* show the relaxation spectra in the 'dry'

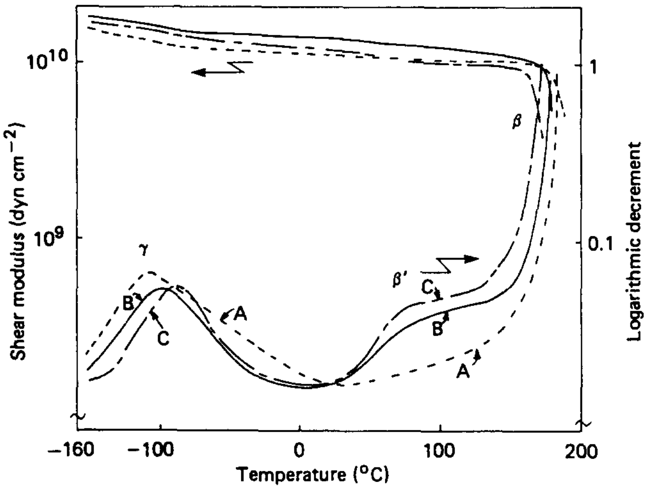

Figure 3 Mechanical relaxation spectra of U-PS irradiated with various doses in the 'wet' state: A, unirradiated; B, with 2 MGy; C, with 5 MGy

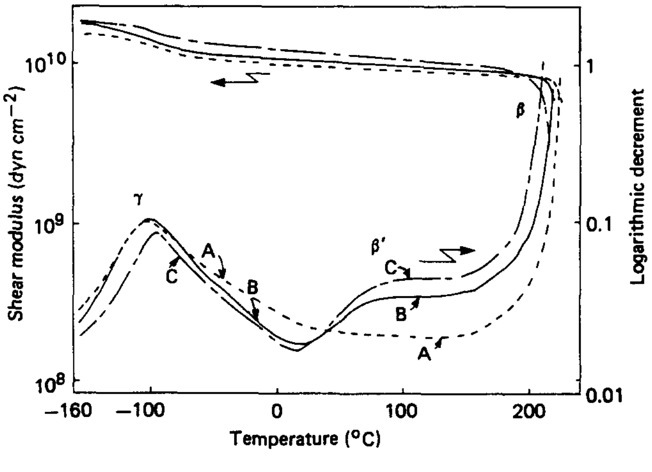

Figure 4 Mechanical relaxation spectra of PES irradiated with various doses in the 'wet' state: A, unirradiated; B, with 2 MGy; C, with 5 MGy

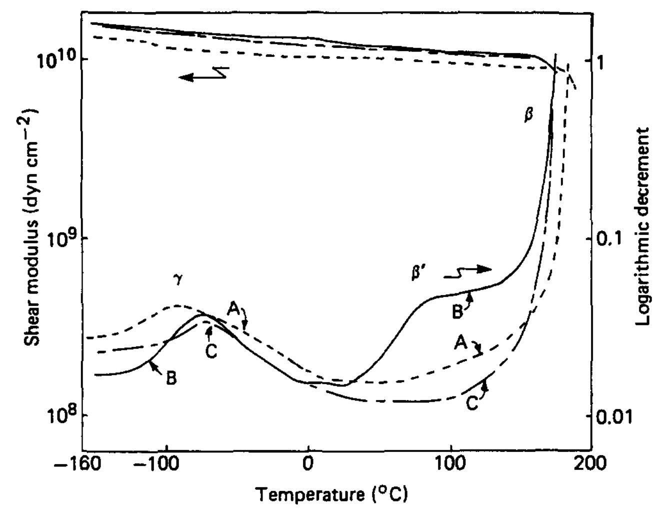

Figure 5 Mechanical relaxation spectra of U-PS irradiated with 5 MGy in the 'dry' state: A, unirradiated; B, first run; C, second run of B

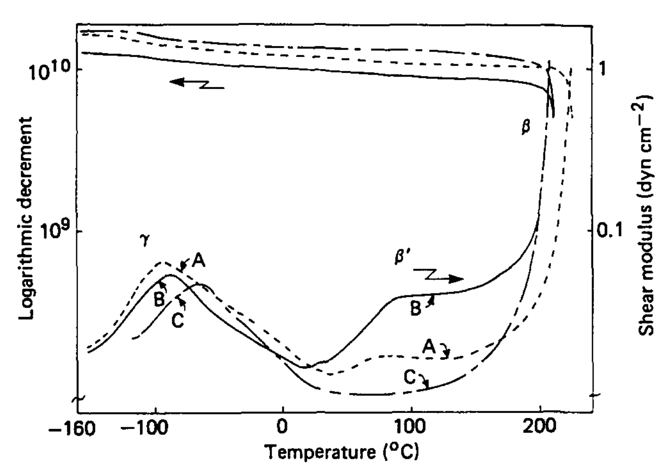

Figure 6 Mechanical relaxation spectra of PES irradiated with 5 MGy in the 'dry' state: A, unirradiated; B, first run; C, second run of B

state of U-PS and PES irradiated with 5 MGy, respectively. Curve A represents the spectrum for the unirradiated specimen, curve B for the irradiated specimen, and curve C exhibits the result of the second run for the irradiated specimen. In the case of U-PS, the γ relaxation peak shifts to a higher temperature and its profile becomes narrower upon irradiation, whereas in PES these changes are less. In the second run, the γ relaxation behaviour of U-PS is scarcely different from that in the first run, but for PES it changes markedly. The β' relaxation is observed also in the 'dry' state for both irradiated specimens and it disappears in the second run.

Figure 7 shows the relaxation spectra in the 'wet' state for U-PS which was subjected to various heat treatments after 5 MGy irradiation. Curve A represents the result in the first run and curve B is for the specimen annealed at 150°C in vacuum for 1 h and then kept in normal humidity (specimen B). Curve C shows the result for the specimen which was quenched from 220°C after the first run of specimen B. The γ and β relaxations are scarcely affected by annealing and quenching, but the magnitude of loss in the β' relaxation region is decreased by annealing and reappears again after quenching.

The same experiments for unirradiated U-polymer are shown in *Figure 8*. The notations of the curves are the same as in *Figure 7*. The β' relaxation is observed in the untreated specimen but it disappears with annealing and reappears again after rapid quenching from 220°C.

DISCUSSION

γ relaxation

The γ relaxation of U-PS is affected by water sorption (*Figures 1* and *2*). The same phenomena were reported for various aromatic polysulphones[7–10]. Assignments of the low-temperature relaxation of polysulphones in the 'wet' state differ between researchers. Baccaredda *et al.*[8] concluded that the low-temperature relaxation of 'wet' polysulphone is due to rotational movement of water molecules bound to polar groups along polymer chains. Kurz *et al.*[9] interpreted the low-temperature relaxation of polysulphone as arising from a molecular process directly involving the $-SO_2-$ group and concluded that its magnitude is enhanced by water sorption. Robeson *et al.*[10] pointed out that the low-temperature relaxation of 'wet' polysulphone is due to the complex motion of water bound to the $-SO_2-$ moiety and the aryl ether relaxation. Although detailed assignment differs in each case, the

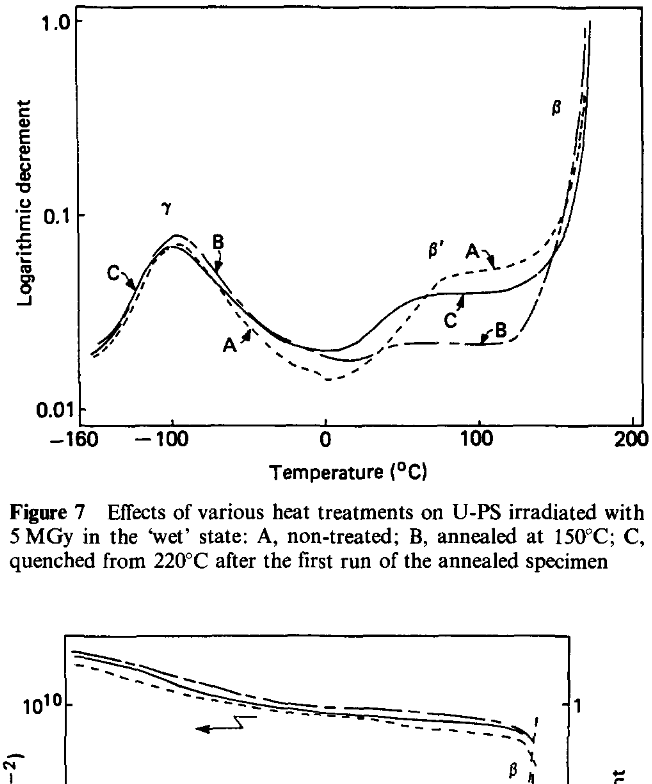

Figure 7 Effects of various heat treatments on U-PS irradiated with 5 MGy in the 'wet' state: A, non-treated; B, annealed at 150°C; C, quenched from 220°C after the first run of the annealed specimen

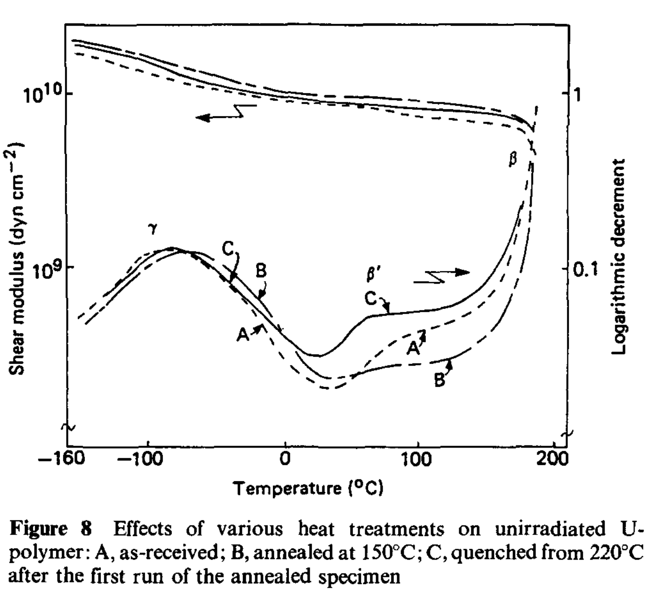

Figure 8 Effects of various heat treatments on unirradiated U-polymer: A, as-received; B, annealed at 150°C; C, quenched from 220°C after the first run of the annealed specimen

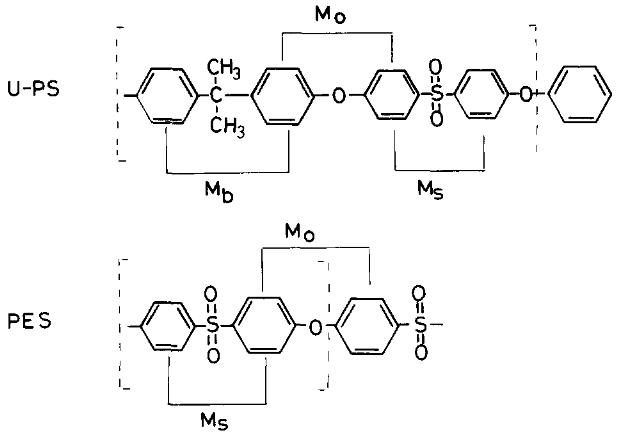

Figure 9 Chemical structures of repeating units for U-PS and PES

low-temperature relaxation of 'wet' polysulphone should be related to the molecular motion of water bound to the main chains. It can be considered that the change in the γ relaxation behaviour of U-PS on drying results from the desorption of water molecules.

In the case of PES the change in profile of the γ relaxation on drying is less than in U-PS. Hinkley[6] reported that the peak temperature of the low-temperature relaxation of PES dried above the glass transition temperature is -80°C (11 Hz). The γ peak temperature of PES dried by the method in this work is -95°C and it shifts to -80°C after more harsh drying is suffered in the second run. The effect of water molecules may remain in the γ relaxation of 'dry' PES, i.e. 'dry' PES may contain a very small amount of water even after vacuum drying at room temperature.

The low-temperature relaxation of rigid polymers such as aromatic polysulphones and poly(aryl ether) is attributed to local motion of the phenylene units that make up the main chains in the glassy state. *Figure 9* shows the chemical structures of repeating units of U-PS and PES, respectively. Elemental motions responsible for the γ relaxation in the 'dry' state should be motions of diphenyl sulphone (M_s), bisphenol A (M_b) and diphenyl ether (M_o), but it is reasonable to consider that the γ relaxation is responsible for their complex motion.

As shown in *Figures 3* to *6*, the γ relaxation peak shifts to higher temperature and the peak profile becomes narrower after irradiation. The change in peak temperature and profile of the relaxation should be related to changes in mode of local motion. A change in mode of molecular motion may be introduced by disintegration of some moiety among M_s, M_b and M_o.

We have evaluated brief radiation susceptibility of various aromatic units composing the main chains from comparison of radiation resistance of polymers themselves and their chemical structures[1]. The order of the susceptibility is:

diphenyl sulphone > bisphenol A > aromatic amide > diphenyl ether, diphenyl ketone > aromatic imide

Brown and O'Donnell[12] reported the *G* value of crosslinking (G_c) and scission (G_s) for U-PS and PES: $G_c = 0.04$, $G_s/G_c = 0.75$ for U-PS (*in vacuo* at 35°C); and $G_c = 0.07$, $G_s/G_c = 1.1$ for PES (*in vacuo* at 220°C). Further they reported that the main volatile gas in irradiation of U-PS and PES is sulphur dioxide[13,14]. It can be seen from these data that crosslinking and chain scission reactions take place simultaneously and chain scission occurs in the sulphone moiety during irradiation. The change in the γ relaxation behaviour could be explained in terms of disintegration of the sulphone moiety.

In the case of PES, the radiation-induced change in the γ relaxation region is less than in U-PS even in the 'dry' state. However, in the second run the γ peak shifts markedly to higher temperature and its profile is narrower. It is considered that the radiation-induced change in the γ relaxation may be masked by a very small amount of water molecules, because drying under vacuum at room temperature is not sufficient for PES. Also in the case of PES, the sulphone moiety should be disintegrated during irradiation.

β' relaxation

A new mechanical loss appears upon irradiation in the range from 40°C to just below the glass transition temperature and its magnitude increases with increasing dose. This relaxation is not affected by drying but is affected by heat treatment, indicating that the β' relaxation is affected only by thermal history. As shown in *Figures 7* and *8*, the magnitude of the loss factor in the β' relaxation region decreases with annealing, and it reappears with rapid quenching. Such behaviour with thermal treatment indicates that the β' relaxation is closely related to changes in chain conformation, such as molecular packing. Since U-PS and PES are non-crystalline polymers, the β' relaxation could be assigned to molecular motion during rearrangement of the main chain from a loosened chain packing towards a more rigid packing.

When main chain scission takes place during irradiation, the newly formed chain ends should loosen the packing of the surrounding molecules. It can be concluded that the β' relaxation observed in the irradiated specimens is due to molecular rearrangement from the loosened packing created during irradiation to a more rigid packing. Appearance of the β' relaxation on irradiation would be proof of the occurrence of main chain scission.

Unirradiated U-polymer (*Figure 8*) and 'dry' unirradiated PES (*Figure 2*) also show β' relaxation. These β' relaxations disappear after thermal treatment and reappear after rapid quenching. It is supposed that these polymer sheets are cooled with a relatively high cooling rate in production and that they have a loose chain packing.

Glass transition temperature

From studies of the radiation effects on molecular motion[11,16] during crystallization of non-crystalline poly(ether ether ketone) (PEEK) by X-ray diffraction[15], the following conclusions have been made: crosslinking occurs by high-dose-rate electron beam irradiation, whereas only chain scission takes place by oxidative irradiation (low-dose-rate γ-rays under oxygen pressure). At the same time, it was revealed that the β relaxation is affected by the radiation conditions. The β relaxation of PEEK shifts to higher temperature on electron beam irradiation; in contrast, it shifts to lower temperature fafter oxidative irradiation. It can be seen from these results that the glass transition temperature is increased by crosslinking and is lowered by chain scission (lowering of the molecular weight). Also, decrease of the glass transition temperature in the case of polysulphones would be related to lowering of the molecular weight.

The mechanism of deterioration of of polysulphones by electron beam irradiation is summarized as follows: deterioration of mechanical properties is mainly brought about by chain scission in the sulphone moiety.

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