

The Effects of 3-MeV Proton Radiation on an Aromatic Polysulfone*

DANIEL R. COULTER, MARK V. SMITH, FUN-DOW TSAY, and AMITAVA GUPTA, *Applied Mechanics Technology Section, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109*, and R. E. FORNES,[†] *North Carolina State University, Raleigh, North Carolina 27607*

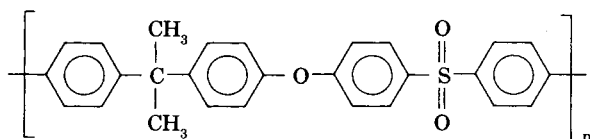
Synopsis

3-MeV proton beam irradiation studies have been carried out on a commercial aromatic polysulfone (Udell 1700). Physical and mechanical property changes have been monitored as a function of dose. Chemical and spectroscopic analyses have also been performed on the irradiated samples. Results have been compared to those from previous studies with electrons and γ -radiation. A mechanism of proton-induced degradation is proposed.

INTRODUCTION

Polysulfones are tough, high temperature thermoplastic materials. Because of these properties, they have been identified as possible matrices for fiber/polymer composite materials which may be utilized to build large structures in space. The durability of such materials in the space radiation environment, however, is still open to some question. It may be anticipated that aryl sulfones would show good radiation resistance due to their high aromatic content. Several reports on the effects of γ -radiation¹⁻⁴ and energetic electrons⁵⁻⁷ on polysulfones are found in the literature; however, only limited work on proton irradiation effects is reported.⁵

We have performed a brief study in which films of the polysulfone of bisphenol A (Udell 1700) were irradiated with a 3-MeV proton beam for different periods. The chemical structure is shown below. Structure and molecular weight determination were made through sol-gel studies, high performance liquid chromatographic analysis, FTIR, and fluorescence spectroscopy. Changes in physical and mechanical properties were also monitored as a function of the applied dose level. A proton-induced degradation mechanism has been developed from these data.



Udell 1700

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EXPERIMENTAL

Materials

Udell 1700 polysulfone was obtained from Union Carbide in pellet form. Prior to use, the pellets were vacuum dried for ~ 150 h at 130°C . Thin films (~ 0.01 cm) were then formed by compression molding for 10 min at $\sim 295^\circ\text{C}$ and 1500 psi followed by cooling in air at room temperature. In order to avoid the use of mold release agents which could complicate analysis of irradiated samples, the films were pressed between two pieces of Teflon-coated Kapton, from which they could be easily removed.

Irradiation

Samples were irradiated at room temperature in vacuum ($\leq 10^{-6}$ torr) with 3 MeV protons from the Tandem Van de Graff Accelerator at the Kellogg Radiation Laboratory of the California Institute of Technology. The 3 MeV value was chosen because at this energy the target depth is comparable to the sample thickness (0.01–0.013 cm), and yet it is still below the threshold for generation of neutrons from carbon nuclei (3.2 MeV). Furthermore, this energy is typical of proton energies found in various earth orbits.

The focused (~ 1 mm²) proton beam was scattered by a 10000 Å thick Ni foil approximately 100 cm upstream of the sample. This produced a Gaussian intensity distribution with respect to angular deviation relative to the beam axis which resulted in spreading the beam over several cm² of sample. Using the multiple scattering theory of Marion and Zimmerman,⁸ an estimate of radiation dose vs. distance off axis could be made. Total beam intensity was measured before and after the sample with Faraday cups. Doses were calculated by integrating beam currents.

Sample doses ranged from 100 to 5000 Mrad at rates ranging from 0.5 to 1.5 Mrad/s, which are quite high compared to what would be encountered in space. The accelerated dose rate could affect results in two ways. First, it could cause the sample temperature to rise, thus increasing degradation rates. In order to minimize this problem, samples were mounted in contact with brass or aluminum plates to facilitate heat dissipation. Estimates based on calculated radiative heat loss and conduction through the mounts indicate a maximum temperature rise on the order of 10°C is possible. This is consistent with thermocouple⁹ and infrared emission¹⁰ measurements made on polymers during electron irradiation at comparable dose rates. Secondly, high dose rates could affect results by creating a steady state concentration of transient intermediates high enough to allow secondary reactions, i.e., radical-radical reactions, which would not occur under more moderate conditions. This is an important consideration only for species which live long enough to allow a second proton track to occur within the "interaction region" of the first track. At the highest dose rates, assuming an interaction distance of 20 Å, only intermediates with lifetimes of 10–100 s or more would have a significant chance of undergoing such secondary reactions. There are some radical species generated with lifetimes in this range; however, estimating their long term contribution to observed damage is difficult.

Analysis

Sol-gel studies were carried out on films extracted with methylene chloride. Molecular weight distributions in the soluble fraction were recorded on a Waters 6000 Modular High Pressure Liquid Chromatograph equipped with microstyrigel columns (10, 10^2 , 10^3 , 10^4 Å pores). Narrow molecular weight distribution polystyrene was used as a standard for calibration.

Tensile modulus data were recorded on a temperature-controlled Rheovibron operated in a static mode. Dynamic viscoelastic measurements were made on a DuPont 1090 DMA apparatus. Infrared spectra of irradiated films were recorded on a Digilab FTIR Spectrometer operated in attenuated total reflectance mode. Spectra of the soluble fractions were recorded in the diffuse reflectance mode following their extraction with methylene chloride and deposition on KCl powder. Free radical species were monitored by electron spin resonance spectroscopy using a Century series E-15 Varian ESR spectrometer. Electronic absorption spectra were recorded on a Cary 219 spectrometer and post-irradiation fluorescence studies were performed on a Perkin-Elmer MPF-3 fluorescence spectrophotometer. *In situ* emission spectra were recorded during actual irradiation through a quartz window with the samples mounted at 45°. Emitted light was dispersed by a 0.25 m Jobin-Yvon monochromator and detected with a RCA 1P28 photomultiplier tube. Resolution was ~ 2 nm.

RESULTS

Sol-Gel Studies

Proton irradiation of polysulfone results in both the fracture of single polymer macromolecules (chain scission) and the fusion of two or more polymer macromolecules (crosslinking). Sol-gel studies on irradiated films show that the initial formation of insoluble material occurs at doses somewhere between 250 and 600 Mrad. The fraction of insoluble material increases with dosage. Results of sol-gel measurements on six typical samples as a function of dose are given in the inset of Figure 1. The molecular weight distributions in the soluble fractions have been determined by high pressure liquid chromatography. Chromatograms of material extracted from irradiated samples are shown in Figure 1. The calculated number average and weight average molecular weights are listed in Table I. The molecular weights in the soluble fractions drop as a function of dose. The structure apparent at low molecular weight (even in the control sample) arises from the presence of oligomeric species of order $n = 3-6$.

A measure of the crosslinking and chain scission yields can be obtained from the sol-gel data. Charlesby and Pinner¹¹ have shown that the change in soluble fraction (S) of a polymer as a function of radiation dose (r) is given by the expression

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

In eq. (1), p_0 is the fraction of polymer chains undergoing scission per unit dose, q_0 is the fraction of chains undergoing crosslinking per unit dose, and N_0 is the initial number average degree of polymerization given by

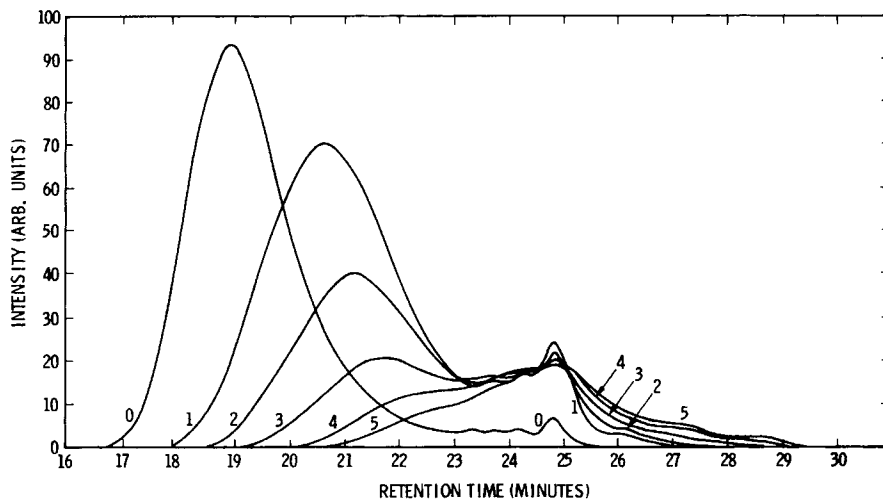


Fig. 1. HPLC chromatograms of the soluble fractions of proton irradiated polysulfone films at various doses. The relative intensities are directly comparable except for the control sample which has been multiplied by 0.5 in order to fit it on scale.

Sample no.	Dose (Mrad)	Soluble fraction (<i>S</i>)
0	0	1.0
1	672	0.592
2	1285	0.284
3	2281	0.212
4	3427	0.167
5	4680	0.149

$$N_0 = \bar{M}_n/w \quad (2)$$

where w is the molecular weight of the repeating unit (442 g/mol). If the dose is given in Mrad, then the expressions for the radiation yields of crosslinking and chain scission are¹²

$$G_{\text{chain scission}} = 9.6 \times 10^5 p_0/w \quad (3a)$$

$$G_{\text{crosslink}} = 4.8 \times 10^5 q_0/w \quad (3b)$$

A Charlesby-Pinner plot of the sol-gel data is shown in Figure 2. From the slope and the intercept, p_0 and q_0 are calculated to be $5.69 \times 10^{-6} \text{ Mrad}^{-1}$

TABLE I
Molecular Weight Distributions in Soluble Fractions of Irradiated Polysulfone

Sample no.	Dose (Mrad)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
0	0	46000	71600	1.56
1	672	5889	10605	1.80
2	1285	4309	7771	1.80
3	2281	2739	5026	1.83
4	3427	2227	3213	1.44
5	4680	1783	2650	1.48

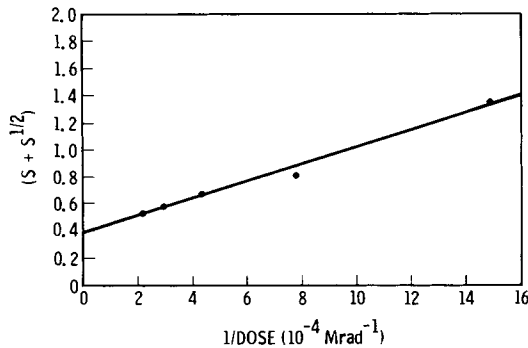


Fig. 2. Charlesby-Pinner plot for proton-irradiated polysulfone. Slope = 642 Mrad; intercept = 0.38.

and $1.50 \times 10^{-5} \text{ Mrad}^{-1}$, respectively. Using expressions (3a) and (3b), the G values for crosslinking and chain scission are calculated to be

$$G_{\text{crosslink}} = 0.016$$

$$G_{\text{chain scission}} = 0.012$$

The radiation induced gel point is the point where the line in Figure 2 intersects $S + S^{1/2} = 2$. This corresponds to a gel dose (r_{gel}) of 396 Mrad, which is consistent with our observation that insoluble material is present in all samples receiving doses of more than several hundred Mrad. Charlesby¹² has shown that $G_{\text{crosslink}}$ may be related to \bar{M}_w by the following expression:

$$G_{\text{crosslink}} = 4.8 \times 10^5 / r_{\text{gel}} \bar{M}_w \quad (4)$$

Substitution of r_{gel} into eq. (4) gives $G_{\text{crosslink}} = 0.017$, which agrees well with that calculated from the slope of the Charlesby-Pinner lot.

Physical and Mechanical Property Measurements

Polysulfone samples receiving high doses of proton radiation show considerable embrittlement, making them difficult to handle. Stress-strain data have been recorded on several samples of relatively low dose and typical data recorded at 100°C are presented in Figure 3. It is seen that the tensile modulus increases with increasing dose, which is consistent with the observation of embrittlement.

Dynamic viscoelastic properties of irradiated films have been studied by dynamic mechanical analysis. Due to small sample size, reliable *quantitative* measures of the storage modulus and loss tangent could not be obtained. The T_g and the γ -relaxation temperature, however, can clearly be seen in the plot of frequency (storage modulus) vs. temperature shown in Figure 4. These data are consistent with those reported in the literature except that no β -transition was observed at 75°C.¹³ The measured T_g increases from $\sim 150^\circ\text{C}$ in the control sample to $\sim 220^\circ\text{C}$ at 1366 Mrad. This finding is again consistent with earlier observations of embrittlement and increases in the

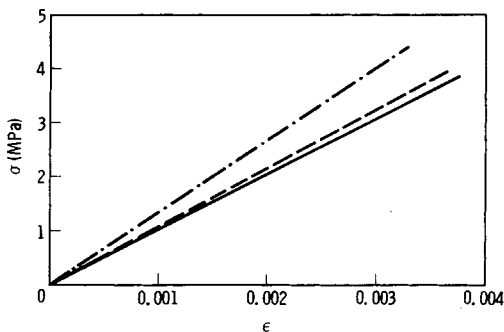


Fig. 3. Plot of stress-strain data for proton-irradiated polysulfone recorded at 100°C showing increase in tensile modulus with dose (Mrad): (—) 0; (---) 772; (- · -) 1084.

tensile modulus. The γ -relaxation temperature of $\sim -90^\circ\text{C}$ is seen to be insensitive to irradiation. The damping ($\tan \delta$) measurements show essentially the same results except that a weak β -relaxation peak, which did not change with irradiation, was observed near 50°C .

Spectroscopic Studies

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR studies have been carried out on proton-irradiated polysulfone films and their extracts. Measurements on the films themselves were performed in the attenuated total reflectance (ATR) mode. Figure 5 shows the ATR-FTIR spectra of a typical irradiated film (1366 Mrad) and a control film in the region $400\text{--}2000\text{ cm}^{-1}$. There is essentially no difference in the two spectra in this region. ATR-FTIR may not be an optimum technique for studying damage in irradiated samples because it probes only the first few microns below the surface. The films, however, are far too thick to allow transmission FTIR spectra to be recorded.

In an effort to detect chemical changes resulting from irradiation, exposed films were extracted with methylene chloride and the resulting solutions

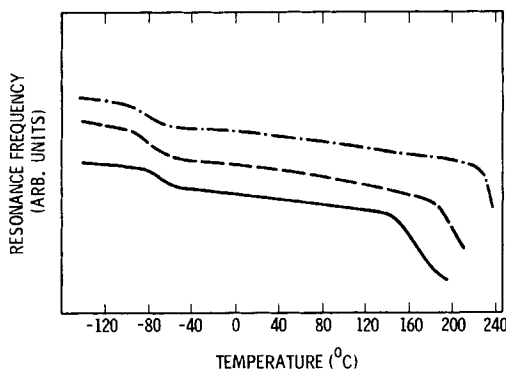


Fig. 4. Plot of the resonance frequency (storage modulus) vs. temperature as recorded by DMA for proton irradiated polysulfone showing T_g and γ -relaxation temperatures: (—) control; (---) 772 Mrad; (- · -) 1366 Mrad.

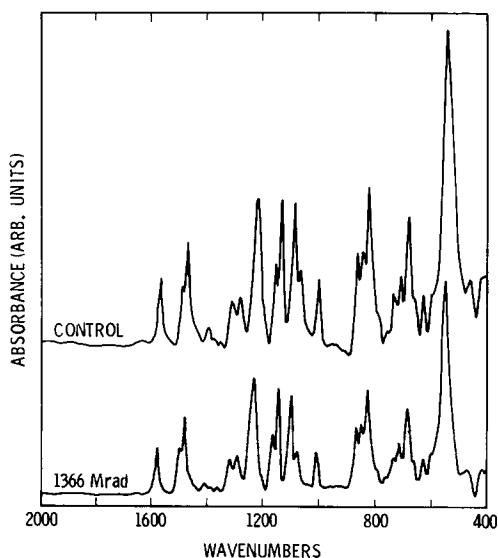


Fig. 5. Attenuated total reflectance-FTIR spectra of control and proton-irradiated polysulfone films.

evaporated on KCl powder. FTIR spectra were then recorded in the diffuse reflectance (DR) mode. Typical DR-FTIR spectra are shown in Figure 6. The most obvious change occurring as a function of dose is the appearance and growth of an —OH absorption band at 3400 cm^{-1} . Other more subtle changes can be observed including small decrease in bands around 1150 cm^{-1} , 1300 cm^{-1} , and 1400 cm^{-1} , which are associated with $\text{—SO}_2\text{—}$ vibrations⁶ and the appearance of features at 1035 cm^{-1} and $\sim 750\text{ cm}^{-1}$, which may be associated with monosubstituted phenyl rings, although this assignment is not certain.

Electron Spin Resonance (ESR) Spectroscopy

The ESR spectrum of irradiated polysulfone is shown in Figure 7. This spectrum was recorded ~ 20 h after irradiation (1366 Mrad), during which time the sample was stored at room temperature and exposed to air.

Electronic Spectroscopy

The UV-visible absorption spectra of irradiated films were recorded as a function of dose and are shown in Figure 8. The absorption edge moves progressively to the red as dose increases.

In situ emission spectra were also recorded during the irradiation of films as a function of dose. One set of these spectra is shown in Figure 9. The proton-excited emission spectrum of polysulfone appears to show two bands. A short wavelength band with a maximum near $340\text{--}350\text{ nm}$ is seen to disappear rapidly as the accumulated dose approaches $300\text{--}400\text{ Mrad}$. A longer wavelength band with a maximum near $380\text{--}390\text{ nm}$ appears to be relatively insensitive to dose up to 630 Mrad . UV excitation of films after proton irradiation produces similar emission spectra. At very high proton doses (3000 Mrad) even the long-wavelength emission disappears.

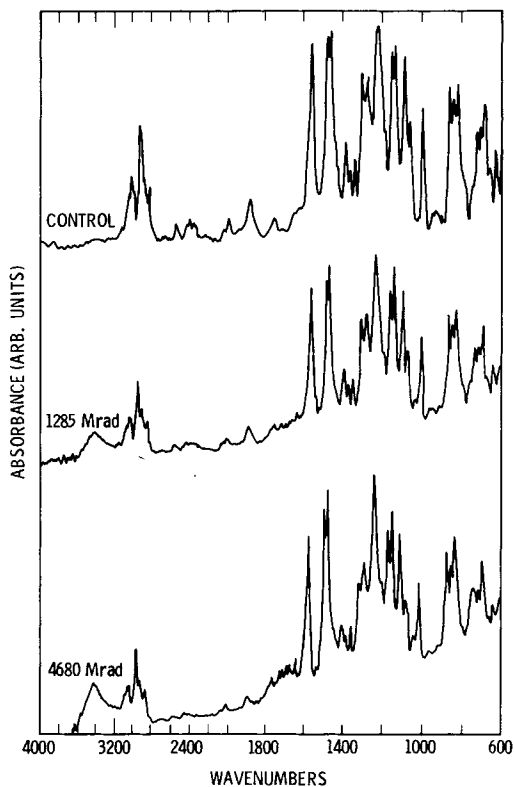


Fig. 6. Diffuse reflectance-FTIR spectra of evaporated sol fractions (methylene chloride extracted) from proton-irradiated polysulfone.

DISCUSSION AND CONCLUSIONS

The results of this study indicate that polysulfone (Udell 1700) is relatively stable to proton bombardment. This generally agrees with results from other exposure studies¹⁻⁷ with γ -radiation or electrons, although some specific results differ. It is not surprising that the details of the radiation effects are different with protons since the nature of the particle/matrix interactions are not the same. With the heavier particles, ionization is no longer the *only* likely initial event. Displacement of the "lattice" atoms due to

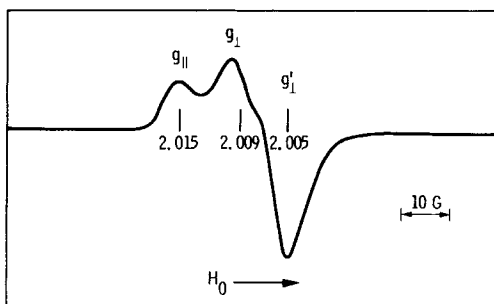


Fig. 7. ESR spectrum of proton irradiated polysulfone.

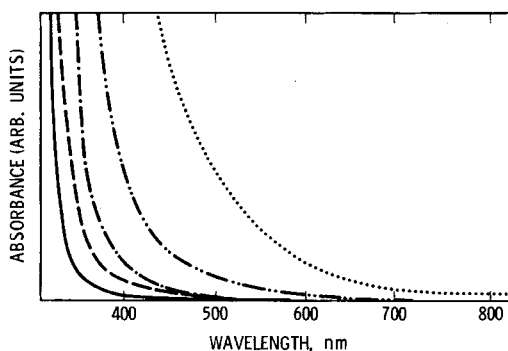


Fig. 8. UV-VIS absorption spectra of proton irradiated polysulfone as a function of dose (Mrad): (—) 0; (---) 197; (-·-) 772; (- - -) 1084; (· · ·) 3125.

proton bombardment resulting in broken bonds, nonvertical transitions, and significant local "heating" might be expected to cause much more heterogeneous damage than that observed with electron or γ -irradiation.

Proton bombardment is found to result in both crosslinking and chain scission in polysulfone, as has been previously reported in proton,⁵ electron,⁵ and γ -radiation³ studies. Santos and Sykes⁵ have suggested that with electrons and protons, chain scission dominates at low doses while crosslinking dominates at higher dose levels. They report a threshold of 1000 Mrad for crosslinking. No evidence of such a threshold is found in this work. Rather, based on sol-gel studies it appears that both processes occur simultaneously. Crosslinking seems to be occurring from the onset of exposure resulting in initial gel formation near 400 Mrad while chain scission continues to reduce the molecular weight of the soluble fraction even at the highest doses. The radiation yields of $G_{\text{scission}} = 0.012$ and $G_{\text{crosslink}} = 0.016$ measured in this study are in reasonable agreement with the results from γ -radiation studies³ of $G_{\text{scission}} = 0.012$ and $G_{\text{crosslink}} = 0.05$. The measured gel dose of ~ 400 Mrad is also in reasonable agreement with the γ -radiation value of ~ 250 Mrad.³ The near equality of scission and crosslinking yields from proton irradiation may be indicative of the more heterogeneous nature of the damage compared to that resulting from γ -radiation.

The crosslinking and chain scission reactions occurring in polysulfone alter the physical and mechanical properties of the material. Irradiated

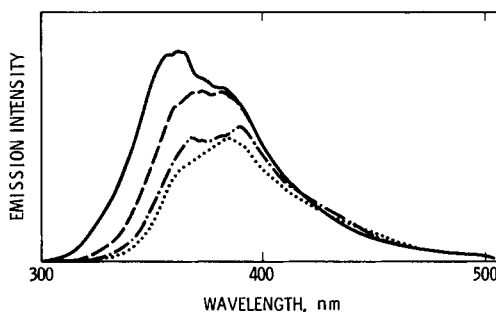


Fig. 9. Emission spectra of polysulfone recorded *in situ* during proton irradiation. Dose (Mrad) at 300 and 500 nm, respectively: (—) 30, 180; (---) 210, 330; (-·-) 360, 480; (· · ·) 510, 30.

samples become brittle and show increases in the tensile modulus and T_g . The embrittlement phenomena, probably resulting from crosslinking, is consistent with that observed previously.^{3,5}

Earlier proton and electron studies in vacuum⁵ found that the modulus showed an initial decrease followed by an increase at higher doses (> 5000 Mrad for protons), while electron bombardment in air resulted in the modulus increasing monotonically.⁷ γ -Radiation exposure produced no change in modulus up to 400 Mrad.³ The nature of the reported⁵ initial drop in modulus ($\sim 20\%$) is not clear. In general, it must be concluded that, at least at higher dose levels, proton and electron bombardment results in an increased tensile modulus in polysulfone.

The glass transition temperature has been reported to drop following proton exposure.⁵ With electron bombardment, T_g increases with vacuum irradiation⁵ and decreases with irradiation in air.⁷ We observe a monotonic increase in T_g with dose to a level similar to that observed in electron exposure studies in vacuum.⁵ This would seem to be consistent with the embrittlement and modulus increases discussed above.

FTIR studies on polysulfone films showed few if any changes after proton bombardment. The extracted fraction of irradiated films, however, did show formation of $-\text{OH}$ groups and loss of $-\text{SO}_2-$ groups after irradiation. Several authors^{5,6} have observed disappearance of $-\text{SO}_2-$ bands after irradiation of polysulfones, which correlates well with the observation that SO_2 is a major volatile product trapped during γ -irradiation.³ No other instances of $-\text{OH}$ formation have been reported in the literature; however, previous authors have not reported FTIR results above 2000 cm^{-1} .^{5,6}

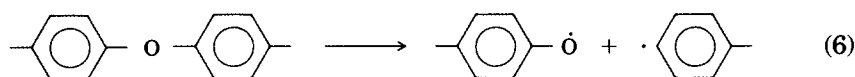
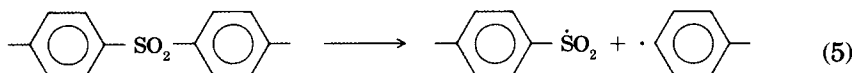
The observed ESR spectrum of irradiated polysulfone is typical of that resulting from randomly oriented radicals with an anisotropic g -tensor in a rigid matrix.¹⁴ The relatively high g values of the spectrum are indicative of nonhydrocarbon radicals. It has been suggested² that polysulfone irradiated with γ -radiation at low temperature produces phenoxy and aryl-sulfonyl radicals with g values in the range 2.005–2.007. This is consistent with the present observation; however, it is unlikely that phenoxy radicals would have a lifetime of 20 h, particularly when the sample is exposed to air. Consequently, it is believed that the observed spectrum is probably due to randomly oriented aryl-sulfonyl radicals which might be expected to be more stable at room temperature, as has been found to be the case for alkyl-sulfonyl radicals.¹

The results of the UV-VIS absorption spectroscopy are similar to those reported for polysulfone which was γ -irradiated in air and vacuum.⁴ For samples irradiated in air, yellowing was probably mainly due to oxidation. In vacuum the yellowing is probably due to generation of species with extended conjugation which causes their excited states to shift to lower energies. Reaction of the samples with oxygen after removal from vacuum, however, cannot be completely ruled out.

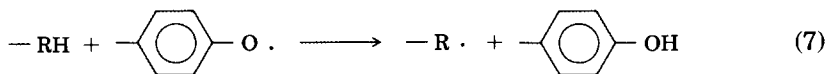
The changes in electronic absorption and emission spectra observed on proton irradiation are qualitatively similar to those found in an UV irradiation study.¹⁵ The implications of the absorption and emission data are that, initially, there are at least two emissive species present in polysulfone. During the early stages of irradiation new, conjugated, nonemissive species

are created whose excited states lie between those of the two emissive species. Formation of these new species leads to the appearance of a longer wavelength absorption feature and quenching of the high energy emitting state with little or no change of the long wavelength emission. As irradiation continues, species with increasingly lower energy excited states are produced, resulting in further red shifts in the absorption spectrum. Ultimately both of the emissive states are quenched when the energy of the excited states of the product species fall below the energy of the lower emissive state.

The mechanism of damage to polysulfone by protons is probably quite complex. γ -Irradiation studies^{2,3} have indicated that scission of C—S and C—O bonds in the main chain as shown in eqs. (5) and (6) are the principal steps in the radiolysis:

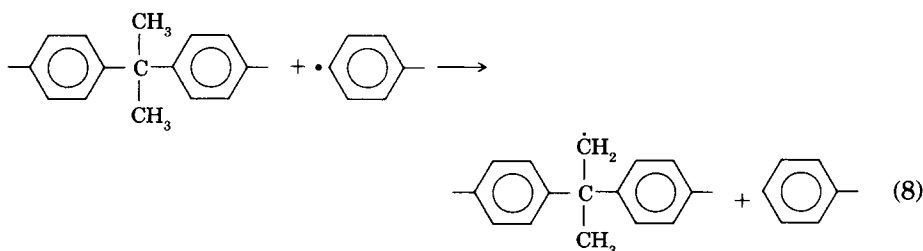


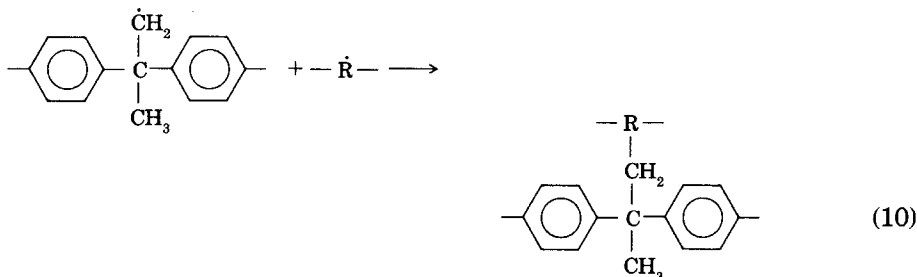
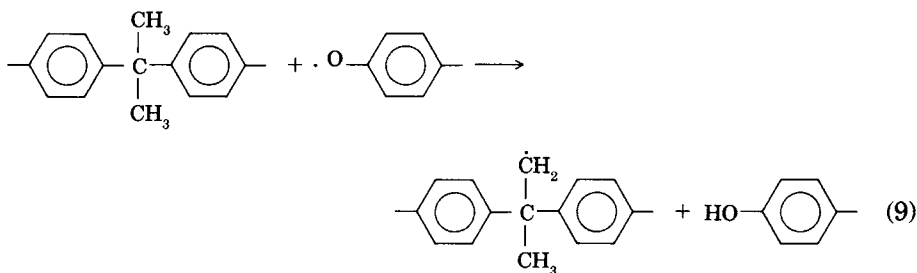
Observation of the phenyl sulfonyl radical by ESR and the appearance of —OH groups in the FTIR spectra, probably resulting from breaking of the ether linkage followed by hydrogen abstraction [eq. (7)] suggests that C—O and C—S bond cleavage may also be major damage mechanisms during proton exposure.



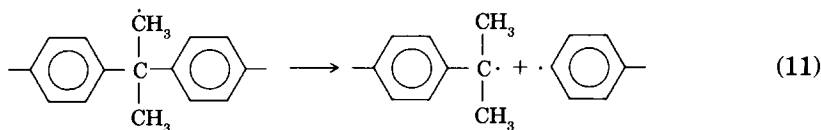
Loss of SO₂ bands in the FTIR spectra probably indicate that the phenyl-sulfonyl radicals slowly decay by elimination of SO₂, leaving behind a phenyl radical. This is consistent with the results of product analysis in earlier work.³

Brown and O'Donnell³ have shown that the isopropylidene linkage in polysulfone is involved in both chain scission and crosslinking processes. It is possible that it is primarily the methyl protons that are abstracted by phenyl and phenoxy radicals leaving behind a methylene radical which may participate in crosslinking. A possible reaction sequence is shown below:

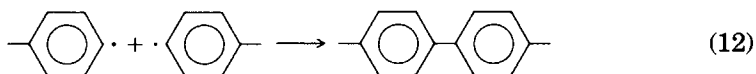




The isopropylidene linkage may also represent a point of main chain scission as shown in eq. (11), although no direct evidence of this reaction has been observed in this study:



Phenyl radicals created as in eq. (5), (6), and (11) may simply abstract hydrogen atoms forming monosubstituted aromatics or two of them may recombine forming a strained biphenyl linkage, as shown below:



A number of other possible radicals and radical reactions have been postulated in the literature.¹⁻⁴ Indeed it is expected that some or all of these as well as other previously unknown reactions occur as a result of proton irradiation. However, no direct evidence has been observed for these in this work.

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