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γ Radiolysis of Poly(butene-1 sulfone) and Poly(hexene-1 sulfone)

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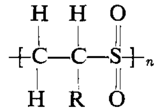
ABSTRACT: It has been shown that poly(butene-1 sulfone) and poly(hexene-1 sulfone), which are 1:1 alternating copolymers of the type $\left[CH_2CHR\text{-}SO_2 \right]_n$, undergo rapid degradation upon irradiation in the solid state in air and *in vacuo*. *G*(fracture) = 10.7 for poly(butene-1 sulfone) at 0° and 9.8 for poly(hexene-1 sulfone) at 30°, both *in vacuo*. The values of *G*(fracture) were higher for irradiation in air. The main volatile product at 0° was sulfur dioxide, in comparable yield to *G*(fracture), suggesting specificity of C–S fracture and stabilization of main-chain fracture by SO_2 elimination. Increasing irradiation temperatures resulted in increasing depropagation to the two comonomers as a result of the thermodynamic instability of the polymer. Hydrogen was the other main volatile product, and there were very small amounts of saturated hydrocarbons. The broad initial molecular weight distributions were only slightly reduced toward the most probable distribution, indicating that some cross-linking occurred.

There is very little information available on the effects of high-energy radiation on compounds containing $-SO_2-$, and particularly on polymers. The poly(olefin sulfones) (**1**) are of interest because preferential scission of main-chain C–S bonds has been observed by electron spin resonance,[1] instead of the usual C–H scission. Recombination of the geminate polymeric radicals within the "cage" could result in a high radiation resistance.



$$\left[\begin{array}{ccc} H & H & O \\ | & | & \| \\ C- & C- & S \\ | & | & \| \\ H & R & O \end{array} \right]_n$$

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In a study of the γ-radiation-initiated copolymerization of a variety of olefins with SO_2, Bray[2] observed that the polysulfones obtained after high radiation doses had lower limiting viscosity numbers than those which had been produced with lower doses, suggesting that the polymers were degraded by radiation. Eaton and Ivin,[3] in an experiment involving the grafting of styrene onto poly(butene-1 sulfone) with X-rays, found that the polysulfone was degraded. We have reported that the limiting viscosity number of poly(butene-1 sulfone) decreases rapidly with dose of γ radiation and that the two comonomers are the major volatile products.[4]

This paper describes a detailed investigation of the changes in molecular weight and of the amount and composition of volatile products resulting from the γ irradiation of poly(butene-1 sulfone) and poly(hexene-1 sulfone) in the solid state. In particular, the temperature dependence was examined to elucidate the importance of depropagation.

The polysulfones of the lower olefins are insoluble in organic solvents, and higher olefins have a low volatility and monomer production cannot be conveniently determined. The polysulfones of butene-1 and hexene-1 are particularly suitable for investigation, since they are readily soluble and the monomers have adequate volatility.

Experimental Section

Preparation. Poly(butene-1 sulfone) and poly(hexene-1 sulfone) were prepared by copolymerization of equimolar liquid mixtures of butene-1 (Matheson pure grade) or hexene-1 (Koch-Light) and sulfur dioxide (British Drug Houses) using distilled monomers with *tert*-butyl hydroperoxide and ultraviolet initiation at −78°. The polymers were purified by precipitation from acetone solution into methanol and dried under vacuum at ambient temperatures. The microanalysis values corresponded to the 1:1 copolymers. *Anal.* Calcd for poly(butene-1 sulfone): C, 39.98; H, 6.71; O, 26.63; S, 26.68. Found: C, 39.99; H, 6.67; O, 26.6; S, 26.7. Calcd for poly(hexene-1 sulfone): C, 48.62; H, 8.16; O, 21.59; S, 21.63. Found: C, 48.56; H, 8.21; O, 21.7; S, 21.5.

Irradiation. Polymer samples (1 g) of finely divided powder were sealed under vacuum (18 hr of pumping at room temperature 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 at Lucas Heights at a dose rate of about 0.5 Mrad/hr. Ferrous sulfate dosimetry was used with $G(Fe^{3+}) = 15.5$ and the dose (*D*) in the polymer was calculated from the energy absorption coefficients.[5] *D*(polymer)/*D*(dosimeter) = 0.96 for poly(butene-1 sulfone) and 0.97 for poly(hexene-1 sulfone). Irradiations were carried out at −196, −78, and 0° by immersing the samples in a vacuum flask containing liquid nitrogen, Dry Ice–acetone, and ice–water, respectively. Variable-temperature rigs circulating liquid nitrogen for the temperature range −100 to 10°[6] or water from 10 to 40°C and an electrically heated oil bath from 40 to 100° were used to provide a wide range of irradiation temperatures.

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

(2) B. G. Bray, *Diss. Abstr.*, **19**, 494 (1958).

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

(4) J. R. Brown and J. H. O'Donnell, *Macromolecules*, **3**, 265 (1970).

(5) J. H. O'Donnell and D. F. Sangster, "Principles of Radiation Chemistry," Edward Arnold, London, 1970.

(6) J. H. O'Donnell, *Chem. Ind.* (*London*), 481 (1968).

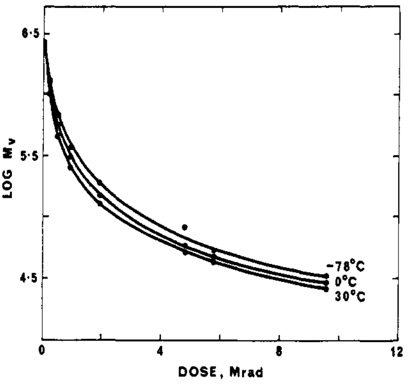

Figure 1. Log $\bar{M}_v$ *vs.* radiation dose for poly(butene-1 sulfone) irradiated in air.

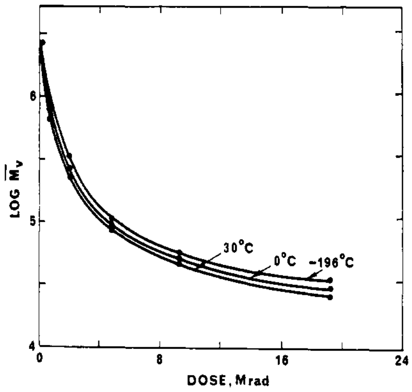

Figure 2. Log $\bar{M}_v$ *vs.* radiation dose for poly(butene-1 sulfone) irradiated *in vacuo.*

Table I
Number-Average and Viscosity-Average Molecular Weights of Poly(butene-1 sulfone) after γ Irradiation *in vacuo* at 0°

Dose, Mrad	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$
0	2,751,000	410,000	6.71
0.19	1,514,000	221,000	6.85
0.38	912,000	130,000	7.02
0.76	513,000	96,000	5.34
1.5	331,000	51,000	6.49
3.1	178,000	34,000	5.24

Irradiated samples were stored in liquid nitrogen after irradiation to minimize postirradiation effects. At ambient temperatures these effects were shown to cause appreciable increases in gas yields as a result of depolymerization, but no changes in viscosity.

Solution Properties. Solution viscosities were measured in acetone at 30°. Problems of shear dependence were overcome by using spiral capillary viscometers and by making measurements down to low polymer concentrations.[7] Shear rate effects were only significant in the unirradiated poly(butene-1 sulfone), which was found to have $\bar{M}_v = 2{,}751{,}000$, using the K and a values for the Mark–Houwink equation which we have reported elsewhere,[8] and $\bar{M}_v/\bar{M}_n = 7$. $\bar{M}_n$ values were obtained by membrane osmometry (Mechrolab model 501 membrane osmometer with S and S 0.8 membranes) in cyclohexanone at 37°.

Gel permeation chromatography measurements of molecular weight distributions were made with a Waters 200 instrument, calibrated with narrow-distribution polystyrene samples and calculated using the method described by Cazes.[9]

Volatile Products. Volatile radiolysis products were measured in a gas buret by transfer on a vacuum line. They were analyzed with an F and M Model 810 gas chromatograph which had the inlet carrier gas flow passing through a loop at the exit of the buret. A Porapak Q column was used at 110° with thermal conductivity and flame ionization detectors. The analyses were checked on an Atlas CH4 mass spectrometer.

Other Techniques. Electron spin resonance (esr) spectra of irradiated poly(butene-1 sulfone) were obtained with a Varian V4502 spectrometer, and radical yields at −170° were measured by double integration of recorded first-derivative spectra using a computer and comparison with DPPH–KCl and pitch–KCl standards. A Perkin-Elmer differential scanning calorimeter, Model 1B, was used to examine the relative thermal stability of irradiated and unirradiated poly(butene-1 sulfone).

Results

Poly(butene-1 Sulfone). Molecular Weight Changes. Viscosity measurements after irradiation in air showed that the polymer undergoes rapid degradation. The reduction in the viscosity-average molecular weight, $\bar{M}_v$, with radiation dose, using the K and a values determined for the unirradiated polymer, is shown in Figure 1. The rate of degradation increased slightly with increase in temperature.

Viscosity measurements after irradiation in vacuum showed that rapid degradation was also occurring under these conditions, but not as rapidly as in air, indicating that air does enhance the degradation. Again, the rate of degradation increased slightly with increase in irradiation temperature as shown in Figure 2.

The use of $\bar{M}_v$ values for irradiated polymers, derived from measured limiting viscosity numbers $[\eta]$ with K and a values for the Mark–Houwink relationship between $[\eta]$ and $\bar{M}_v$ obtained with unirradiated polymer, cannot be strictly justified. Branching and cross-linking, and especially intramolecular cross-linking, can alter the hydrodynamic behavior and hence the relationship between $[\eta]$ and M. None of these effects is expected to occur significantly in comparison with the rate of degradation in poly(butene-1 sulfone). Also, the interpretation of changes in $\bar{M}_v$ is more complex if the molecular weight distribution changes, but as shown later this is almost unaltered by irradiation. In any case, the rapid decrease in limiting viscosity number on irradiation shows that main-chain scission is predominant and that it occurs more rapidly in air than vacuum.

The change in number-average molecular weight, $\bar{M}_n$, with dose was determined by membrane osmometry for one set of irradiation conditions—vacuum irradiation at 0°. Values of $\bar{M}_n$ obtained are compared with values of $\bar{M}_v$ for the same radiation dose in Table I. It is evident that the molecular weight distribution remains broad, despite the substantial reduction in molecular weight.

G(**fracture**). The number-average molecular weight, $\bar{M}_n$, after irradiation is related to the initial number-average molecular weight, $\bar{M}_n'$, by the equation[10]

$$1/\bar{M}_n = (1/\bar{M}_n') + (p_0/w)(r + r_0)$$

where p_0 is the fraction of chain-repeat units fractured per unit dose, w is the molecular weight of the chain unit, r is the radiation dose, and r_0 is the dose which would be required to produce a polymer with the observed initial distribution from one which is infinitely long. This relationship holds whatever the initial molecular weight distribution. Thus a plot of $1/\bar{M}_n$ against dose is linear. The slope is p_0/w and $G(\text{fracture}) = (0.96 \times 10^6)p_0/w$.

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[7] J. R. Brown and J. H. O'Donnell, *Polymer*, **9**, 567 (1968).

[8] J. R. Brown and J. H. O'Donnell, in preparation.

[9] J. Cazes, *J. Chem. Educ.*, **43**, A567, A625 (1966).

[10] A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, London, 1960.

A plot of $1/\bar{M}_n$ *vs.* dose for poly(butene-1 sulfone) irradiated in vacuum at 0° is shown in Figure 3. The plot is linear up to a dose of 1.5 Mrad. From the slope, *G*(fracture) = 10.7 ± 0.4. The value at 3.1 Mrad suggests that the fracture yield may decrease at higher doses.

Plots of $1/\bar{M}_v$ *vs.* dose for irradiation in air and vacuum at three different temperatures were linear up to the doses given (10 Mrad in air and 20 Mrad *in vacuo*).

If the value of $\bar{M}_v/\bar{M}_n$ characterizing the breadth of the molecular weight distribution remains constant and is known, then plots of $1/\bar{M}_n$ *vs.* dose can be used to determine *G*(fracture). In the case of poly(butene-1 sulfone), this requirement is met, at least to a satisfactory approximation, as indicated in Table I. If an average value of $\bar{M}_v/\bar{M}_n$ of 6.6 is taken (from Table I), then the *G*(fracture) values shown in Table II are obtained. The *G*(fracture) value for irradiation *in vacuo* at 0° obtained in this way from the viscosity measurements is the same as the value derived directly from osmometry measurements of $\bar{M}_n$, indicating that the method has a reasonable validity.

Gel Permeation Chromatography. The molecular weight distributions of poly(butene-1 sulfone) samples irradiated *in vacuo* at 0° were checked by gel permeation chromatography in tetrahydrofuran at 40°. The differential molecular weight distributions are shown in Figure 4 and illustrate clearly that (a) the molecular weight is rapidly reduced by irradiation and (b) the distribution remains broad and does not approach a random distribution within the range of doses studied.

Volatile Radiolysis Products. The volatile products formed on irradiation of poly(butene-1 sulfone) were sulfur dioxide, butene-1, hydrogen, and very small amounts of methane and ethane. The three major components were quantitatively resolved on a Porapak Q column at 110° using a thermal conductivity detector. The methane and ethane were measured with a flame ionization detector. Mass spectrometric analysis confirmed the identification of the products.

Temperature Dependence of Total Gas Yield. The yield of volatile radiolysis products showed a very strong temperature dependence between −10 and 72°. This is shown in Table III for a dose of 5 Mrad with *G*(gas) increasing from 11.5 to 478.

Temperature Dependence of Gas Composition. The relative proportions of the three major radiolysis products, sulfur dioxide, butene-1, and hydrogen, showed a marked temperature dependence, as shown in Table III for a dose of 5 Mrad. The yields of sulfur dioxide and butene-1 increased rapidly with increase in irradiation temperature, while the hydrogen yield showed a small rise. At low temperatures the predominant product was sulfur dioxide (88%). As the temperature increased, the gas approached an equimolar mixture of the comonomers butene-1 and SO_2, with only a small amount (0.2%) of hydrogen and trace amounts of methane and ethane.

Dose Dependence of Total Gas Yield and Composition. The total gas yields were measured after various doses at 0 and 30°. At 30°, *G*(gas) decreased from 50.0 after 0.96 Mrad to 30.4 after 12.1 Mrad. Similarly, at 0°, *G*(gas) decreased from 18.7 after 0.47 Mrad to 8.6 after 9.6 Mrad. These *G* values are calculated as the total gas evolved divided by the radiation dose. The "instantaneous" *G*(gas) values, taken as the slope of the gas yield *vs.* dose curves, decreased even more rapidly, especially at 30°.

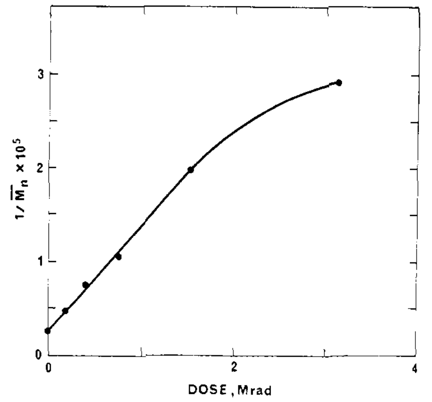

Figure 3. $1/\bar{M}_n$ *vs.* radiation dose for poly(butene-1 sulfone) irradiated *in vacuo* at 0°.

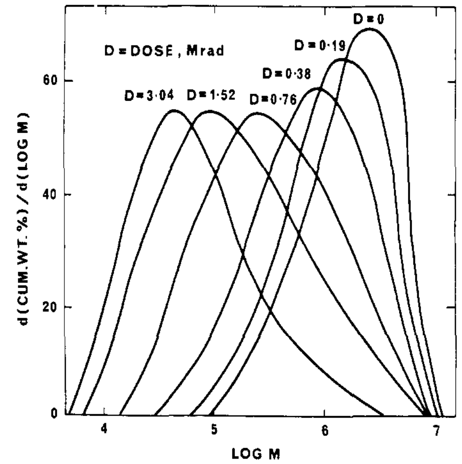

Figure 4. Differential molecular weight distributions of poly(butene-1 sulfone) after various radiation doses determined by gel permeation chromatography.

Table II

G(fracture) Values for Poly(butene-1 sulfone) from Viscosity Measurements

Temp, °C	*G*(fracture)
In vacuo	
−196	9.2
0	10.7[a]
30	12.2
Air	
−78	18.1
0	22.2
30	23.7

[a] *G*(fracture) = 10.7 from $\bar{M}_n$ values determined by membrane osmometry.

Table III

Temperature Dependence of Total Gas Yield and Composition from Poly(butene-1 sulfone) after ~5 Mrad

Temp, °C	Dose, Mrad	*G*(gas)	Yield, μmol g^{-1}	Composition, % SO_2	Butene-1	H_2
−10	4.9	11.5	59	88.2	9.3	2.5
0	5.0	12.0	63	88.0	10.0	2.0
10	5.1	15.1	81	80.8	18.3	1.6
22	5.4	24.7	140	77.2	21.5	1.3
30	5.1	39.0	209	73.3	25.8	0.9
50	4.8	137.1	699	53.3	46.3	0.4
72	5.0	478	2521	50.4	49.4	0.2

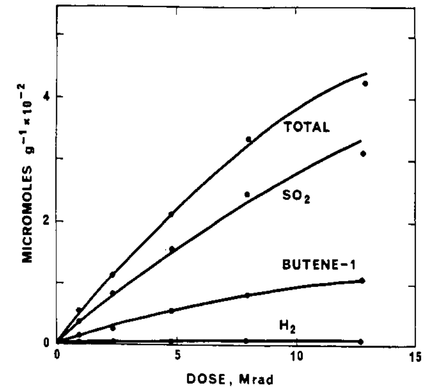

Figure 5. Gas yields *vs.* dose for poly(butene-1 sulfone) irradiated *in vacuo* at 30°.

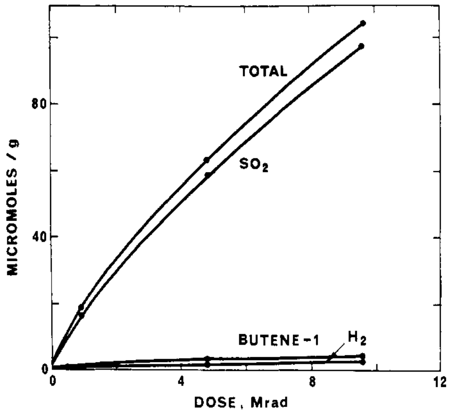

Figure 6. Gas yields *vs.* dose for poly(butene-1 sulfone) irradiated *in vacuo* at 0°C.

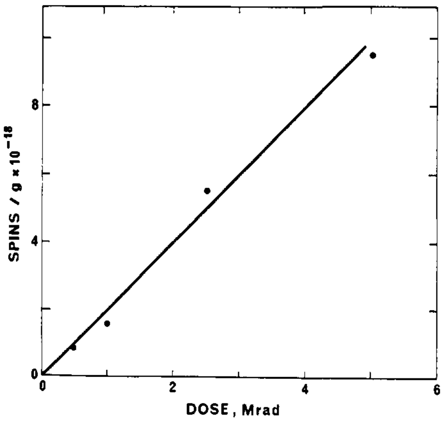

Figure 7. Trapped radical concentration *vs.* dose for poly(butene-1 sulfone) irradiated *in vacuo* at −196° and measured at −170°.

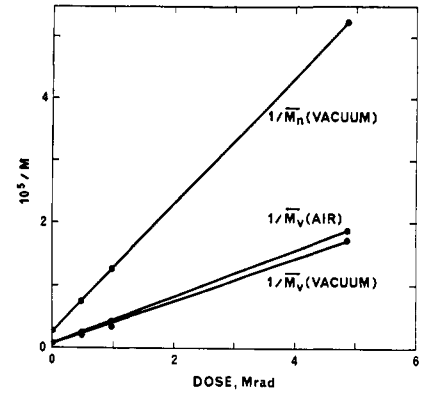

Figure 8. $1/\bar{M}$ *vs.* dose plots for poly(hexene-1 sulfone) irradiated *in vacuo* and in air at 30°.

The variations of the yields of sulfur dioxide, butene-1, and hydrogen with radiation dose at 30 and 0° are shown in Figures 5 and 6, respectively. The hydrogen yield is a linear function of dose at both 30 and 0°, but *G*(sulfur dioxide) and *G*(butene-1) decrease with increasing dose.

Radical Concentration. The electron spin resonance spectrum of poly(butene-1 sulfone) irradiated at −196° and measured at −170° was the same as that reported earlier by Ayscough, *et al.*[11] Radical yields after doses from 0.5 to 5.0 Mrad are shown in Figure 7, and the slope of this plot gives *G*(radicals) = 3 ± 1.

Differential Thermal Analysis. Differential thermal analysis curves for unirradiated poly(butene-1 sulfone) and a sample given 20 Mrad in air at 30° showed that the irradiated polymer was much less stable than the unirradiated polymer, decomposition occurring at 150° compared with 215°.

Poly(hexene-1 sulfone). Molecular Weight Changes. Viscosity measurements on poly(hexene-1 sulfone) after irradiation in air and *in vacuo* at 30° showed that the polymer behaves similarly to poly(butene-1 sulfone), *i.e.*, rapid degradation in both air and vacuum with enhanced degradation in air. The decreases in limiting viscosity number for doses up to 10 Mrad are shown in Table V. $\bar{M}_v$ values have been derived from the relationship

$$[\eta]\ (\mathrm{cm^3\ g^{-1}}) = 0.0059\bar{M}_v^{0.74}\ (\text{acetone, } 25°)$$

obtained by Ivin, *et al.*[12] $\bar{M}_n$ values for samples irradiated *in vacuo* were determined by membrane osmometry. These values and the ratio $\bar{M}_v/\bar{M}_n$ are given in Table IV. The distribution is narrower than for the poly(butene-1 sulfone), but again is only slightly reduced by irradiation.

A plot of $1/\bar{M}_n$ *vs.* radiation dose is linear, as shown in Figure 8, and the slope gives *G*(fracture) = 9.8 ± 0.4. Plots of $1/\bar{M}_v$ *vs.* radiation dose for irradiation *in vacuo* and in air are also linear, as shown in Figure 8. Correcting to $\bar{M}_n$ values from the known breadth of the distribution, as for poly(butene-1 sulfone), gives *G*(fracture) = 10.6 ± 0.4 in air. This assumes that $\bar{M}_v/\bar{M}_n$ remains the same during irradiation in air, as has been shown *in vacuo*.

Volatile Radiolysis Products. The volatile products formed on irradiation of poly(hexene-1 sulfone) were sulfur dioxide, hexene-1, hydrogen, and traces of methane and butane.

The total gas yields after 5 Mrad of irradiation at tempera-

Table IV
Viscosity and Molecular Weight Changes in Poly(hexene-1 sulfone) on Irradiation *in vacuo* and Air at 30°

	In vacuo				Air	
Dose (Mrad)	[η], cm^3 g^{-1}	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$	[η], cm^3 g^{-1}	$\bar{M}_v$
0.0	200.3	1,327,000	352,000	3.77	200.3	1,327,000
0.49	98.2	507,000	133,000	3.78	89.6	448,000
0.97	64.3	286,000	79,000	3.61	57.2	244,000
4.9	19.2	56,000	19,000	2.95	18.8	54,000
9.7	11.9	29,000			11.4	28,000

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[11] P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, *Proc. Chem. Soc.*, 71 (1961).

[12] K. J. Ivin, H. A. Ende, and G. Meyerhoff, *Polymer*, 3, 129 (1962).

tures from 0 to 50° are shown in Table V. *G*(total gas) increased from 17.5 at 0° to 321 at 50°. The gas composition at each temperature is also given in Table V. At 0°, sulfur dioxide is the predominant product (75%), with smaller amounts of hexene-1 (21.1%) and hydrogen (3.9%). The composition changes with increasing temperature similarly to poly(butene-1 sulfone), approaching an equimolar mixture of the comonomers sulfur dioxide and hexene-1, with small amounts of hydrogen. The yield of methane and butane was less than 0.3% under all conditions.

Table V
Temperature Dependence of Total Gas Yields and Composition from Poly(hexene-1 sulfone) after ~5 Mrad

Temp, °C	Dose, Mrad	*G*(gas)	Yield, μmol g^{-1}	Composition, %		
				SO$_2$	Hexene-1	H$_2$
0	5.0	17.5	52	75	21.1	3.9
15	5.3	28.6	158	73.4	24.1	2.5
30	5.1	71.4	500	65.4	32.8	1.8
50	4.2	321	1408	53.1	45.9	1.0

Discussion

Poly(butene-1 sulfone) and poly(hexene-1 sulfone) have been clearly shown to undergo rapid degradation (main-chain fracture) on irradiation, both in air and *in vacuo*. The values of *G*(fracture) = 10.7 for poly(butene-1 sulfone) *in vacuo* at 0° and of *G*(fracture) = 9.8 for poly(hexene-1 sulfone) *in vacuo* at 30°, derived from osmotic pressure measurement of $\bar{M}_n$, show that they are two of the most rapidly degraded of all polymers.

The high degradation rates of poly(butene-1 sulfone) and poly(hexene-1 sulfone) can be attributed to the relative weakness and specificity of fracture of the carbon–sulfur bonds in the main chain. This is in contrast to the usual picture of radiation damage in polymers, with carbon–hydrogen fracture as the main process, and little permanent main-chain fracture owing to the low mobility of the geminate polymeric fragments causing recombination within the "cage."

In the poly(olefin sulfones) fracture of C–S bonds in the main chain is evidently a permanent process, because the adjacent C–S bond is also fractured, either simultaneously or immediately afterward, with the liberation of SO$_2$ and the creation of a "hole" between the adjacent polymeric radicals, which provides a barrier to recombination. Ivin and coworkers[13] have shown for dimethyl sulfone, CH$_3$SO$_2$CH$_3$, that (1) the C–S bond is relatively weak, with *D*(CH$_3$–SO$_2$CH$_3$) = 254 kJ mol^{-1}; (2) the second C–S bond is much weaker still, with *D*(CH$_3$–SO$_2$) = 97.5 kg mol^{-1}; and (3) C–S fracture is the predominant thermal decomposition reaction.[14]

Studies of the esr spectra of irradiated dialkyl sulfones and poly(olefin sulfones) by Ayscough, Ivin, and O'Donnell[1] have shown that in both classes of compounds the main radical species trapped at −196° is the alkyl radical corresponding to C–S fracture. The absence of an RSO$_2$ radical in comparable concentration suggested that both C–S bonds were fractured. The greater *G*(fracture) of 10.7 in poly(butene-1 sulfone) compared with *G*(radicals) of 3 suggests that radical-termination reactions have occurred at −196°. However, the possibility of a chain reaction for fracture cannot be excluded.

Depropagation of the poly(olefin sulfone) to the comonomers, olefin and SO$_2$, does occur, and increases with increase in irradiation temperature. This would assist in stabilization of main-chain fractures if it occurred to a small extent in many chains rather than as extensive unzipping of a few chains. However, this is an unnecessary requirement, as the value of *G*(fracture) is only slightly temperature dependent and is not significantly reduced at 0° when depolymerization is small (10%) compared with SO$_2$ elimination (80%).

The similarity of the *G* values for fracture (10.7) and SO$_2$ elimination (10), corrected for depropagation, at 0° in poly(butene-1 sulfone) and similar observations in poly(hexene-1 sulfone) suggest that each elimination must result in a permanent main-chain fracture.

An increase in *G*(fracture) for irradiation in air compared with vacuum is a common phenomenon and is usually attributed to the formation of peroxy radicals. The effect of air was more pronounced in poly(butene-1 sulfone), for which *G*(fracture) values were 10.7 and 22.2 *in vacuo* and air, respectively, at 0°, than in poly(hexene-1 sulfone), for which *G*(fracture) values were 9.8 and 10.6 *in vacuo* and air, respectively, at 30°. The reason for this difference is not known.

The molecular weight distributions of polymers undergoing rapid, random main-chain fracture only should quickly approach most probable distributions. This is not the case for the two poly(olefin sulfones), as the initial broad distributions are not appreciably narrowed, although the average molecular weight is reduced from 10^6 to 10^4. Therefore, it is probable that a small amount of radiation-induced cross-linking is occurring. Irradiation of poly(butene-1 sulfone) up to 40 Mrad *in vacuo* produced no observable gel, which indicates that, relative to fracture, any cross-linking must be ineffective. However, poly(butene-1) and poly(hexene-1) both form insoluble gels on irradiation,[15,16] so it is reasonable to assume that cross-linking can take place to a small degree in the polysulfones.

G(total gas) increases rapidly with increase in irradiation temperature for both polymers although *G*(fracture) only increases slightly. The composition of the gas approaches an equimolar mixture of the two comonomers with increase in temperature, whereas at low temperature it is predominantly SO$_2$. Therefore, depropagation must be increasing rapidly in this temperature range. The equilibrium or ceiling temperatures for the liquid-phase polymerizations are about 60°, depending on the comonomer composition,[17] and above this temperature long-chain polymer will not be formed.

If there is an equilibrium between solid polymer and monomer vapor, an equilibrium vapor pressure of olefin and sulfur dioxide will exist above the polymer, which will increase rapidly over the temperature range 0–70° for the two poly(olefin sulfones).[18] Such an equilibrium has been demonstrated for poly(methyl methacrylate) by Ivin.[19] Hence, the polymer would be expected to depolymerize until equilibrium conditions were reached once active sites such as free radicals were established by the irradiation. However, side reactions and recombination of radicals would prevent complete depolymerization and the overall result would be a rapidly increasing production of monomer with increasing temperature.

The decrease in *G*(total gas) with increasing dose for poly-

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(13) W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *Trans. Faraday Soc.*, 57, 1064 (1961).

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(butene-1 sulfone) was shown to be due to a reduction in *G* values for SO_2 and butene-1 production. This is the result of the reversibility of the polymerization reaction. Radiation-induced copolymerization of butene-1 and SO_2 in the gas phase, with the concurrent formation of sulfinic acids, has been investigated in detail.[18]

Permanent chain fracture was only slightly temperature dependent. This could be explained by radicals trapped during irradiation at low temperatures reacting on warming. However, the *G*(fracture) values are much higher than the yield of trapped radicals, *G*(radicals) = 3 ± 1, and it is probable that the fracture reaction occurs during irradiation.

The present investigation was restricted to two poly(olefin sulfones) for which similar results were obtained. It can be predicted that high *G*(fracture) values will be obtained for all poly(olefin sulfones). However, as the size of the olefin increases, the importance of cross-linking reactions, which are characteristic of long-chain alkanes and of polyalkanes, will increase. Depropagation to the two comonomers would also be expected to increase with irradiation temperature and to show a correlation with the ceiling temperature.

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Radiation-Cross-Linked Poly(vinyl chloride). Phase Studies

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ABSTACT: The presence of multiple phases in a mixture of poly(vinyl chloride) and tetraethylene glycol dimethacrylate was investigated by electron microscopy, calorimetry, and dynamic viscoelasticity studies. The glass-transition temperatures of these phases increased with increasing doses of electron irradiation until finally only a single transition was observed at a dose of about 1 Mrad. The relationship between the extent of radiation-induced polymerization reaction and the viscoelastic and calorimetric properties of the system was elucidated.

In another paper,[1] the mechanism of radiation cross-linking of poly(vinyl chloride) (PVC) with tetraethylene glycol dimethacrylate (TEGDMA) was investigated. Rapid polymerization took place to form a three-dimensional network onto which PVC was grafted. The rate of disappearance of the double bond in the monomer and the rate of gel formation were measured as a function of radiation dosage. In the present investigation morphological, calorimetric, and dynamic-mechanical studies have been undertaken in order to elucidate the interrelation between the extent of chemical reaction and the physical properties of the system.

Experimental Section

(1) Materials. Tetraethylene glycol dimethacrylate from Ware Chemical Corp. and PVC (Opalon 660) from Monsanto Co. were used. All the mixtures investigated contained 33% by weight of monomer. The monomer was added slowly to PVC in a high-speed blender at 80°; from these powders, sheets were compression molded at 140° for 3 min. Irradiation was carried out at 80° under nitrogen using 1-MeV electrons from a van de Graaff generator. The dose rate was 0.01 Mrad/sec. Unsaturation was determined by infrared absorption. Gel content was measured by extraction; in addition, the gel was analyzed for chloride content to determine the extent of PVC grafting.

(2) Calorimetry. The glass transitions and changes in specific heat, ΔC_P, of the samples were studied by a differential scanning calorimeter, Perkin-Elmer DSC-1. All measurements were made at a heating rate of 40°/min in a manner which has been reported in detail elsewhere.[2]

(3) Dynamic Modulus. Measurement of dynamic viscoelasticity was made by the use of a direct-reading dynamic viscoelastometer from the Toyo Measuring Instrument Co., Vibron DDV-II, at a frequency of 110 Hz.

(4) Electron Microscopy. The state of mixing of TEGDMA in PVC before irradiation was studied under the electron microscope. The technique used here was based on Kato's method of staining double bonds with osmium tetraoxide (OsO_4).[3] However, an additional step was introduced for obtaining thin sections of soft materials. In the two-step sectioning method,[4] slices as thick as 10 μ were first cut with a hand microtome at liquid nitrogen temperature, stained with OsO_4 vapor, and then embedded in an epoxy resin. Ultrathin sections of about 800 Å in thickness were obtained by the use of Reichert ultramicrotome, and electron micrographs were taken by direct observation of the ultrathin sections.

(5) Absorption–Desorption Studies. Compression-molded PVC sheets were immersed in TEGDMA at various temperatures for at least 3 days. Each specimen was pat dried quickly at the temperature of the experiment and the weight gain determined. Desorption experiments were carried out by allowing the swollen specimens to cool, in the presence of the monomer, to lower temperatures for at least 5 days.

Results

(1) Recapitulation of Previous Results. The disappearance of the double bond and the formation of insoluble gel as a function of radiation dosage are shown in Figure 1. The gelation dose was reached at 0.05 Mrad. During this period, 45% of the unsaturation was consumed. In the

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