comparison with the lower spectrum recorded after the sample was photobleached with red light (λ >640 nm). In contrast to the esr spectrum of the quenched sample which showed no change on illumination with visible light and little or no angular dependence in the magnetic field, the esr spectrum of the slowly cooled sample exhibited changes due to magnetic anisotropy both before and after photobleaching. By selecting the particular orientation which offered the best resolution, it has been found that the difference between the spectra taken before and after photobleaching gives a triplet spectrum having approximately 1:1:1 intensity ratios. From the results of several such experiments with aligned samples, the triplet hyperfine splitting is determined as being between 10 and 11 G. Hence it is clear that a different paramagnetic species is produced by γ irradiation of the low-temperature phase. The parallel with the triplet spectrum[4] for the low-temperature phase of CD_3CN is very striking, and the magnitude of the nitrogen hyperfine splitting is almost identical in the two systems. Also both centers are photobleached by red light. Recent work[5] with aligned samples of $CD_3{}^{13}CN$ has revealed an isotropic ^{13}C splitting of *ca.* 60 G which strongly implies that the excess-electron center in the low-temperature phase of acetonitrile is the anion radical with appreciable spin density in an sp^2 orbital on the carbon atom of the nitrile group. A similar assignment of the triplet spectrum for acrylonitrile to the anion radical is therefore suggested by the correspondence in the spectra.

Previous work[7,8] has not succeeded in identifying the active species responsible for initiating the "in-source" polymerization of acrylonitrile in the low-temperature phase. No evidence for free radical propagation has been obtained from esr studies between 83 and 121°K, and it has been frequently suggested that the anion radical is formed and initiates anionic polymerization. Hitherto, the failure to detect the anion radical could be attributed to its reactivity in polymerization or to the lack of sufficient resolution in the esr spectrum. In the present study we have observed that the triplet spectrum largely disappears if the sample either is allowed to stand for 2 days at 77°K in the dark, or is warmed to 93°K (this was the lowest temperature obtainable in this series of experiments with our variable-temperature equipment), and the resulting spectrum is very similar to the one recorded after photobleaching.

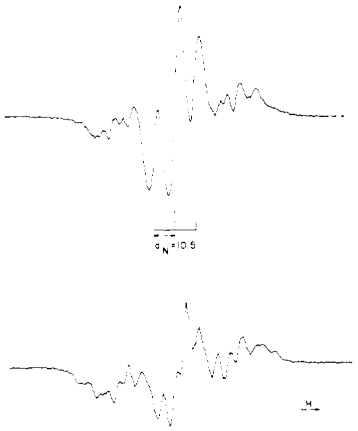
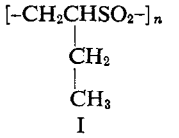


Figure 1. Electron spin resonance first-derivative spectra of γ-irradiated acrylonitrile in the low-temperature phase at 77°K. The hyperfine splitting is in gauss. Upper and lower spectra were recorded at the same microwave power (0.016 mW) and at the same spectrometer gain settings before and after photobleaching with filtered light (λ >640 nm) from a tungsten lamp (Corning filter No. 2030). The γ-irradiation dose was 1 Mrad (6.2 × 10^{19} eV g^{-1}).

Communications to the Editor

The Degradation of Poly(butene-1 sulfone) during γ Irradiation

This communication presents preliminary results of a study of the effect of γ radiation on poly(butene-1 sulfone) (I), a regularly alternating copolymer of butene-1 and sulfur dioxide.



$$[-CH_2\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{C}}}HSO_2-]_n$$

I

The polymer is shown to degrade rapidly under irradiation. Cross-linking is relatively unimportant, no gel being formed, even at quite high doses. Sulfur dioxide is the main volatile product at 0°, together with some butene-1, hydrogen, methane, and ethane. The gas yield increases rapidly with increasing irradiation temperature and approaches equimolar proportions of sulfur dioxide and butene-1, indicating depropagation.

Electron spin resonance studies of the radiolysis of poly(olefin sulfones) at −196° by Ayscough, Ivin, and O'Donnell[1] indicated preferential scission of C–S bonds. Also, initial C–S bond scission was shown to be the predominant effect in the radiolysis of dialkyl sulfones (RSO_2R).[1] These bonds are weak and bond cleavage is evidently energy selective. However, it was not clear whether both C–S bonds were broken, either simultaneously or successively, as the final radiolysis products were not determined.

No other information on the effects of γ radiation on poly(olefin sulfones) has been reported. However, Eaton and Ivin,[2] in an experiment involving the grafting of styrene on to poly(butene-1 sulfone) with X-rays, showed that the poly(butene-1 sulfone) was degraded.

Poly(butene-1 sulfone) is the first soluble polymer in the olefin series,[3] hence the first for which changes in molecular weight can be followed. Also, the olefin (bp −6.3°), if produced during radiolysis, can be

---

(1) P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, *Trans. Faraday Soc.*, **61**, 1110 (1965).

(2) E. C. Eaton and K. J. Ivin, *Polymer*, **6**, 339 (1965).

(3) H. A. Ende, K. J. Ivin, and G. Meyerhoff, *ibid.*, **3**, 129 (1962).

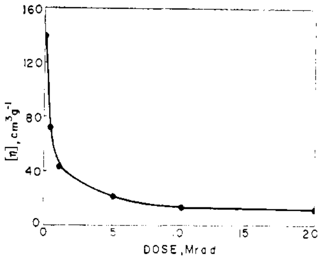


Figure 1. Decrease in limiting viscosity number with radiation dose. Irradiation under vacuum at 30°. Viscosity in acetone at 30°.

measured readily in the gas phase. Therefore, this polymer was selected for investigation.

Experimental Section

Poly(butene-1 sulfone) was prepared by initiation with *t*-butyl hydroperoxide or uv irradiation of approximately equimolar mixtures of sulfur dioxide and butene-1 (Matheson pure grade). The polymer was dissolved in acetone and precipitated in methanol and dried under vacuum for 48 hr at ambient temperature. Microanalysis confirmed that it was the 1:1 alternating copolymer.

Samples of polymer were sealed under vacuum (18 hr pumping on a high vacuum line), or in air, in glass tubes fitted with break-seals. Irradiations were carried out with cobalt-60 γ radiation, in the pond facility of the Australian Atomic Energy Commission Research Establishment at Lucas Heights.

The changes in molecular weight with irradiation were measured by solution viscometry in acetone at 30°, and by osmometry in cyclohexanone at 37°. Volatile radiolysis products were compressed into a gas buret with a Toepler pump and the yield was measured from the volume, pressure, and temperature. The gases were analyzed with an F & M Model 810 gas chromatograph using a Poropak column and checked with an Atlas CH4 mass spectrometer.

Results

Chain Degradation. Irradiation of poly(butene-1 sulfone) with doses up to 40 Mrad produced no observable gel, indicating that any cross-linking must be relatively ineffective. Viscosity measurements of the irradiated polymer showed rapid initial degradation for doses up to about 2 Mrad, but a decrease in degradation rate for higher doses, as shown in Figure 1.

The degradation was only slightly affected by the irradiation temperature, increasing a little with increasing temperature. The presence of oxygen also resulted in only slightly enhanced degradation. Typical results are shown in Table I.

Values of $\bar{M}_n$ for the irradiated samples, obtained by membrane osmometry, gave G(scission) = 11 for irradiation under vacuum at 0°. The molecular weight distributions are being investigated by gel permeation chromatography and $\bar{M}_w$ values are being obtained by light scattering.

Gas Production. The yield and composition of the gases evolved during irradiation showed a very strong temperature dependence from 0 to 70°. The volatile material consisted mainly of the two monomers (sulfur dioxide and butene-1) and smaller amounts of hydrogen, methane, and ethane. Typical results are summarized in Table II.

TABLE I
EFFECT OF IRRADIATION TEMPERATURE AND OXYGEN ON THE DEGRADATION OF POLY(BUTENE-1 SULFONE) BY γ IRRADIATION

		Limiting viscosity number, cm³/g	
Dose, Mrad	Temp, °C	Vacuum	Air
0		139.0	139.0
0.5	−196	66.1	
	−80		61.2
	0	63.4	53.6
	30	60.0	48.5
5.0	−196	25.2	
	−80		20.1
	0	24.1	16.4
	30	22.0	15.5
10.0	−196	15.9	
	−80		12.1
	0	15.0	11.2
	30	14.7	11.0

TABLE II
TEMPERATURE DEPENDENCE OF THE YIELD AND COMPOSITION OF THE GASES EVOLVED ON γ IRRADIATION OF POLY(BUTENE-1 SULFONE). RADIATION DOSE 5 MRAD; ANALYSIS BY GAS CHROMATOGRAPHY

Irradiation temp, °C	G(gas)	Composition, mole %			
		SO_2	Butene-1	H_2	CH_4 and C_2H_6
0	12.0	88	9	2	<1
30	39.0	71	28	1	<0.5
70	478	50	49	0.5	<0.5

The gas yield and composition depended on the temperature and duration of storage after irradiation, indicating the occurrence of post-irradiation reactions, especially depropagation. They were minimized by storage at −196°. The value for the total gas yield at a particular temperature was found to decrease slightly with increasing radiation dose.

Discussion

In most long-chain polymers, the predominant effect of high-energy radiation is either the formation of cross-links with an increase in the average molecular weight and the ultimate formation of a three-dimensional, insoluble, network structure, or the fracture of main-chain bonds, resulting in a reduction of the average molecular weight. These processes are accompanied by the formation of gaseous products and frequently by changes in unsaturation. Both cross-linking and main-chain fracture can occur simultaneously in the same polymer, although polymers are usually classified as either of the cross-linking or degrading type, depending on the process which predominates under the irradiation conditions.

Poly(butene-1 sulfone) has been clearly shown to be of the degrading type at all temperatures under vacuum and in air from the solution viscosity measurements. The value of G(scission) = 11 derived from osmotic pressure measurements of $\bar{M}_n$ shows that it is one of the most rapidly degraded polymers. The rate of radiation degradation under vacuum at ambient temperature is comparable with that of cellulose[4] in which anhydroglucose units are linked together by weak 1,4-glycosidic bonds. It is greater than degrading polymers with a carbon–carbon backbone chain such as poly(isobutene),[5–7] poly(methyl methacrylate),[8,9] and poly(α-methylstyrene).[10] The high degradation rate of poly(butene-1 sulfone) can be attributed to the relative weakness and specificity of scission of the C–S bonds in the main chain.

At 0° the predominant gaseous product is SO_2 (88%). Therefore C–S scission, followed by SO_2 elimination, must be the principal reaction occurring. The total yield of gaseous products is G(gas) = 12.0. As the irradiation temperature is increased, the rapidly increasing G(gas) value, the increasing butene-1 to SO_2 ratio, and the very high proportion of monomer (99% at 70°) in the gas indicate that the chain scission and SO_2 elimination is accompanied by increased chain depropagation to equal amounts of the two comonomers.

Only a very small proportion of the chain scissions resulting from SO_2 elimination must disappear by recombination of the fragments to form C–C links, the majority remaining as permanent fractures since G(scission) = 11 and $G(SO_2)$ = 10, exclusive of depropagation, at 0°.

The explanation of the rapid rise in the production of monomer with increase in irradiation temperature from 0 to 70° must lie in the thermodynamic stability of the polymer. The equilibrium or ceiling temperature for the formation of poly(butene-1 sulfone) in the liquid phase is 68° for an equimolar mixture of butene-1 and sulfur dioxide (calculated from the heat and entropy of polymerization data of Dainton and Ivin[11]). If there is an equilibrium between solid polymer and monomer vapor then there will be an equilibrium vapor pressure of butene-1 and SO_2 above the polymer which will increase rapidly over the temperature range 0–70°.

In contrast to depropagation, permanent main-chain scission, which produces the decrease in molecular weight and hence in viscosity, is only slightly temperature dependent. This can be explained by radicals trapped during irradiation at low temperatures reacting on warming. However, the G(scission) value is much higher than normal yields of trapped radicals and it is probable that the scission reaction actually occurs during irradiation and is reasonably temperature independent.

Scission of C–C bonds is not important as the main other product is hydrogen, resulting from C–H scission; methane and ethane yields are very small. These results confirm that the high-energy radiation cleaves main-chain C–S bonds with high specificity.

The poly(olefin sulfones) are relatively unstable to heat, the principal mode of thermal decomposition being depolymerization to the monomers.[12,13] This is due to the low ceiling temperature, above which the polymer is thermodynamically unstable. Our results show that when there is a suitable source of free radicals the polymers are likely to be unstable even at ambient temperatures.

Acknowledgments. We are pleased to acknowledge the Australian Atomic Energy Commission for supporting this work, and Mr. B. M. O'Leary and Mr. J. Bolton for organizing the irradiations. We wish to thank Professor I. Lauder for mass spectrometric analysis and Dr. E. Senogles for the osmometry measurements.

J. R. Brown, J. H. O'Donnell*
Department of Chemistry
University of Queensland
Brisbane, Australia

Received October 15, 1969

---

(4) A. Charlesby, *J. Polym. Sci.*, **15**, 263 (1955).

(5) D. T. Turner, *ibid., Part A*, **2**, 1699 (1964).

(6) P. Alexander, R. M. Black, and A. Charlesby, *Proc. Roy. Soc.* (London), **A232**, 31 (1955).

(7) A. Henglein and C. Schneider, *Z. Physik. Chem.*, **19**, 367 (1969).

(8) L. A. Wall and D. W. Brown, *J. Phys. Chem.*, **61**, 129 (1957).

(9) A. R. Shultz, P. I. Roth, and G. B. Rathmann, *J. Polym. Sci.*, **22**, 495 (1956).

(10) A. M. Kotliar, *J. Appl. Polym. Sci.*, **2**, 134 (1959).

(11) F. S. Dainton and K. J. Ivin, *Quart. Rev.* (London), **12**, 61 (1958).

(12) M. A. Naylor and A. W. Anderson, *J. Amer. Chem. Soc.*, **76**, 3962 (1954).

(13) D. O. Hummel, H-D. R. Schueddemage, and U. Pohl, *Kolloid-Z.*, **210**, 106 (1966).