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Trevor N. Bowmer[a][b]; James H. O'donnell[a]
[a] Department of Chemistry, University of Queensland, Brisbane, Australia [b] Bell Laboratories, Murray Hill, New Jersey, USA

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Radiation Degradation of Poly(olefin Sulfone)s: A Volatile Product Study

TREVOR N. BOWMER* and JAMES H. O'DONNELL†

Department of Chemistry
University of Queensland
Brisbane 4067, Australia

ABSTRACT

The predominant degradation reaction in the γ-irradiation of nine poly(olefin sulfone)s was found to be C–S bond scission with elimination of SO_2 and olefin. The extent of depolymerization, measured by the yields of the two comonomers, increased over five irradiation temperatures from 0 to 150°C and could be correlated with the ceiling temperature. Thus G (total volatile products) increased from 10 to 10,000 over this temperature range. Minor radiolysis products included the alkanes corresponding to (1) loss of the side chain group and (2) scavenging of the side chain radical by monomer olefin. There was a deficiency of olefin relative to SO_2, except at high temperatures, and isomerization of the product olefin in some cases. These observations are attributed to reactions of radiation-induced polymeric cations.

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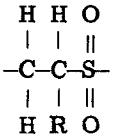
*Present address: Bell Laboratories, Murray Hill, New Jersey 07974, USA.

†To whom correspondence should be addressed.

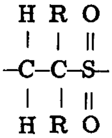
INTRODUCTION

Poly(olefin sulfone)s, I, II, III are copolymers of olefins with sulfur dioxide and therefore have a hereroatom in the main chain. Both these features place them outside the generalization that polymers containing a tetra-substituted carbon atom in the main chain repeat unit will predominantly undergo chain scission on irradiation, whereas all other polymers will predominantly cross-link [1].



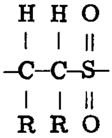
$$\begin{array}{ccc} H & H & O \\ | & | & \| \\ -C- & C- & S- \\ | & | & \| \\ H & R & O \end{array}$$

I



$$\begin{array}{ccc} H & R & O \\ | & | & \| \\ -C- & C- & S- \\ | & | & \| \\ H & R & O \end{array}$$

II

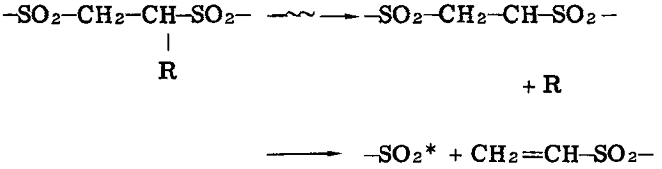


$$\begin{array}{ccc} H & H & O \\ | & | & \| \\ -C- & C- & S- \\ | & | & \| \\ R & R & O \end{array}$$

III

There is already evidence from the gamma radiolysis of poly(1-butene sulfone) [2] and poly(1-hexene sulfone) [3] that C–S bond scission with SO_2 elimination is the predominant radiation chemical reaction in poly(olefin sulfone)s. However, this conclusion has not been tested for more complex olefins, including branched olefins and 1,2-disubstituted olefins, such as 2-butene and cyclohexene.

It is also uncertain whether C–S scission is the initial step in the radiation-induced degradation. Elimination of the side-branch may occur first, followed by adjacent fracture of the main chain, as in



$$-SO_2-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-SO_2- \xrightarrow{\sim\sim} -SO_2-CH_2-\dot{C}H-SO_2- + R \longrightarrow -SO_2{*} + CH_2{=}CH-SO_2- \qquad (1)$$

Although the main volatile radiolysis product from polyethylene is hydrogen [4], small quantities of hydrocarbons (~2%) emanate from chain-end fragmentation and short-branch elimination. The hydrocarbon yield has been used to provide information about the nature and frequency of short branches in both polyethylene [4] and poly(vinyl chloride) [5] after reduction to the corresponding polyethylene. We may therefore anticipate that a close examination of the minor volatile products from the gamma irradiation of poly(olefin sulfone)s will show a relationship to the structure of the olefin.

In the present paper we report the volatile products from radiolysis of nine poly(olefin sulfone)s at temperatures between 0 and 150°C. The magnitude and temperature dependence of the radiation chemical yields have been correlated with the polymer structure and the ceiling temperatures. In addition, the minor products, which include alkanes produced by (1) loss of the alkyl side chain and subsequent hydrogen abstraction by the ensuing radical, (2) scavenging of the side chain radical by monomer olefin, and (3) dimerization and trimerization of olefin are considered in relation to the polymer structure.

EXPERIMENTAL

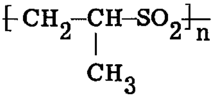
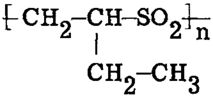
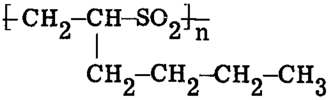
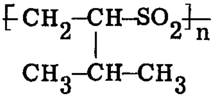
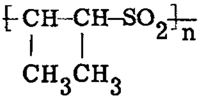
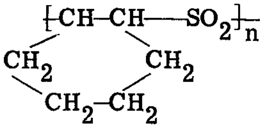
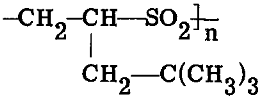
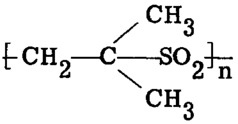
Poly(olefin sulfone)s were prepared from pure grade ethylene, propylene, isobutene (C.I.G. Aust.), 1-butene, cyclohexene (Matheson), 1-hexene, 3-methyl-1-butene (Phillips 66), 2-butene (Fluka), and 4,4-dimethyl-1-pentene (City Chemical Co.). The olefin and SO_2 were distilled and dried over molecular sieves on a vacuum line and condensed in equimolar proportions into a glass polymerization vessel. tert-Butyl hydroperoxide initiator was used for the copolymerizations, which were normally carried out at -78 to -40°C [6]. Poly(ethylene sulfone) was prepared at 20°C using a stainless steel pressure vessel. The polymers were precipitated into methanol and dried under vacuum at 45°C for 60 h. Table 1 lists the structures of the poly(olefin sulfone)s used in this work and their codes.

Elemental microanalyses confirmed that all the polysulfones have 1:1 olefin:SO_2 compositions. IR spectra with KBr disks and ^1H and ^{13}C NMR spectra of PPS, PBS, PHS, P2BS, and PCHS, which were soluble in dimethylsulfoxide, confirmed that the olefins had not undergone any rearrangement during polymerization [7].

Powdered samples (20-40 mg) of the polymers were evacuated at $< 10^{-2}$ Pa for 50 h at 25°C and sealed in thin-walled glass ampules (45 mm × 4.5 mm diam). The ampules were irradiated with ^{60}Co rays in a Gammacell 220 unit at ~0.4 Mrd/h to doses from 1 to 10 Mrd. Fricke dosimetry [8] and mass-energy absorption coefficients [9] were used to determine the absorbed doses. Irradiations were carried out at 0°C (ice water), 20°C (ambient), and at 50, 75 and 150°C (aluminum block heater).

The volatile radiolysis products were analyzed by gas chromatography by crushing the ampule containing the irradiated polymer in a special injection port on the chromatograph [4]. The post-irradiation, pre-analysis thermal treatment was found to affect significantly the volatile product yields and therefore the temperature of the injection port was maintained below the irradiation temperature. A Porapak Q column was used for most analyses with temperature programming from 70 to 220°C. Molecular sieve and alumina columns were used to separate and identify some of the products. Thermal conductivity and flame ionization detectors were used in series. Identification and calibration was performed with pure gases, supplemented by mass spectrometric and ^1H NMR analyses of the elutant. The NMR analyses, after bubbling the elutant through CCl_4, were particularly useful for identification of isomeric olefins.

TABLE 1. Structures, Codes, and Ceiling Temperatures of Poly(olefin sulfone)s. Ceiling Temperatures Determined from Solution Copolymerizations [10]

Olefin	Code	Structure	T_c (°C)
Ethylene	PES	$\left[CH_2-CH_2-SO_2\right]_n$	> 135
Propene	PPS	 $\left[CH_2-CH(CH_3)-SO_2\right]_n$	90
1-Butene	PBS	 $\left[CH_2-CH(CH_2-CH_3)-SO_2\right]_n$	64
1-Hexene	PHS	 $\left[CH_2-CH(CH_2-CH_2-CH_2-CH_3)-SO_2\right]_n$	60
3-Methyl-1-butene	PMBS	 $\left[CH_2-CH(CH(CH_3)-CH_3)-SO_2\right]_n$	36
2-Butene	P2BS	 $\left[CH(CH_3)-CH(CH_3)-SO_2\right]_n$	32-35
Cyclohexene	PCHS		24
4,4-Dimethyl-1-pentene	PDMPS	 $-CH_2-CH(CH_2-C(CH_3)_3)-SO_2\right]_n$	14
Isobutene	PIBS	 $\left[CH_2-C(CH_3)_2-SO_2\right]_n$	5

RESULTS AND DISCUSSION

The general features of the formation of volatile products by γ-irradiation of poly(olefin sulfone)s may be summarized as follows:

(1) the G-value for the total yield of volatile products from all of the poly(olefin sulfone)s is large compared to the values of hydrocarbon polymers; (2) the major products are sulfur dioxide and olefin, i.e., the two monomers; (3) G(olefin)/G(SO_2) increases toward unity–the value in the initial polymer–as the irradiation temperature is raised, starting from a value in the range 0.1-0.5 at 0°C; (4) the yield of volatile products rises rapidly as the irradiation temperature is increased; and (5) depolymerization producing the two monomers dominates the irradiation process with side chain fracture and fragmentation reactions, and secondary reactions, being of minor importance.

G(total gas) values of 10-200 at 0°C, increasing to 10,000-15,000 for irradiation at 150°C, indicate that a chain reaction has been initiated, leading predominantly to depolymerization and producing sulfur dioxide and olefin–the parent monomers. At high temperatures the depolymerization to free olefin and sulfur dioxide is thermodynamically favored, resulting in a rapid increase in G(total gas) values.

The absolute differences between G(SO_2) and G(olefin) for the irradiation of a particular polymer vary up to 1400. Such differences are too large to arise from single irradiation events, and therefore imply that a chain reaction leads to the reduction in the G(olefin)/G(SO_2) ratio from the expected value of 1. This chain reaction has been shown to be homopolymerization of the free product olefin on cationic sites in the irradiated polymer, consequently reducing G(olefin) [11]. The G(olefin)/G(SO_2) ratio is thus determined by competition between the cation undergoing (1) depropagation or (2) olefin homopolymerization, which will depend on its lifetime. At higher irradiation temperatures depropagation is favored. Figure 1 shows the major reaction pathways which we have postulated may occur in the radiolysis of poly(olefin sulfone)s [11].

The minor products were generally 1-3% of the total yield and arose from (1) side-chain fracture and fragmentation producing hydrogen and low molecular weight hydrocarbons, (2) addition of these alkyl fragments to free olefin, (3) dimerization and trimerization of the product olefin, and (4) fragmentation of the alkyl free radical and cation intermediates. The small yields of the above minor products are remarkable considering the large degree of degradation of the polymer induced by the radiation. The C–S bond has the lowest bond dissociation energy (230-250 kJ/mol compared with 330-355 kJ/mol for C–C bonds and 375-420 kJ/mol for C–H bonds), but the high specificity of main-chain C–S bond scission is unexpected in comparison with C–H scission and also elimination of side branches. Poly(olefin sulfone)s are an unusual class of polymer with respect to their radiation sensitivity [12].

Methane and C_2 hydrocarbons (C_2H_2, C_2H_4, and C_2H_6) were observed for all the polymers, independent of olefin type. These small alkyl fragments can result from (1) radiolysis of the olefin monomer produced by the radiation and (2) fragmentation of the free radical and cationic intermediates.

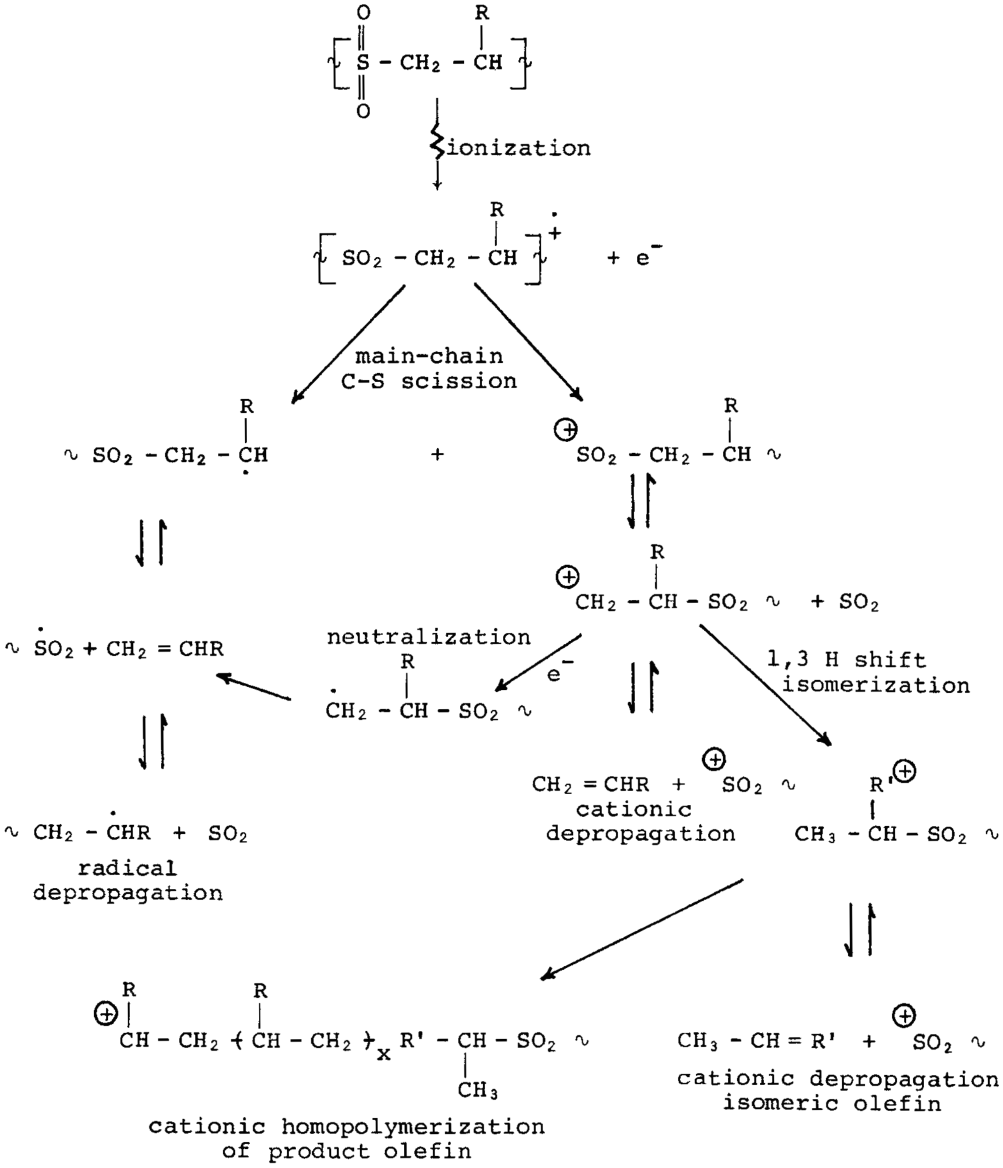


FIG. 1. Overall reaction scheme for radiation degradation of poly(olefin sulfone)s.

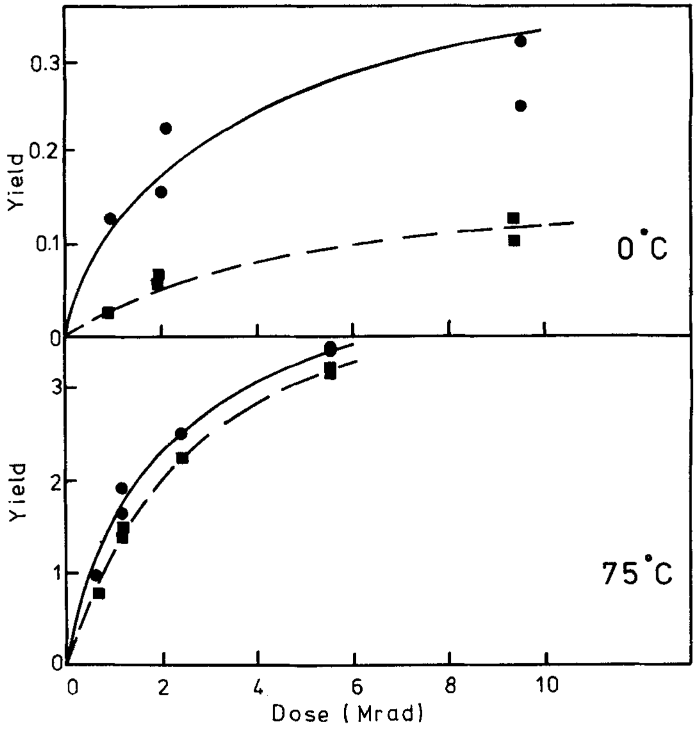


FIG. 2. Dose dependence of the yields (μmol/mg) of the main volatile products, olefin and SO_2, at 0 and 75°C from P2BS. (●) SO_2, (■) olefin.

The dose dependence of the major product yields from P2BS are shown in Fig. 2 as typical examples of the radiolysis of poly(olefin sulfone)s.

A decreasing rate of volatile product production with increasing radiation dose was usually observed. This may arise from (1) substantial degradation of the polymer leading to a noticeable weight loss, (2) the occurrence of secondary reactions between the volatile products and the polymer, and (3) the influence of the monomer-polymer equilibrium at high monomer vapor pressures.

The degradation of the polymer results in a reduction in the mass of the solid polymer, therefore making the measured yield in μmol of product/mg of initial polymer too small. A correction for the resulting curvature of the dose dependence plot can be made for this effect.

Although the loss in mass accounts for a proportion of the curvature,

TABLE 2. G Values of Volatile Radiolysis Products from Poly(ethylene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	2.4-3.0	10.7	9.8	57
Ethylene	0.3-0.4	2.1	3.3	56
$\left(\frac{\text{Ethylene}}{SO_2}\right)$	~0.1	0.2	0.29	1.0
H_2	0.13	0.22	0.19	0.84
CH_4	0.013	0.047	0.036	0.34
C_2H_6	0.004	0.02	0.04	0.2
$C_3H_6 + C_3H_8$	0.003	0.01	0.01	
Butadiene n-Butene } C_4	0.05	0.15	0.23	~4.0
C_5 hydrocarbons C_6	-	0.03	0.024	0.20
Total	3.3	13.25	14.0	115

the effects of secondary reactions and monomer/polymer equilibrium were of greater importance. Sulfur dioxide may also react with the polymer to form sulfinic or sulfonic acids. The effect of the equilibrium will become more important at high irradiation temperatures and high radiation doses. The values for the radiation chemical yields in this paper are initial G-values, i.e., slopes of the yield versus doses plots extrapolated to zero dose. Comparison with previously reported G(volatile products) [2, 3] for PBS and PHS are in agreement after taking account of the dose dependence.

Tables 2 to 10 give the G values for the individual volatile radiolysis products over the range of irradiation temperatures.

During irradiation at 150°C, volatile products were formed in significant yields from radiation-induced thermal degradation. Contributions to the yields of the small alkyl fragments of up to 60% arose from these thermal reactions at 150°C.

Poly(ethylene Sulfone). The yields of volatile products from PES are shown in Table 2. It was the most radiolytically stable of the poly(olefin sulfone)s studied. The products included (1) hydrogen from C–H scission followed by dimerization ($H\cdot + H\cdot \rightarrow H_2$) or hydrogen abstraction ($H\cdot + RH \rightarrow H_2 + R\cdot$); (2) methane,

TABLE 3. G Values of Volatile Radiolysis Products from Poly(propene Sulfone)

Product	Irradiation temperature (°C) 0	50	75	150
SO_2	13.2	60	110	3500
Propene	1.70	24.5	58	3500
$\left(\frac{\text{Propene}}{SO_2}\right)$	0.13	0.4	0.53	1.0
H_2	0.36	0.28	0.1	0.51
CH_4	0.0105	0.014	0.012	~0.25
C_2 C_2H_2	-	-	-	0.1
C_2 C_2H_4	0.004	0.0055	0.007	
C_2 C_2H_6	0.001	0.006	0.004	0.011
C_3H_8	0.1	-	0.005	-
Isobutene	0.015	0.08	0.15	1-2
C_5/C_6 hydrocarbons	0.012	0.04	0.05	0.6
Total	15.4	85	170	7003

ethane, propene, and propane, derived principally from fragmentation of the alkyl units in the main chain with subsequent addition and/or abstraction reactions; and (3) C_4 and C_6 hydrocarbons, which are oligomers of the original monomer, and are formed in small yields via dimerization and trimerization, respectively.

Poly(propene Sulfone). Propene and sulfur dioxide, the major products of radiolysis, were produced in much higher yields than from PES. There were a variety of minor products (Table 3) including hydrogen and methane from side branch fracture, isobutene *from the secondary reaction between methyl radicals and propene,* and C_6 hydrocarbons formed via dimerization of the propene monomer.

Poly(1-butene Sulfone). The major products were the original monomers, 1-butene and sulfur dioxide, but the presence of 2-butene in significant amounts (5-10%) shows that isomerization occurred during degradation (Table 4). Other products included n-butane from butyl radicals abstracting and/or reacting with hydrogen atoms, C_2 hydrocarbons and methane from the fracture and fragmentation of the alkyl side branch, C_5 and C_6 hydrocarbons from

TABLE 4. G Values of Volatile Radiolysis Products from Poly(1-butene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	13.2	70.8	475	4110
1-Butene	1.69	32.6	350	4200
2-Butene	0.3	6.0	55	500
$\left(\frac{\text{Butenes}}{SO_2}\right)$	0.15	0.55	0.85	1.1
H_2	0.4	0.485	0.53	~0.7
CH_4	0.02	0.026	0.025	0.29
C_2 C_2H_2	-	-	0.05	0.06
C_2 C_2H_4	0.0002	0.009	0.08	0.11
C_2 C_2H_6	0.01	0.005	0.008	0.035
n-Butane	0.02	1.2	14.0	300
C_5–C_6 hydrocarbons	0.002	-	0.18	2.3
C_8 hydrocarbons	0.15	0.04	0.12	0.1
Total	16.0	110	890	9115

secondary reactions between butyl products and fragmentation products, and branched C_8 hydrocarbons produced by dimerization reactions. n-Butane was produced in remarkably large quantities at high temperatures [G(n-butane) = 300 at 150°C] and requires large amounts of hydrogen. The source of this hydrogen may be (1) decomposition of sulfinic acids, $\sim\sim RSO_2H \rightarrow \sim R\cdot + SO_2 + H\cdot$, or (2) abstraction from alkyl units on the main chain,

$$\sim\sim CH_2\text{—}\dot{C}H\sim\sim + \text{n-butyl radical} \longrightarrow \sim\sim CH{=}CH\sim\sim + \text{n-butane}$$

Poly(isobutene Sulfone). This copolymer degraded rapidly and almost exclusively into isobutene and sulfur dioxide under irradiation. Minor product formation (< 0.15% of the total volatile products) occurred by the reactions postulated for the other poly(olefin sulfone)s, e.g., methane from alkyl branch fracture, isobutane from

TABLE 5. G Values of Volatile Radiolysis Products from Poly(isobutene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	80.0	485	1625	4900
Isobutene	40.2	445	1300	4400
$\left(\frac{\text{Isobutene}}{SO_2}\right)$	0.5	0.92	0.8	0.9
H_2	0.54	0.26	0.27	1.0
CH_4	0.025	0.042	0.04	
C_2 C_2H_2	-	-	0.04	
C_2H_4	0.008	0.019	0.025	
C_2H_6	0.003	0.005	0.003	
Isobutane	0.065	-	-	
Neopentane	0.10	1.2	3.2	
C_6 hydrocarbon	0.011	0.04	0.4	
Total	122.5	932	2950	9400

hydrogen atom abstraction by an isobutyl radical (derived from an alkyl unit from the main chain), and neopentane from secondary reactions between isobutyl and methyl fragments. The yields are given in Table 5. The isobutane yield was small (cf. the butane yield from PBS), suggesting that steric hindrance by the methyl groups attached to the central carbon atom hinder abstraction of hydrogen atoms.

Poly(1-hexene Sulfone). The original monomers, 1-hexene and sulfur dioxide, were the major products for all irradiation temperatures (Table 6). However, in contrast to the other copolymers the G(olefin)/G(SO_2) ratio was ≈ 1.0 for all irradiation temperatures. The minor products included those from alkyl branch fracture and fragmentation (C_1 to C_4 hydrocarbons), a C_5 hydrocarbon and hydrogen.

Poly(4,4-dimethyl-1-pentene Sulfone). The major products were SO_2 and 4,4-dimethyl-1-pentene, the parent monomers, with fracture and fragmentation reactions producing small amounts (0.5% of total yield) of methane, C_2 hydrocarbons, isobutene and neopentane (Table 7). In PDMPS and PHS the minor product distribution can be correlated with the alkyl branch degradation. The neopentyl branch, $(CH_3\!-)_3C{-}CH_2{-}$, of PDMPS yields neopentane from

TABLE 6. G Values of Volatile Radiolysis Products from Poly(1-hexene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	21.1	450	1610	4500
1-Hexene	23.1	490	1225	3775
$\left(\frac{\text{1-Hexene}}{SO_2}\right)$	1.1	1.1	0.8	0.85
H_2	0.94	0.92	0.80	1.5
CH_4	0.025	0.034	0.032	0.098
C_2H_2		0.008	0.05	0.3
C_2 C_2H_4	0.01	0.10	0.30	
C_2H_6	0.025	0.019	0.016	0.03
C_3H_6 + C_3H_8	0.002	0.05		
n-Butene	0.03	3.3	2.5	20
n-Butane	0.03	0.75	0.6	
C_5 hydrocarbon	0.01	0.02		1.0
Total	46	950	2840	8300

fracture, and methane and isobutene from fragmentation, while PHS provided butane, ethane, and methane in approximately the expected quantities from the fragmentation of an n-alkyl branch (the expectations arise from studies of α-olefin-ethylene copolymers [13]).

Poly(3-methyl-1-butene Sulfone). Isomerization occurred during radiolytic degradation. The major products were sulfur dioxide and the three isomers: 3-methyl-1-butene, 2-methyl-2-butene and 2-methyl-1-butene (Table 8). The dose dependence of the yields was generally linear up to 5 Mrd with a small curvature at higher doses. All the isomers showed the same dose dependence, implying that the isomers were primary radiolysis products, and not derived from secondary irradiation of the 3-methyl-1-butene product. Isomerization increased with increasing irradiation temperature. Using free radical and cation scavengers we have shown that the isomerization proceeds primarily via a cationic intermediate and have proposed the mechanism shown in Fig. 1 [14]. This general mechanism is also applicable to PBS in which isomerization produces 2-butene.

TABLE 7. G Values of Volatile Radiolysis Products from Poly(4,4-dimethyl-1-pentene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	115	645	1,200	6,500
4,4-Dimethyl-1-pentene	53	375	860	5,950
$\left(\frac{\text{4,4-Dimethyl-1-pentene}}{SO_2}\right)$	0.5	0.6	0.7	0.9
H_2	0.52	0.60	0.57	~1.0
CH_4	0.30	0.36	0.32	0.05
C_2 C_2H_2	-	0.009	0.028	
C_2H_4	0.0007	0.01	0.04	
C_2H_6	0.008	0.018	0.01	
$C_3H_6 + C_3H_8$	0.003	-		
Isobutene	0.11	0.9	5	20
Neopentane or (4-methyl-1-pentene)	0.1	0.1	0.7	
Total	170	1,025	2,060	12,400

Hydrogen, methane, and C_2 hydrocarbons were observed from fragmentation reactions, but yields of C_3 hydrocarbons were small, although the propyl unit would be expected from alkyl branch fracture from the main-chain.

The two polymers (PBS and P3MBS) which showed substantial isomerization in olefin production during radiolysis gave abnormally low yields of products from branch elimination. Thus there was no significant propane yield from PMBS which contains isopropyl branches, and the ethane yield from PBS was smaller than the methane yield. This may be a result of the competition between isomerization and fragmentation of the intermediates favoring isomerization.

Poly(2-butene Sulfone). Sulfur dioxide and 2-butene were the main radiolytic products with small yields of products from fracture reactions (methane, hydrogen) and secondary reactions (butane, C_2 hydrocarbons, C_8 hydrocarbons) making up 1% of the total yield (Table 9). There was isomerization during the degradation which

TABLE 8. G Values of Volatile Radiolysis Products from Poly(3-methyl-1-butene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	31	175	550	2200-2500
3-Methyl-1-butene	3.6	22.0	68.4	80-100
2-Methyl-2-butene	2.3	15.7	58.4	410-500
2-Methyl-1-butene	0.25	1.2	4.6	50
$\left(\frac{\Sigma \text{ methyl-butenes}}{SO_2}\right)$	0.2	0.22	0.24	0.30
H_2	0.63	0.53	0.2	~0.5
CH_4	0.049	0.050	0.047	0.28
C_2 C_2H_2	-	0.0036	0.012	0.083
C_2 C_2H_4	0.0005	0.0054	0.018	
C_2 C_2H_6	0.0011	0.0024	0.003	0.04
C_3H_6 + C_3H_8	-	-	-	0.7
C_4 isobutene	0.11	0.13	0.7	~10.0
C_4 isobutane	-	0.02	0.05	~0.2
Neopentane	0	0.1	0.2	2.0-4.0
C_7, C_8 hydrocarbons	0.01	0.08	0.025	5.0
Total	44	215	685	3000

produced 1-butene, but the yields were small and disappeared at high irradiation temperatures in contrast to the isomerization observed in PBS.

The secondary reactions involve mainly the olefinic product (2-butene) dimerizing or reacting with alkyl fragments. Similar to PBS radiolysis results, the butane yield requires a hydrogen source—a sulfinic acid decomposing or double bond formation in the main-chain.

The methyl-branched polymers (PPS, PIBS, and P2BS) showed lower than expected methane yields, while yields of the secondary products G(original olefin + methane) were larger than expected. For example, PPS gave $G(CH_4) \simeq 0.01$ and G(isobutene) = 0.05-0.2 depending on the irradiation temperature, suggesting that the branch fracture products were reacting with the olefin monomer.

TABLE 9. G Values of Volatile Radiolysis Products from Poly(2-butene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	80.6	900	1,800	8,125
2-Butene	40.4	862	1,610	8,300
$\left(\frac{\text{2-Butene}}{SO_2}\right)$	0.5	0.96	0.90	1.0
H_2	0.41	0.40	0.55	~1.0
CH_4	0.02	0.029	0.032	0.11
C_2 C_2H_2	-	0.08	0.12	0.2
C_2 C_2H_4	0.001	0.035	0.09	
C_2 C_2H_6	0.0015	0.0022	0.002	0.012
1-Butene	0.06			
n-Butane	0.79	33	150	100 (± 50)
C_7–C_8 hydrocarbons			0.2	3.0
Total	122.5	1,775	3,700	16,500

Poly(cyclohexene Sulfone). Cyclohexene and sulfur dioxide constituted 99.5% of the radiolysis products with 0.5% derived from fragmentation reactions (Table 10). There were small yields of hydrogen, methane, and C_2 hydrocarbons.

The cyclic olefin unit in PCHS requires cleavage of at least two bonds to give a volatile product. Ethylene and ethane appear in the radiolysis of a variety of hydrocarbons [15, 16].

The C_4 hydrocarbon is either cyclobutane, butene, or butadiene and would be formed by scission of the two branch points simultaneously or successively:

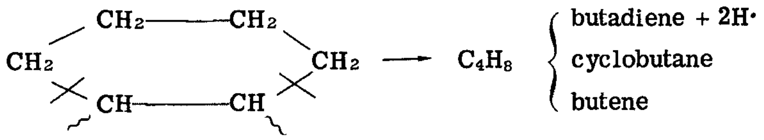


TABLE 10. G Values of Volatile Radiolysis Products from Poly(cyclohexene Sulfone)

	Irradiation temperature (°C)			
Product	0	50	75	150
SO_2	210	1,400	2,000	9,000
Cyclohexene	36.5	950	1,400	7,400
$\left(\frac{\text{Cyclohexene}}{SO_2}\right)$	0.17	0.68	0.70	0.82
H_2	0.06	0.60	0.63	~1.0
CH_4	0.085	0.009	0.02	0.2
C_2 C_2H_2	-	-	0.08	0.3
C_2 C_2H_4	0.003	0.18	0.18	
C_2 C_2H_6	0.016	0.0012	0.064	0.02
C_4 hydrocarbon	0.19	1.1	0.6	10
n-Butane n-Butene		0.12		
C_5 hydrocarbon	0.1		0.25	0.8
RSO_2	~0.2	~6.0	~5.0	~12.0
Total	250	2,350	3,410	16,410

If the two scissions occurred simultaneously, the four carbon atoms could be in a favorable orientation to produce cyclobutane.

The unidentified product lay between cyclohexene and butane in retention time on the Porapak Q column. The ratio of FID response to TCD response on the gas chromatograph showed that the product was not a pure hydrocarbon. It is likely to be (1) a sulfinic or sulfonic acid of RSO_2H or RSO_3H structure, known to be formed during radiolysis of olefin/sulfur dioxide mixtures [18, 19], or (2) an adduct of sulfur dioxide with butadiene.

Ceiling Temperature

The main reaction in the radiation degradation of all the poly(olefin sulfone)s is the depropagation shown:

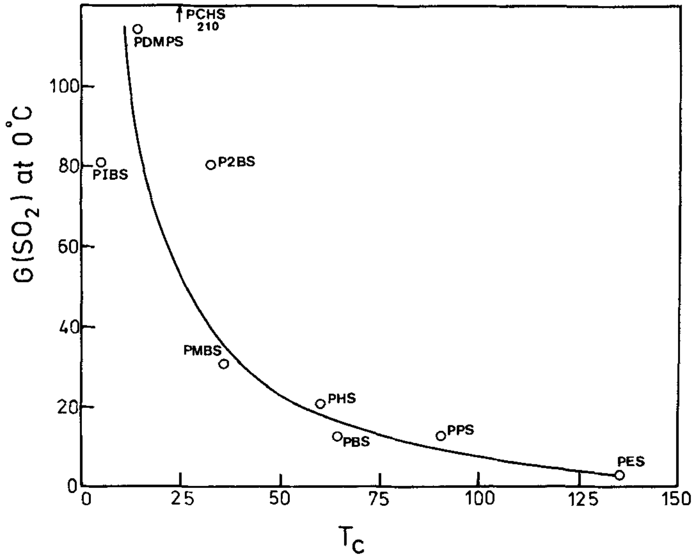


FIG. 3. Variation of G(SO$_2$) at 0° C with ceiling temperature T_c for the nine poly(olefin sulfone)s.

$$-(MS)_n- \rightleftharpoons -(MS)_{n-x}- + xM + xS \qquad (2)$$

The thermodynamic potential for monomer production should increase with temperature in accord with the equilibrium constant for Eq. (2). Dainton and Ivin [29] have shown that the ceiling temperatures, T_c, for the liquid-phase copolymerizations are mainly in the range 0-100°C. Above the respective T_c's the polymers are thermodynamically unstable with respect to the appropriate monomer concentrations. The ceiling temperatures for the solid polymer ⇌ gaseous monomer equilibria will vary with the monomer vapor pressure and have a maximum at the saturation vapor pressure for the monomer liquid ⇌ vapor equilibrium.

The applicability of these concepts has been indicated quantitatively in the electron beam copolymerization of 1-butene and SO$_2$ in the gas phase [19]. In a consideration of depropagation, liquid-phase T_c values should provide a reasonable basis for comparison [30].

G(SO$_2$) values are probably the best criteria of the extent of depropagation, since part of the olefin yield is consumed in secondary, cationic homopolymerization. They will depend on (1) the number of primary, main-chain C–S scissions which are stabilized; and (2) the average kinetic chain length for depropagation. Figure 3 shows that

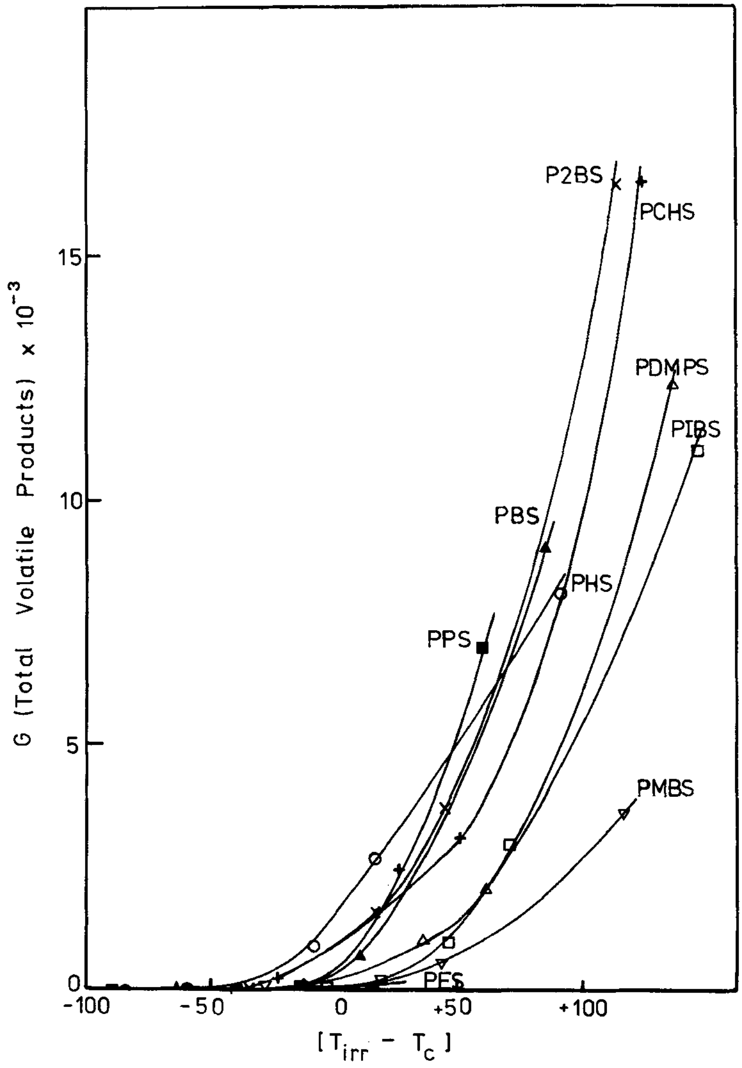


FIG. 4. Temperature dependence of the total yield of volatile products. T_{irr} = irradiation temperature. (●) PES, (■) PPS, (▲) PBS, (□) PIBS, (○) PHS, (△) PDMPS, (▽) PMBS, (×) P2BS, (+) PCHS.

$G(SO_2)$ increases with decreasing T_c. Although kinetic factors must be involved in the depropagation, and they should also lead to an increase in G(monomer) with increasing temperature, they would not give the observed correlation with T_c.

The variation in total volatile product yields with irradiation temperature is shown in Fig. 4 for the nine poly(olefin sulfone)s. The G values increase very rapidly with increasing temperature for all the polymers. The normalized temperature scale in Fig. 4 compresses the degradation rates into a similar profile, although a single, master curve is not achieved. The differences may be due to (1) inappropriate T_c values; (2) configurational, conformational, and steric interactions beyond those reflected in T_c; (3) local solid-state morphology; and (4) reactions competing with depropagation. Competing reactions include (1) SO_2 expulsion [21-25] in which C–S scission and formation of a new C–C bond occur concurrently and (2) sulfinic acid formation [18, 19, 26, 27].

It is notable that the Type III poly(olefin sulfone)s, and particularly PCHS, show excessive depolymerization. Evidently the higher steric strain favors depropagation.

CONCLUSIONS

Poly(olefin sulfone)s of Types I, II and III all degrade similarly during γ-irradiation, the principal reaction being C–S scission and depropagation. There is a deficiency of olefin compared with SO_2 and in some cases isomerization of the product olefin which can be attributed to homopolymerization and hydride shift reactions, respectively, of polymer cations. Generally, the rate of depolymerization, which increases rapidly with increasing temperature, can be correlated with the ceiling temperature for propagation/depropagation equilibrium. However, polymers of Type III show enhanced degradation; this may be associated with steric rigidity in the chain. The yields of side-branch products are relatively low, indicating that main-chain C–S scission does not occur as a secondary reaction following side-chain elimination.

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