Effects of Gamma Radiation on Two Aromatic Polysulfones. II. A Comparison of Irradiation at Various Temperatures in Air-Vacuum Environments.*

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Synopsis

The aromatic polysulfone poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneiso-propylidene-1,4-phenylene) (I) showed no change in flexural yield strength after doses of γ-radiation up to 600 Mrad in vacuum at 35, 80, and 125°C (T_g = 190°C). However, the flexural strength decreased markedly with doses above 100 Mrad on irradiation in air, to 40–60% of the initial value after 200–400 Mrad, depending on the sample and the irradiation conditions. Chain crosslinking was predominant over scission for irradiation in vacuum at all temperatures; $G(X)$, $G(S)$, and $G(S)/G(X)$ increased with the irradiation temperature, but $G(S)/G(X)$ decreased to zero above T_g. Poly-(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (II) behaved similarly, except that the flexural strength was found to be very dependent on the thermal treatment of the sample. This polymer showed a remarkable retention of its mechanical properties on irradiation up to 200°C (T_g = 230°C) in the absence of air, the flexural strength being retained up to 500 Mrad. Radiation annealing occurred at 35°C in vacuum and air and combined radiation and thermal annealing at 125 and 220°C. Progressive removal of surface layers from flexural test bars of I irradiated in air showed that the decrease in flexural strength with dose could be explained by a decrease in the molecular weight towards the surface resulting from radiation-oxidation reactions.

INTRODUCTION

In recent years there has been increasing interest in the development and utilization of organic polymeric materials which show durability in service at temperatures in excess of 100°C. These polymers usually contain a substantial proportion of aromatic structures, which leads to high mechanical strength and high modulus. Such high-temperature "engineering" plastics must also contain flexible segments to permit conventional processing and to prevent brittleness. It has been suggested that substitution in the aromatic ring would improve processability but only at the expense of thermal stability.[1] Aromatic polymers containing –COO–, –O–, and –SO$_2$– linkages are produced commercially, and it has been reported that the thermal stability of these materials is superior or comparable to poly(phenylene).[1] Aromatic polysulfones containing both –O– and –SO$_2$– linkages appear to offer particularly high performance characteristics.[2–5]

Radiation resistance is becoming an increasingly important consideration in the design of much equipment for nuclear instrumentation and for aerospace and military purposes. Therefore, the effect of radiation on the mechanical

properties of these polysulfones is of practical importance. We have previously published results[6,7] showing the high resistance of poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene), polysulfones I and II, respectively, to γ-irradiation in vacuum and air, measured by changes in limiting viscosity numbers and volatile product yields. However, the tensile and flexural strength of polysulfone I decreased rapidly above ca. 100 Mrad on irradiation in air, which we suggested could result from a decrease in the molecular weight at the surface of the test bars due to radiation-oxidation reactions.

In the present paper we report results of the effects of γ-irradiation on polysulfones I and II at various temperatures in both vacuum and air environments.

I

II
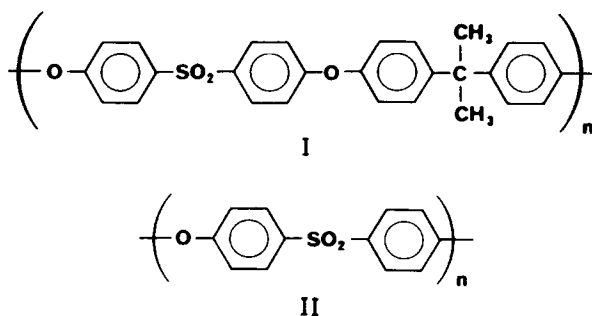
EXPERIMENTAL

Polysulfone I was supplied by Union Carbide Corporation (P-1700 and P-3500 resin) and polysulfone II by I.C.I. (200 P and 300 P resin), both polymers being in the form of granules. Sheet (3 mm thick) was compression molded at 250°C (I) and 300°C (II) at 4.8 MPa between Teflon-coated stainless-steel glazing plates, after removing absorbed water by drying at 150°C for 5 days. Bars (75 × 12 × 3 mm^3 and 50 × 6 × 3 mm^3) for flexural strength measurements were cut from the sheet and the edges polished with a rotating disk coated with carborundum paper and cooled in a stream of water. Some bars were thermally annealed in a vacuum oven at 150°C for 5 days. Bars or granules of both polymers were sealed in glass tubes after evacuation for 48 hr on a high-vacuum line for irradiation in vacuum or placed in open glass tubes for irradiation in air. The samples were irradiated in the cobalt-60, γ-irradiation pond facility of the Australian Atomic Energy Commission at 35 ± 3°C at a dose rate of 2–4 Mrad/hr, determined by ceric dosimetry.[8] An aluminum block thermostat was used for above-ambient irradiations. Dose rates were measured at the sample positions in the thermostat and corrections made for the absorption coefficients of the polymers relative to the dosimeter.[7,9]

Flexural strength measurements were made with an Instron model 1026 tensometer (75-mm bars: 50-mm span, crosshead speed 2 mm/min; 50-mm bars: 38-mm span, crosshead speed 1 mm/min). No significant size effect was noted in the flexural strength, which was determined according to ASTM D 790. Limiting viscosity numbers [η] were measured in chloroform (polysulfone I) and

dimethylformamide (polysulfone II) at 25°C with an Ubbelohde viscometer. The $[\eta]$ values can be converted into molecular weights for unirradiated polymer samples, and less reliably so for irradiated samples with increasing crosslinking, due to changes in hydrodynamic volume characteristics, using the relationship in eq. (1) derived by Allen et al.[10] and in eq. (2) due to Allen and McAinsh[11]:

$$\text{Polysulfone I } [\eta] = 0.024 \, \overline{M}_v^{0.72} \text{ cm}^3 \text{ g}^{-1} \text{ in chloroform at 25°C} \qquad (1)$$

$$\text{Polysulfone II } [\eta] = 0.033 \, \overline{M}_v^{0.64} \text{ cm}^3 \text{ g}^{-1} \text{ in dimethylformamide at 25°C} \quad (2)$$

Gel fractions were obtained by repeated extraction in a Soxhlet apparatus or a stainless-steel mesh bag using the above solvents and vacuum drying at 50°C and then at slightly above T_g until constant weight was obtained.

RESULTS

Polysulfone I

Irradiation in Vacuum. The flexural strength of polysulfone I was unaffected by doses of γ radiation up to 600 Mrad in vacuum at 35°C [Fig. 1(A)]. After all doses in this range, the flexural strength was a yield stress, i.e., measured at the yield point. Irradiation at 80°C in vacuum also had no effect on the flexural strength [Fig. 1(B)]. The flexural strength after irradiation from 100
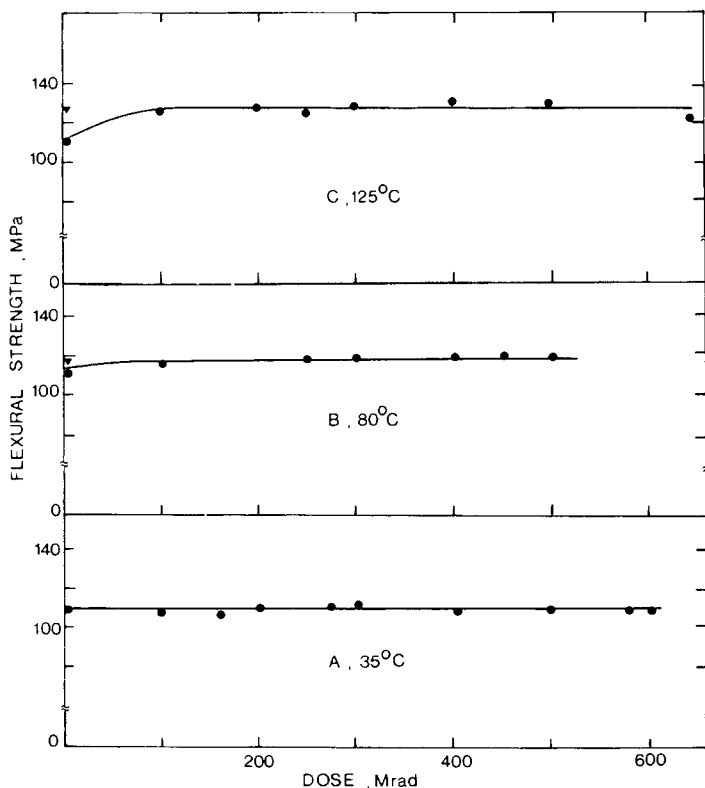

Fig. 1. Flexural strength of polysulfone I after irradiation in vacuum at 35, 80, and 125°C (▼, unirradiated annealed specimen).

to 645 Mrad at 125°C in vacuum remained constant, but was significantly higher (15%) than the value for the unirradiated sample, and also corresponded to ductile yield [Fig. 1(C)]. This increase was also achieved by heating at 125°C for 50 hr without irradiation, and thus associated with a thermal annealing process.

Irradiation in Air. Irradiation of polysulfone I in an atmosphere of air at 35°C resulted in a marked reduction in the flexural strength; it decreased to 50% of the initial value after 200 Mrad [Fig. 2(A)]. Irradiation at 125°C caused a similar decrease in flexural strength [Fig. 2(B)].

Viscosity and Solubility. The limiting viscosity number $[\eta]$ of polysulfone I increased on irradiation in vacuum and indicated gel doses of ca. 400 Mrad at 35°C, 360 Mrad at 80°C, and 100 Mrad at 125°C (Fig. 3). These gel doses are higher than those measured previously,[7] due to the higher initial molecular weight of the previously reported material. Irradiation at 220°C, i.e., above the glass-transition temperature of 190°C, resulted in a rapid increase in viscosity to a gel dose of ca. 30 Mrad. Measurements of the nongel or soluble fractions after irradiation in vacuum at 35, 80, 125, and 220°C are also shown in Fig. 3.

Polysulfone II

Irradiation in Vacuum. The effect of irradiation up to 600 Mrad in vacuum at 35°C on the flexural strength of polysulfone II is shown in Fig. 4(A). An initial increase in flexural strength occurred, with the measured strength up to 300 Mrad corresponding to a yield stress. However, at higher doses failure occurred by brittle fracture, and the flexural strength decreased to the initial value. Thermal
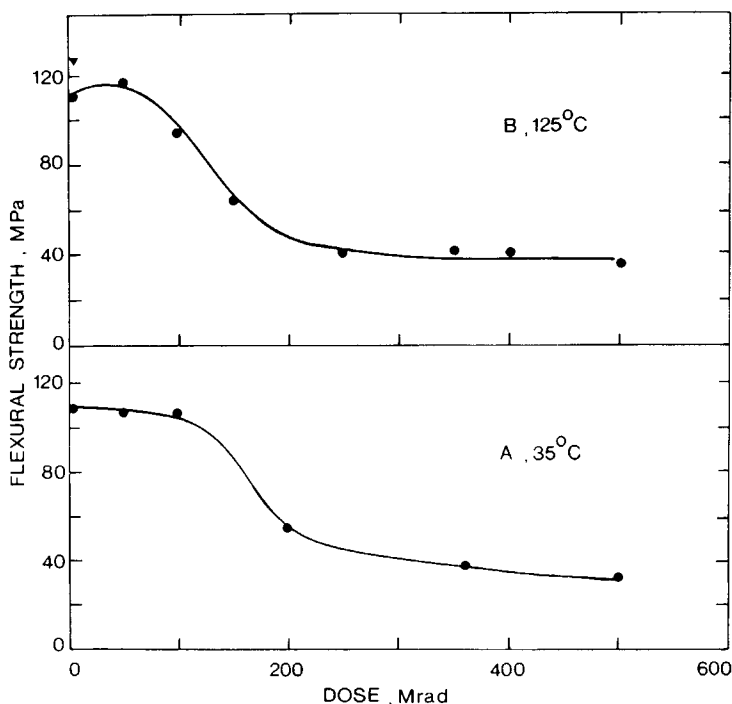

Fig. 2. Flexural strength of polysulfone I after irradiation in air at 35 and 125°C (▼, unirradiated annealed specimen).
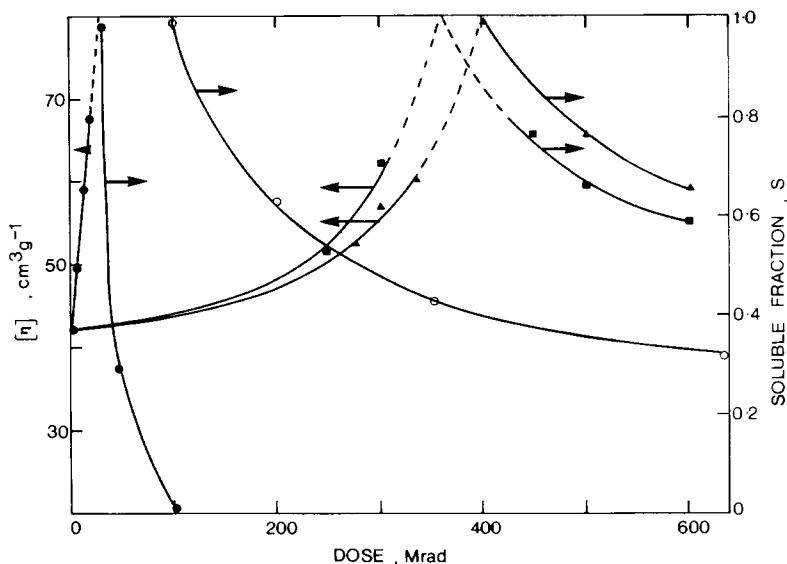
Fig. 3. Solution viscosity and soluble fraction measurements on polysulfone I after irradiation in vacuum at 35 (▲), 80 (■), 125 (O), and 220°C (●).

annealing of the unirradiated bars at 150°C for 50 hr also caused a substantial increase in flexural strength, although the experimental values showed considerable variation, with failure occurring sometimes by ductile yield and sometimes by brittle fracture.   Similar large increases in the tensile strength of polysulfone II as a result of aging in air at 150°C have been reported,[12] and it is evident that the mechanical properties are peculiarly sensitive to the thermal history of the sample.[13]   Irradiation at 35°C to moderate doses apparently causes changes in morphology comparable with those produced by thermal treatment, i.e., there is a process of radiation annealing.

Irradiation in vacuum at 125°C caused a similar initial increase of ca. 50% in the flexural strength of polysulfone II over a dose range of 300 Mrad, after which it decreased slightly up to 600 Mrad [Fig. 4(B)].   The maximum flexural strength was similar to that attained by thermal annealing of unirradiated bars; those which had been thermally annealed before irradiation showed only a small decrease in strength on irradiation.

Polysulfone II exhibited remarkable retention of its mechanical properties on irradiation at still higher temperatures.   Figure 4(C) shows that the flexural strength increased to the value attained by thermal annealing at 150°C during irradiation in vacuum over the dose range of 0–500 Mrad at 220°C.   This is above the heat-distortion temperature (203°C at 1.82 MPa)[12] of the polymer, and the mechanical test specimens showed some deformation during irradiation.

Irradiation in Air.   The flexural strength decreased on irradiation in air at 35°C [Fig. 5(A)] for doses up to 600 Mrad.   There was an initial increase in the flexural strength of unannealed samples, similar to the behavior observed in polysulfone II irradiated in vacuum, whereas annealed samples showed a continuous decrease in strength.   There was a reduction to 50% of the flexural strength of annealed, unirradiated bars after ca. 200 Mrad and to 30% after ca. 500 Mrad.   Irradiation in air at 125°C [Fig. 5(B)] resulted in a more rapid de-
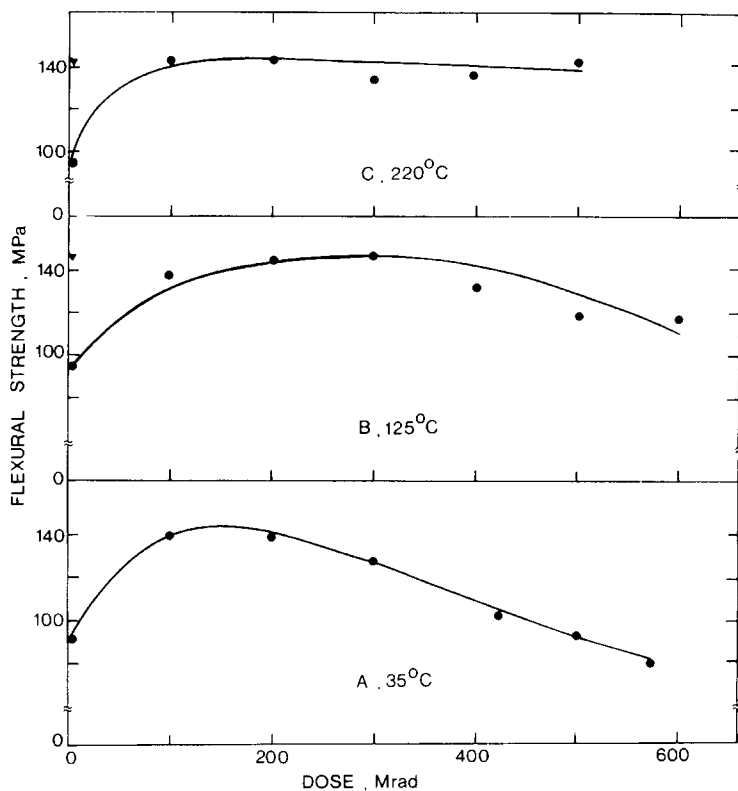
Fig. 4. Flexural strength of polysulfone II after irradiation in vacuum at 35, 125, and 220°C (▼, unirradiated annealed specimen).

crease in strength (to 50% after ca. 150 Mrad) but an apparent leveling-off above 250 Mrad at ca. 30% of the initial value.

Viscosity and Solubility. The limiting viscosity number $[\eta]$ increased with radiation dose in vacuum at 35, 125, and 220°C, and insoluble gel fractions were measured above 160 Mrad for irradiation at 220°C (Fig. 6). The viscosities indicated gel doses of ca. 300 and 450 Mrad for irradiation at 35 and 125°C, respectively.

Color Development. Both polysulfones I and II showed a similar marked color development during irradiation in both air and vacuum. The initial pale yellow polymer deepened and changed to a dark red-brown with increasing dose. The UV absorption band edge of 3-mm sheet, shown in Fig. 7 for polysulfone I irradiated in air, illustrates how the visible tail of the strong absorption of the unirradiated polymer, attributable to the phenylene groups, shifts further into the visible region with higher radiation doses. The wavelength for a constant absorbance A, e.g., $A = 2$, for 3-mm sheet plotted as a function of radiation dose (Fig. 8) gives a continuous curve over a large dose range. Also, the change in absorbance at a suitably chosen wavelength (ΔA at 17,500 cm^{-1} or 570 nm) increases linearly with dose, as shown in Fig. 8. Thus the depth-of-color development is such that these polysulfones could provide useful dosimeters, particularly for the dose range 50–500 Mrad. A suitable specimen size would be $30 \times 10 \times d$, where $d = 0.5$–3 mm. The effect of irradiation temperature and
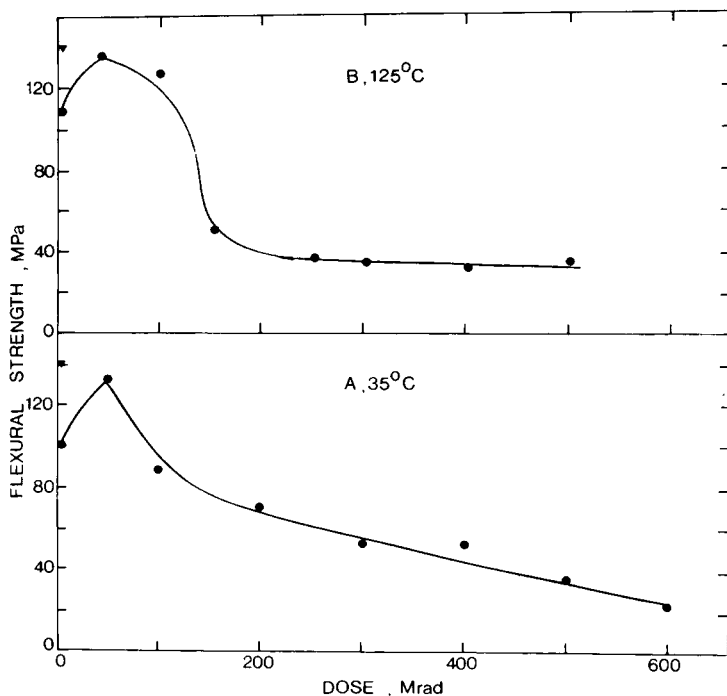
Fig. 5. Flexural strength of polysulfone II after irradiation in air at 35 and 125°C (▼, unirradiated annealed specimen).
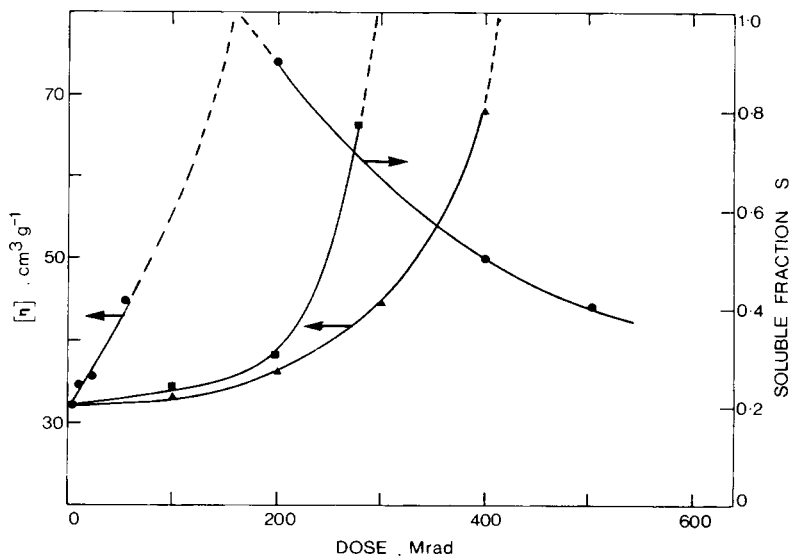

Fig. 6. Solution viscosity and soluble fraction measurements on polysulfone II after irradiation in vacuum at 35 (▲), 125 (■), and 220°C (●).

of post irradiation bleaching on the color development, which would be important for practical use as a dosimeter, has not been studied, but visual observations indicate that the latter is unlikely to be a problem. A similar procedure is also being developed for polysulfone I as a personnel dosimeter to measure exposure of the skin to UV radiation.[14]
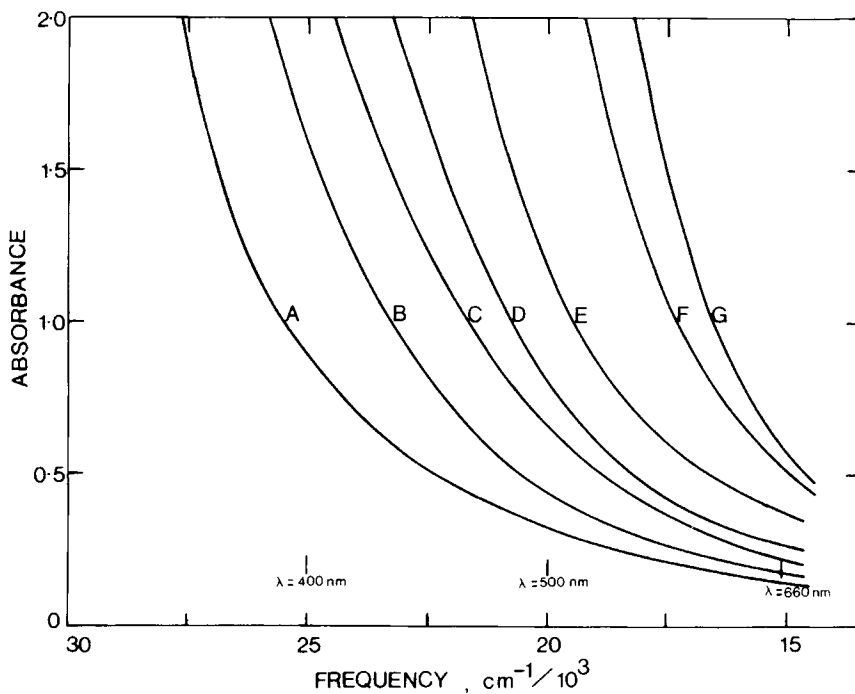
Fig. 7. The UV absorption band edge of polysulfone I (3-mm sheet) after irradiation in air at 35°C. A, unirradiated; B, 20 Mrad; C, 50 Mrad; D, 100 Mrad; E, 195 Mrad; F, 388 Mrad; G, 580 Mrad.
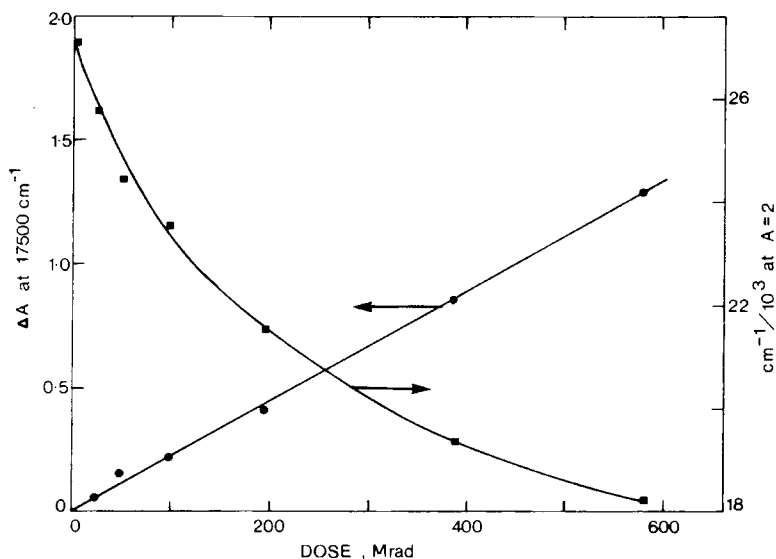

Fig. 8. Dose dependence of UV absorption band edge of polysulfone I (3-mm sheet) after irradiation in air at 35°C: ■, frequency where absorbance $A = 2.0$; ●, ΔA at 17,500 cm^{-1} (570 nm).

DISCUSSION

Mechanical Properties

The practical usefulness of a plastic material depends on its ability to withstand a sufficiently long period of exposure to a service environment without suffering a substantial decrease in the necessary material properties. Polysul-

fones I and II are high-modulus, high-strength materials which retain these properties after exposure to high temperatures. One aspect of the present work is an evaluation of the extent to which these properties are retained after exposure to a high-energy radiation environment.

The flexural strength of polysulfone I is unaffected by γ-irradiation in vacuum at 35°C up to 600 Mrad. We have also shown that there is no reduction in flexural strength after irradiation to similar doses in vacuum at 80 and 125°C. This is in marked contrast to the substantial decreases in strength after irradiation in air at 35 and 125°C.

The flexural strength does not decrease immediately on irradiation in air but after a threshold dose of ca. 100 Mrad, depending on the polymer sample and the irradiation conditions. This behavior is different from that of polystyrene, which shows an immediate decrease in flexural and tensile strength on irradiation in air,[15] probably due to the extent of degradation necessary to reduce the molecular weight (at the surface) into the range where strength is strongly dependent on molecular weight. Glassy polymers usually show a sigmoidal strength-molecular weight relationship; the marked decrease in the flexural strength of copolymers of styrene and methyl methacrylate irradiated in vacuum has been shown to result from a decrease in molecular weight and correlated convincingly with the strength-molecular weight relationships of the homopolymers.[16]

Limiting viscosity numbers of progressive layers removed from 3-mm thick bars of polysulfone I irradiated in air at 35°C to 200 Mrad plotted as a function of depth (Fig. 9) show that the molecular weight is reduced and that it is appreciably lower towards the surface than at the center of the bar. After removal of various surface layers (up to 10% from each side) from similarly irradiated bars, there were no significant changes in the flexural strength, as would be predicted from the molecular weight versus depth measurements in Fig. 9. Therefore, it can be concluded that the decrease in flexural strength of polysulfone I and II on irradiation in air is essentially due to a reduction in molecular weight, resulting from radiation-oxidation reactions.
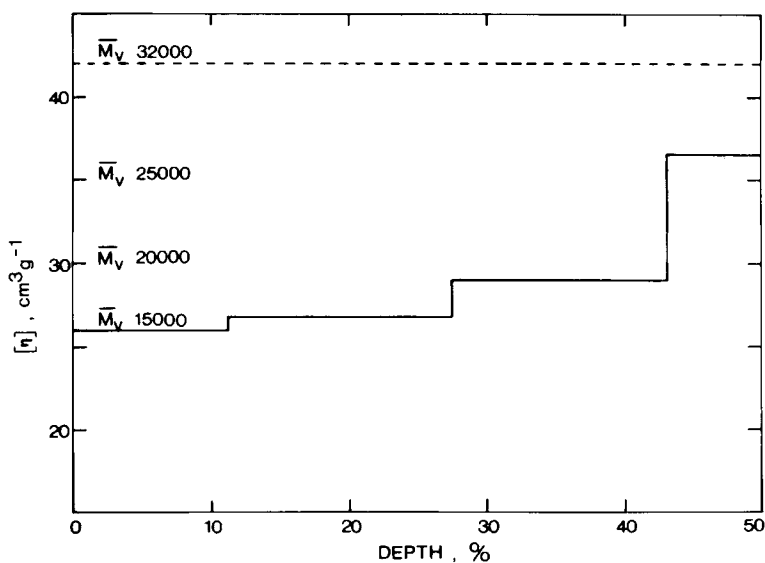

Fig. 9. Molecular weight of polysulfone I versus sample depth after 200 Mrad at 35°C in air.

Gesner and Keller[17,18] have observed a decrease in molecular weight of polysulfone I during UV illumination in air. They found that the tensile elongation was rapidly reduced, which is similar to our observations at low radiation doses.[7] However, UV illumination evidently results in a much more pronounced surface effect than γ-irradiation, in conformity with UV absorption at the surface by the aromatic chromophores. For γ-irradiation, we did not observe any surface "bloom," which was attributed to low-molecular-weight oxidation products (probably disulfonic acids) by Gesner and Keller.

Polysulfone II might be expected to have exceptional radiation stability because of its high aromatic content and the absence of any aliphatic groups. Previous work[7] on volatile product yields and limiting viscosity numbers of irradiated polysulfone II suggested that it was comparable, and possibly superior, to polysulfone I. In the present work, we have shown that the flexural strength is retained after high doses in vacuum, but that thermal and radiation annealing processes complicate the interpretation, especially at low temperatures. However, the radiation resistance at 220°C in vacuum was quite remarkable. This is close to the glass-transition temperature of 230°C and above the heat-distortion temperature (ASTM D648)[12] of 203°C, so that there must be considerable molecular mobility. Nevertheless, crosslinking is predominant, unlike polystyrene in which scission predominates at high temperatures.

There have been some brief reports of high resistance to γ and electron irradiation of polysulfones similar to II. Thus Gillham et al.[5] observed relatively small changes in relative rigidity and mechanical damping index for radiation doses up to 2500 Mrad using torsional braid analysis after irradiation in vacuum and air. Bringer and Morneau[3] found no change in tensile strength and elongation to break or yield after doses of γ radiation up to 120 Mrad. There was no indication whether irradiation was carried out in vacuum or in an inert atmosphere, but their results are quite incompatible with our measurements on polysulfone II after irradiation in air.

Thermal Annealing

The flexural strength of polysulfone II was found to be highly dependent on the thermal history of the sample, including the molding temperature. Thus bar specimens prepared from 200 P resin molded at 300°C gave flexural strengths of 143.2 and 158.4 MPa before and after annealing for 70 hr in vacuum at 150°C. Increases from 94.1 and 103.9 MPa to 149.1 and 158.4 MPa, respectively, were observed in the flexural strengths of bars prepared from sheet molded at 265°C. Moreover, the mode of failure changed from fracture to yield in these latter examples after annealing, indicating that internal stresses had been reduced. Polysulfone I was less dependent on the thermal treatment, but increases in flexural strength of up to 15% were observed after annealing at 125°C. Gotham and Turner[13] have also commented on the effect of thermal history on the mechanical properties of polysulfone II and suggested that applied stress influences the molecular reordering. They noted that failure could occur by ductile yield or brittle fracture in different conditions.

$G(S)$ and $G(X)$

The most suitable method for expressing quantitatively the effect of radiation on the molecular weight of a polymer is to calculate $G(S)$ and $G(X)$, the yield of main-chain scission and crosslinking, respectively. They can be calculated from measurements of the soluble fraction S of the polymer after various radiation doses r in excess of the gel dose r_g by using the Charlesby-Pinner relationship for an initial, most probable molecular size distribution[19–21]:

$$S + S^{1/2} = \dot{\tau}/2\dot{\chi} + 1/2\dot{\chi}ur \qquad (3)$$

where $\dot{\tau}$ and $\dot{\chi}$ are the numbers of main-chain scissions and crosslinks, respectively, formed per monomer unit per unit dose (Mrad in this paper) and u is the initial, number-average degree of polymerization. Thus $\dot{\tau}/2\dot{\chi}$ is the intercept at infinite dose and $\dot{\chi}$ can be obtained from the slope of the linear plot of $S + S^{1/2}$ versus $1/r$. Curved relationships are obtained when the initial distribution is not of the most probable type; the individual values of $\dot{\tau}$ and $\dot{\chi}$ can then be obtained using appropriate modifications of eq. (1).[21]

The gel measurements in the present work are limited by the high gel doses of both polymers, particularly for polysulfone II, except for irradiation at 220°C. Substantial reductions in the gel fractions were observed on the second extraction after vacuum drying at slightly above T_g, which was necessary for complete solvent removal. There is a possibility that scission of weakly crosslinked regions may occur, leading to enhanced $G(S)$ values. $G(S)$ and $G(X)$ have been calculated from eq. (3) and are given in Table I. The limited data preclude accurate determinations of $G(X)$ and $G(S)$; nevertheless, the relative importance and temperature dependence of crosslinking and scission are usefully indicated. The increased G values with increasing temperature support our earlier suggestion[7] that differences between our results at ambient temperature and those of Davis et al.[21] were due to a rise in temperature of their samples due to the high dose rate of 240 Mrad/hr. Both $G(X)$ and $G(S)$, as well as $G(S)/G(X)$, increase with increasing temperature up to 125°C. Above T_g, $G(S)/G(X)$ for polysulfone I fell rapidly towards zero. This remarkable temperature effect is quite different from that observed in polystyrene, where scission predominates over crosslinking above T_g.[22] Although the $G(S)$ and $G(X)$ values for both polysulfones are not greatly different from those for polystyrene at ambient temperature, the gel doses are much higher because the initial molecular weights are ca. 40,000 compared with ca. 200,000 for a typical commercial polystyrene.

TABLE I
Main-Chain Scission $G(S)$ and Crosslinking $G(X)$ Yields for Irradiation of Polysulfones I and II in Vacuum at Various Temperatures

| Polymer	Irradiation temperature, °C	r_g, Mrad	$G(S)$	$G(X)$	$G(S)/G(X)$
I	35	400	0.03	0.04	0.75
I	80	360	0.05	0.05	1.0
I	125	100	0.30	0.20	1.5
I	220	30	0.0	0.67	0.0
II	220	160	0.08	0.07	1.1

Radiation-Induced Reactions

The mechanism of scission and crosslinking in polysulfone I has been discussed previously.[7] The radiation-induced reactions in polysulfone II may be expected to be similar, except that no aliphatic group is available to participate in cross-linking, and the mechanism whereby this occurs remains to be established. Endlinking can be envisaged by the reaction shown in eqs. (4) and (5):

$$-Ar-SO_2-Ar- \longrightarrow -Ar\cdot + -ArSO_2\cdot$$
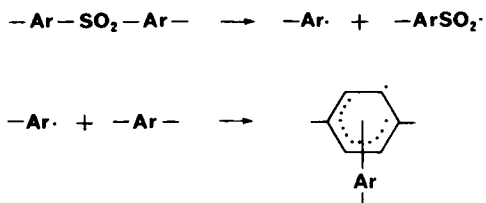
which is analogous to the attack of substituted phenyl radicals on benzene solvent molecules observed by Khodair et al.[23] in the photolysis of aromatic sulfones in benzene. Whereas they postulated that the Ar-$SO_2\cdot$ radical had a low probability of reacting with an aromatic ring or eliminating SO_2 in photolysis, our volatile product analyses[7] indicate that SO_2 is a major product from γ-irradiation (probably due to the higher energy of the radiation), similar to thermal degradation of polysulfone I.[24] Therefore, irradiation of polysulfone II can be expected to give reaction (6),

$$-ArSO_2\cdot \longrightarrow -Ar\cdot + SO_2$$
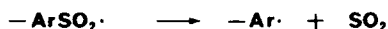
which may be followed by reaction (7), providing an effective crosslinking mechanism:
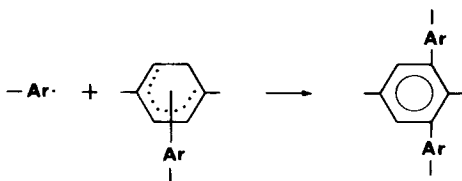
The radiolytic formation of $ArSO_2\cdot$ radicals has been demonstrated in disulfones by Geoffroy and Lucken[25] and in polysulfone I by Lyons et al.[26], who also observed cyclohexadienyl radicals, indicating the involvement of the aromatic rings in the crosslinking reactions.

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