Effects of Gamma Radiation on
Two Aromatic Polysulfones

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Synopsis

Two aromatic polysulfones, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (I) and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (II), undergo crosslinking and chain scission at 30°C during γ-irradiation, the former being predominant in vacuum and the latter in air. Both processes occurred more readily in I, which contains isopropylidene linkages. Gel measurements gave G(crosslink) = 0.051, G(scission) = 0.012 for this polymer at 30°C in vacuum. Increased irradiation temperatures resulted in higher crosslinking and gas yields, especially above the glass transition temperature. The tensile strength, flexural strength, and modulus of I were unaffected by γ-irradiation up to about 50 Mrad in air, but the strength decreased markedly at higher doses. The elongation at break decreased progressively with dose. For both polymers, G(gas) = 0.04 at 30°C with the main products being SO_2, H_2, CO_2, CH_4, and H_2O.

INTRODUCTION

The incorporation of aromatic groups into the structure of polymers greatly reduces their sensitivity to high-energy radiation. Thus, polystyrene,[1] poly(ethylene terephthalate),[2] and poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyl),[3] and poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-2-hydroxytrimethylene)[4] all show considerable resistance to radiation. The G values for crosslinking, main-chain scission, and gas production are all considerably less than for polymers which do not contain aromatic structures.

Aromatic polysulfones have recently been introduced to the commercial plastics field and are of technological importance because of their high glass transition temperatures and high thermal stability in both inert and oxidizing atmospheres.[5-10] They would be expected to combine high radiation resistance with their desirable thermal properties because of their aromatic content. We have published preliminary results[11] showing the high resistance of polysulfone I to γ-irradiation at 30°C, as measured by solution viscosity, gel formation, and gas production. Davis, Gleaves, Golden, and Huglin[12] have reported that polysulfone I is resistant to electron irradiation at ambient temperature.

This paper reports a comparison of the effects of γ-radiation on poly-sulfones I and II,

I

II
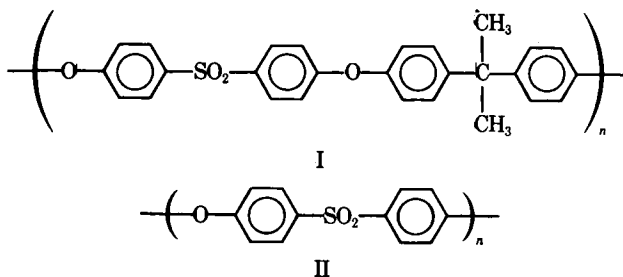
to determine the importance of the isopropylidene linkage in crosslinking reactions. The effect of irradiation temperature was examined for poly-sulfone I by irradiating at 125°C and 240°C, i.e., below and above the glass transition temperature (T_g = 190°C).[5]

EXPERIMENTAL

Polysulfone I was supplied by Union Carbide Corporation as granules and injection-molded ASTM test specimens (P-1700 resin). Some of the polymer was purified by repeated precipitation into methanol from a chloroform solution and dried under vacuum at 110°C for 24 hr. It was then in the form of small, white, fibrous flakes. Microanalysis results were in good agreement with the given structure (found: C = 72.93%, H = 5.40%, O = 14.5%, S = 7.0%; theor.; C = 73.28%, H = 5.01%, O = 14.46%, S = 7.25%).

Polysulfone II was provided by Dr. J. McAinsh. It was prepared by condensation polymerization of phenyl sulfonyl chloride and phenol in sulfolane[13] and was in the form of a white powder which was dried under vacuum at 110°C for 24 hr. Microanalysis corresponded to the given structure (found: C = 61.43%, H = 3.47%, O = 20.4%, S = 13.9%; theor.: C = 62.06%, H = 3.4%, O = 20.6%, S = 13.81%).

Samples (0.6 to 1.0 g) of both polymers were either sealed in glass tubes with breakseals after evacuation for 18 hr on a high-vacuum line or sealed in air. Irradiations were carried out in the cobalt-60 γ-irradiation pond facility of the Australian Atomic Energy Commission at 30° ± 2°C at a dose rate of 0.5 Mrad/hr, determined by a Fricke dosimeter,[14] $G(Fe^{3+})$ = 15.5. An aluminum block heater with temperature control to ±0.5°C was used for irradiations at 125°C and 240°C. Dose corrections[15] gave D(polymer)/D(dosimeter) = 0.944 for polysulfone I and 0.930 for polysulfone II.

Solution viscosity measurements were made at 30°C with an Ubbelohde viscometer using chloroform for polysulfone I and dimethylformamide for polysulfone II. Gaseous products of vacuum irradiated samples were measured on a vacuum line with a gas burette and analyzed by gas chromatography using a Porapak column. The identity of the components was checked by mass spectrometry.

Tensile and flexural strength measurements on polysulfone I were made with an Instron tensometer according to ASTM D638 and ASTM D790 at 25°C using 0.125-in.-thick specimens. The gel content of irradiated polymer was measured by extracting the soluble fraction with chloroform in a Soxhlet extractor and drying to constant weight.

RESULTS

Limiting Viscosity Number Changes

Polysulfone I. The effects of irradiation at 30°C in air and under vacuum on the limiting viscosity number have been given previously.[11] Figure 1 shows the limiting viscosity number changes after irradiation in air and under vacuum at 125°C. Irradiation under vacuum caused gel formation on irradiation in air up to 250 Mrad at 30°C and 50 Mrad at 125°C, but there was no gel formation on irradiation in air up to 473 Mrad at 30°C and 95 Mrad at 125°C. Irradiation at 240°C gave an insoluble gel in both air and vacuum after 14 Mrad. The formation of gel was due to the combination of temperature and radiation, no gel being formed by heating alone for an equivalent period in air and under vacuum. The gel fraction was 0.31 for the vacuum-irradiated sample and a function of depth in the sample and of dose rate for the air-irradiated sample. The sample irradiated in air appeared to be extensively oxidized as indicated by a dark-brown coloration of the soluble portion in a chloroform solution.

Polysulfone II. The effect of irradiation at 30°C under vacuum and in air on the limiting viscosity number of polysulfone II is shown in Figure 2.
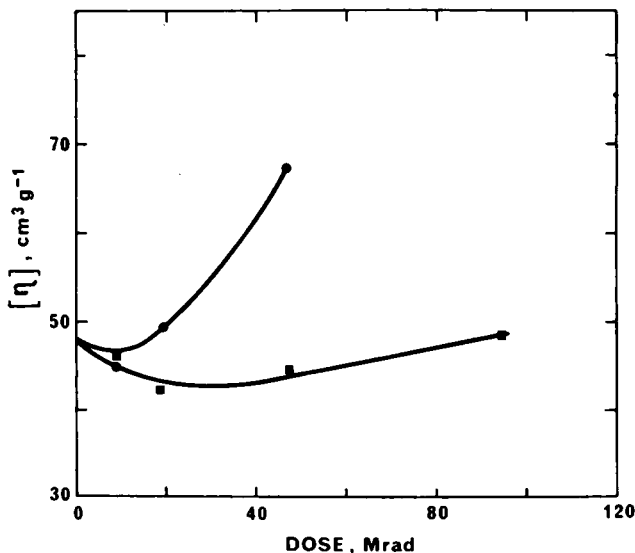

Fig. 1. Limiting viscosity number [η] vs. dose for irradiation of polysulfone I at 125°C: (■) in air; (●) under vacuum.
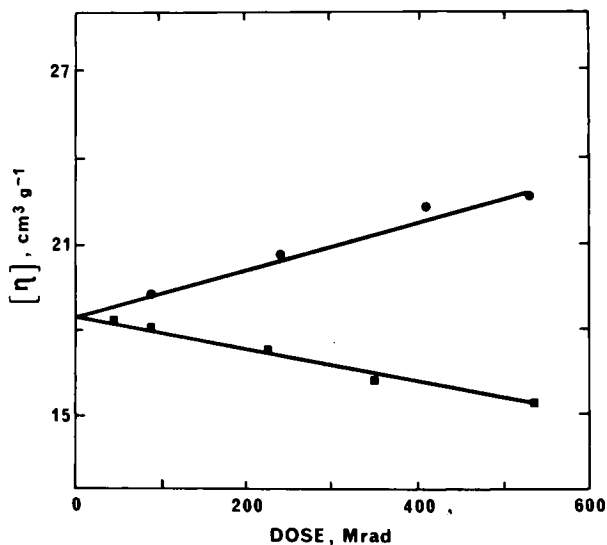
Fig. 2. Limiting viscosity number [η] vs. dose for irradiation of polysulfone II at 30°C: (■) in air; (●) under vacuum.

The [η] value increased slightly after 540 Mrad in vacuum, but there was no gel formation, and decreased slightly for the same dose in air.

Gaseous Products

Polysulfone I. The yields of volatile products versus radiation dose at 30°C are shown in Figure 3. The G(total gas) value at 30°C was 0.04 and showed no significant change with dose in the range of 270–550 Mrad. The gas composition also did not change significantly with dose. Sulfur dioxide was the predominant product (47%), with smaller amounts of water (23%), hydrogen (19%), carbon dioxide (5%), and methane (5%). A trace amount of propane (<0.5%) and a minor product corresponding to $m/e = 60$ in the mass spectrum were observed. This was attributed to carbonyl sulfide. G(total gas) increased to 0.29 at 125°C and 0.65 and 240°C. and the gas composition differed significantly from that at 30°C. At 125°C, sulfur dioxide = 56%, water = 34%, carbon dioxide = 5%, hydrogen = 3%, and methane = 2%. At 240°C, sulfur dioxide = 59%, water = 31%, carbon dioxide = 5%, hydrogen = 3%, and methane = 2%.

Polysulfone II. The volatile product yields for various radiation doses at 30°C are shown in Figure 4. The same components are found as for polysulfone I except that water was absent. G(total gas) = 0.04 was similar to that for polysulfone I. Sulfur dioxide was again the major product (70%) with carbon dioxide (19%), hydrogen (7%), and methane (4%). These are average values in the dose range of 240–540 Mrad. The presence of methane is unexpected, but recent NMR measurements indicate that there is a little residual sulfolane from the preparation which may provide a source of methane on irradiation.[16]
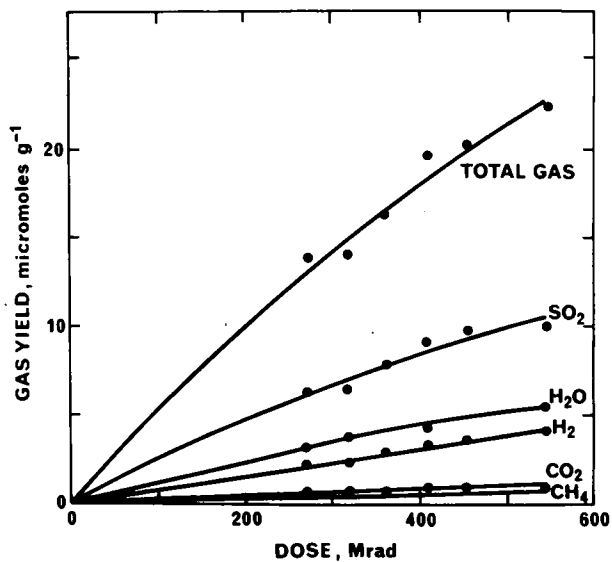
Fig. 3. Volatile product yields vs. dose for irradiation of polysulfone I at 30°C under vacuum.
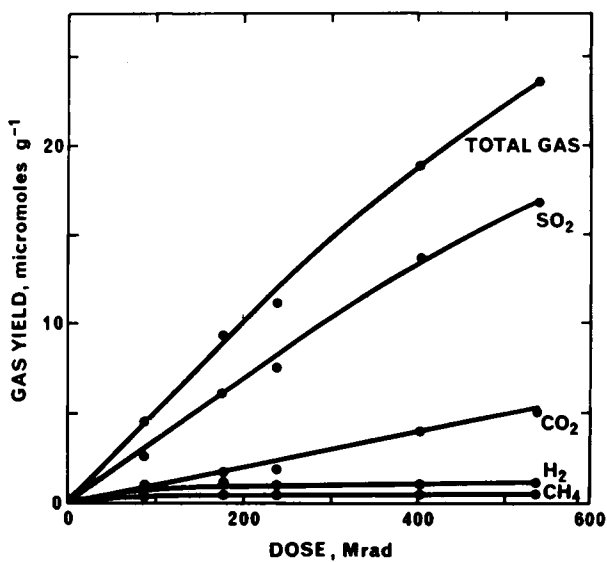

Fig. 4. Volatile product yields vs. dose for irradiation of polysulfone II at 30°C under vacuum.

Gel Formation in Polysulfone I

Charlesby and Pinner[17] derived an expression for the variation of the soluble fraction (S) with dose (r):

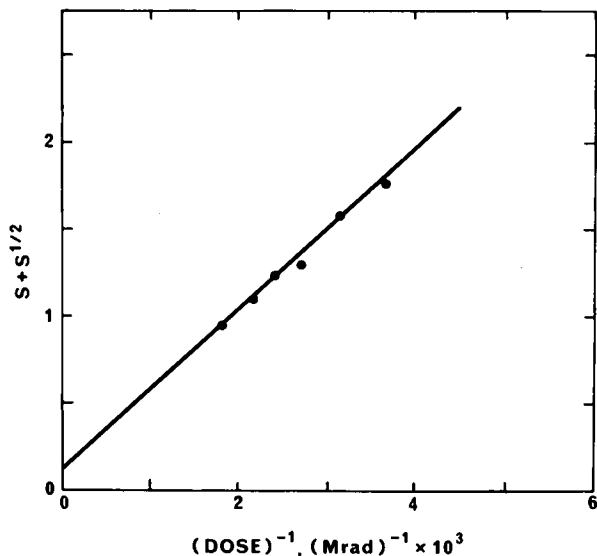$$S + S^{1/2} = p_0/q_0 + 1/(q_0 N_0 r) \tag{1}$$

Fig. 5. Charlesby-Pinner plot for polysulfone I
irradiated at 30°C under vacuum.

where p_0 and q_0 are the fractions of main chains fractured and crosslinked, respectively, per unit dose, and N_0 is the initial number-average degree of polymerization. Figure 5 shows a plot of $S + S^{1/2}$ versus r for our data. Charlesby[18] has shown that

$$G(\text{scission}) = 0.96 \times 10^6 \, p_0/w \qquad (2)$$

$$G(\text{crosslink}) = 0.48 \times 10^6 \, q_0/w \qquad (3)$$

where w is the molecular weight of the repeat unit and the numerical factor allows for the use of Mrad for radiation dose.

We have calculated $\bar{M}_n = 20{,}500$ from $\bar{M}_v$ using the Schulz-Zimm expression

$$\bar{M}_v = \bar{M}_n \, [(a + 1)\Gamma(a + 1)]^{1/a} \qquad (4)$$

for a random distribution where a is the exponent in the Mark-Houwink equation and Γ is the gamma function. The molecular weight (w) of the repeat unit of polysulfone I is 442, giving $N_0 = 46.4$. The slope of the plot in Figure 5 gives $q_0 = 4.7 \times 10^{-5}$, and hence $G(\text{crosslink}) = 0.051 \pm 0.002$. The intercept at $1/r = 0$ is $p_0/q_0 = 0.121$, hence $p_0 = 5.7 \times 10^{-6}$ which gives $G(\text{scission}) = 0.012 \pm 0.003$. The gel dose can be obtained from Figure 5 at $S + S^{1/2} = 2$, which gives 247 Mrad. Substitution into the expression[18]

$$G(\text{crosslink}) = 0.48 \times 10^6/(r_{\text{gel}}\bar{M}_w) \qquad (5)$$

gives $G(\text{crosslink}) = 0.049$, in satisfactory agreement with the value obtained from the slope of Figure 5.

If endlinking occurs, i.e., attachment of polymer fragments produced by chain scission to positions along other polymer chains resulting in branching, the same results will be obtained[19,20] provided cyclization does not occur when the gel fraction may be reduced by up to 10%.

Mechanical Properties of Polysulfone I

Tensile Properties.   Unirradiated polysulfone I showed a high tensile strength of 10,000 psi at yield (5.2% strain) and a high modulus of elasticity in tension of 320,000 psi typical of a rough, rigid plastic.   The effects on tensile properties of irradiation at 30°C in air up to 388 Mrad are shown in Table I.   Irradiation up to 50 Mrad caused the tensile strength at yield to decrease slightly without any change in the per cent strain at the yield point or in the modulus.   However, the elongation to break decreased markedly.   At higher doses, fracture occurred before the yield point had been reached (brittle failure), the tensile strength and the per cent strain at fracture decreasing rapidly with dose.   The modulus, however, was independent of dose up to 388 Mrad, within experimental variation.   It was not possible to make tensile strength measurements after higher doses as brittle fracture of the specimens occurred during the setting of the instrument.

Flexural Properties.   The flexural stress–strain curve for polysulfone I was unaltered within experimental variation by irradiation up to 50 Mrad, but after higher doses the flexural strength and per cent strain at fracture decreased rapidly similar to the tensile strength measurements, and are also shown in Table I.

DISCUSSION

Crosslinking and Scission

Crosslinking and chain scission both occur when polysulfone I and II are subjected to γ-irradiation.   Crosslinking is predominant for irradiation under vacuum since the limiting viscosity number rises; and in I, insoluble gel is formed at high doses.   Irradiation in air results in no gel formation and decrease in $[\eta]$, indicating that scission predominates over crosslinking. Similar behavior is known to occur in polystyrene.[21]   It has been suggested[2] that oxygen suppresses the crosslinking reaction by acting as a free-radical scavenger, and is also involved in a radiation-induced oxidation which increases the number of chain scissions.

The smaller changes in the limiting viscosity number of polysulfone II after irradiation under vacuum or in air compared with polysulfone I and the absence of gel formation indicate that the isopropylidene linkage is a source of both chain scission and crosslinking.   However, the definite evidence of an increase in molecular weight of polysulfone II by irradiation under vacuum shows that crosslinking must also occur between aromatic rings.

TABLE I
Tensile and Flexural Properties of Irradiated Polysulfone I at 30°C

Dose, Mrad	Tensile					Flexural				
	Modulus, psi	Strength, psi		strain, %		Modulus, psi	Strength, psi		Strain, %	
		At yield	At break	At yield	At break		At yield	At break	At yield	At break
0	320,000	10,080	—	5.2	—	228,000	13,380	—	9.5	—
10	306,000	9,790	—	5.5	—	288,000	13,500	—	9.5	—
25	342,000	9,540	—	5.2	—	251,000	13,690	—	9.5	—
50	300,000	9,280	—	5.7	—	236,000	13,100	—	9.5	—
96.5	327,000	—	8,320	—	3.2	262,000	—	10,450	—	4.5
195	297,000	—	3,100	—	0.5	252,000	—	5,850	—	2.6
388	310,000	—	740	—	0.1	254,000	—	3,540	—	1.0
581	—	—	—	—	—	274,000	—	2,050	—	0.7

Temperature

The increased crosslinking yield in polysulfone I at higher irradiation temperatures under vacuum and particularly above T_g can be attributed to increased molecular motion, resulting in a high probability of intermolecular combination reactions. It is interesting that above T_g crosslinking has a high yield and gel formation occurs after a low dose in air, despite the concurrent oxidation processes, which are severe. The effect of irradiation at elevated temperatures on G(crosslink) and the mechanical properties for both polysulfone I and II will be reported in a subsequent paper.

Radiation Resistance

Polysulfone I is more radiation resistant than phenylene polycarbonate[3] and poly(hydroxy ether)[4] where scission is predominant, even under vacuum, causing a decrease in molecular weight and mechanical strength. G(scission) values under vacuum are 0.09 and 0.2, respectively, compared with 0.012 for polysulfone I. It has comparable molecular radiation resistance to polystyrene for which G(crosslink) = 0.034,[1] G(scission) = 0.01[1] and G(gas) = 0.024 (mainly hydrogen)[22] are typical values.

Mechanical Properties

The variation in mechanical properties, especially strength, modulus, and elongation, with radiation dose is a practical measure of the radiation resistance of a polymeric material. The tensile and flexural strengths of polysulfone I were unaffected by γ-irradiation in air up to 50 Mrad, although the elongation to break was progressively reduced. Above 50 Mrad, brittle failure occurred, and the maximum strength and elongation decreased with increasing dose. Reduction to 50% of the initial strength, which is frequently taken as the limit for acceptable deterioration, occurred after 170 Mrad.

These results are consistent with a reduction in molecular weight on irradiation in air. The relationship between strength and molecular weight for polysulfone I has not been published, but one might expect it to be similar to that for polystyrene.[23] The observed molecular weight changes for irradiation in air at $30°C$[11] are not large enough to account for the observed decrease in strength. However, we have shown, by viscosity measurements on layers removed progressively from the surface, that the molecular weight of flexural test specimens was not decreased uniformly, even at the relatively low dose rate (0.5 Mrad/hr) used in these experiments. (These results will be included in a later paper.) Therefore, there must be a dependence on the rate of oxygen diffusion into the sample. Consequently, we postulate that the observed decreases in strength is related to the decrease in molecular weight of the surface layer. Further evidence for this is provided by the fact that the flexural strength was unaffected after radiation doses up to 350 Mrad under vacuum. Under

these conditions there was no molecular weight gradient across the cross section of the sample, and crosslinking was predominant.

Other Work

Our results can be compared with those of Davis et al.[12] on the electron-irradiation stability of polysulfone I. There is qualitative similarity, but considerable quantitative discrepancies. They reported G(crosslink) = 0.16 and G(scission) = 0.08 compared to our values of G(crosslink) = 0.051 and G(scission) = 0.012.
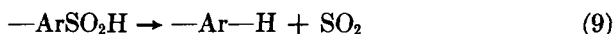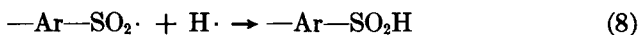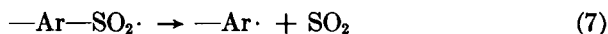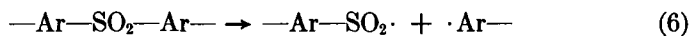
The main cause of the differences between our results and those of Davis et al. is undoubtedly a rise in the temperature of their samples, due to slow removal of heat produced by energy deposition at their relatively high electron dose rate of 240 Mrad/hr. Irradiation at 240 Mrad/hr corresponds to an energy input of 40 J/g, and this would result in a temperature rise of 30°C/min in the polymer in the absence of heat transfer to the surroundings. Even with external cooling, at such a high dose rate, a significant temperature rise is likely. Bell et al.[24] have reported a temperature rise of 41.5°C in a 0.125-in. thick mechanical test specimen of polystyrene during electron irradiation with continuous water cooling. We have shown that the radiation sensitivity of polysulfone I increases rapidly with increasing temperature. The volatile product yields (G = 0.04) are higher than those reported by Davis et al. (G = 0.01), and our analysis showed SO_2 as a major product. Hale et al.[5] have found SO_2 as the major volatile product in the thermal decomposition of polysulfone I under vacuum.

The higher temperature and different physical form of the polymer are probably the main causes of the differences in volatile product yields. Trapping of radiolysis products, especially the polar SO_2, and the retention of H_2O would depend on the physical form of the irradiated polymer. We consider that the yield of volatile products can be expected to be comparable with the yield of scission and crosslinking, and not an order of magnitude lower.

Our results on mechanical strength also differ from those of Davis et al.[12] They found no difference between irradiation in air and vacuum up to 200 Mrad. This is probably due to the difference in dose rates. With the high dose rates used in their work, there would be oxygen depletion in the sample due to relatively slow diffusion, and this would result in enhanced crosslinking.

Radiolysis Mechanism

Irradiation of both polysulfones produced SO_2 as the main volatile product. Therefore, C—S main-chain scission is a principal step in the radiolysis, followed by scission of the adjacent C—S bond liberating SO_2 from the phenylene sulfonyl radical either directly or via phenylene sulfonic acid:

$$-Ar-SO_2-Ar- \rightarrow -Ar-SO_2 \cdot + \cdot Ar- \qquad (6)$$

$$-Ar-SO_2 \cdot \rightarrow -Ar \cdot + SO_2 \qquad (7)$$

$$-Ar-SO_2 \cdot + H \cdot \rightarrow -Ar-SO_2H \qquad (8)$$

$$-ArSO_2H \rightarrow -Ar-H + SO_2 \qquad (9)$$

This mechanism is consistent with the preferred scission of C—S bonds and the liberation of SO_2 in γ-irradiated poly(olefin sulfones) and preferred C—S bond scission in x-irradiated sulfones demonstrated clearly by product analysis[25] and ESR studies.[26,27]

Combination of geminate phenylene radicals formed by the above reaction sequence can then occur. This has been proposed by Hale et al[5] for the thermal decomposition of polysulfone I in vacuum. The postulated reactions of the phenylene sulfonyl radicals have also been shown to occur by Kobayashi, Tanaka and Minato[28] on photolysis of di-p-tolyl disulfide.
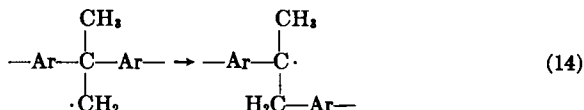
The enhanced scission and crosslinking in polysulfone I compared with polysulfone II indicates that the isopropylidene linkage is involved in both these processes. Possible reaction sequences resulting in crosslinking and scission are given in eqs. (10)–(12):
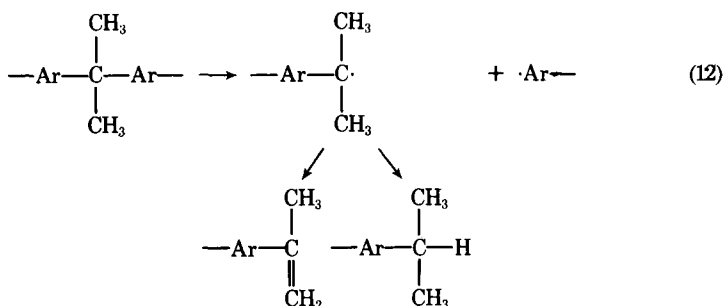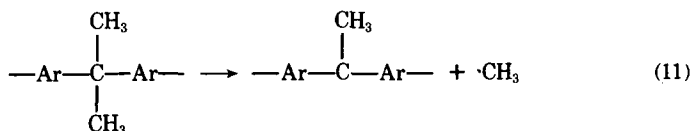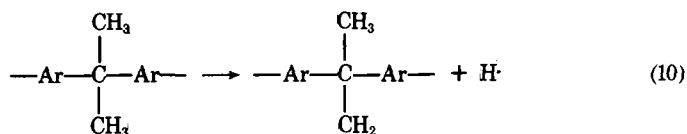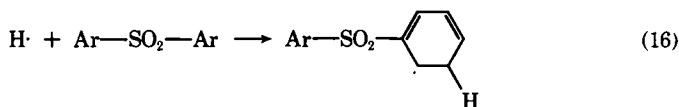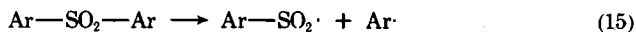

Elimination of $\cdot CH_3$ by C—CH_3 scission is to be expected from the behavior of substituted polymethylenes[29] and the low bond strength (250 kJ/mole), and is confirmed by the yield of methane. Hydrogen abstraction by $\cdot CH_3$ is clearly favored over dimerization since the C_2H_6 yield was negligible. Main-chain C—O scission should also occur in both polysulfones:

$$-Ar-O-Ar- \rightarrow -Ar-O \cdot + \cdot Ar- \qquad (13)$$
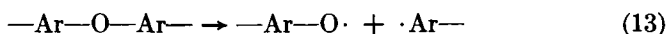
The production of hydrogen from both polysulfones shows that C—H scission in the aromatic rings as well as in the isopropylidene linkages occurs, followed by H· abstraction and combination. Combination of residual polymer radicals will result in crosslinking. Other reactions which may be involved in crosslinking are scavenging of H· and ·CH₃ by aromatic rings to form cyclohexadienyl radicals. A 1,2-phenyl shift of the residual polymer radical after H· elimination may occur and enhance crosslinking:

$$
\underset{\underset{\cdot\text{CH}_2}{|}}{\overset{\overset{\text{CH}_3}{|}}{-\text{Ar}-\text{C}-\text{Ar}-}} \;\longrightarrow\; \underset{\underset{\text{H}_2\text{C}-\text{Ar}-}{|}}{\overset{\overset{\text{CH}_3}{|}}{-\text{Ar}-\text{C}\cdot}} \tag{14}
$$

Our interpretation differs partly from the mechanism for the γ-radiolysis of polysulfone I proposed by Lyons, Symons, and Yandell,[30] based solely on ESR studies. They identified cyclohexadienyl radicals as a major radical species at −196°C together with phenoxy and phenylene sulfonyl radicals which they suggest are formed by reactions with hydrogen atoms released from the pendent methyl groups by the action of the γ-radiation. This is in agreement with our suggested mechanism to account for part of the crosslinking. However, we consider that main-chain C—S scission is a principal primary reaction followed by scission of the adjacent C—S bond and liberation of SO₂ with at least some stabilization of the backbone fracture. This is supported by product analyses of Kevan, Hall, and Kaiser[31] which showed SO₂ and diphenyl to be the main products on γ-irradiation of diphenyl sulfone. The ESR results of Lyons et al. on the model compounds diphenyl sulfone, diphenyl ether, and 2,2¹-diphenylpropane gave, for diphenyl sulfone, phenylsulfonyl and cyclohexadienyl radicals, indicating that C—S scission is a major reaction.

$$
\text{Ar}-\text{SO}_2-\text{Ar} \;\longrightarrow\; \text{Ar}-\text{SO}_2\cdot + \text{Ar}\cdot \tag{15}
$$

$$
\text{H}\cdot + \text{Ar}-\text{SO}_2-\text{Ar} \;\longrightarrow\; \text{Ar}-\text{SO}_2-\underset{\overset{|}{\text{H}}}{\cdot}\!\bigcirc \tag{16}
$$

The source of H atoms in eq. (16) must have been C—H scission in the aromatic rings although the residual radical was not identified. Diphenyl ether gave an ESR spectrum due to phenoxy and possibly phenyl radicals:

$$
\text{Ar}-\text{O}-\text{Ar} \;\longrightarrow\; \text{Ar}-\text{O}\cdot + \text{Ar}\cdot \tag{17}
$$
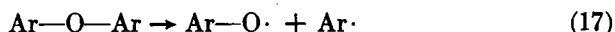
In 2,2¹-diphenylpropane, cyclohexadienyl and Ph₂ĊMe radicals were identified, consistent with our interpretation.

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