Thermal and Photo-oxidation of Polysulfone

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Synopsis

Prolonged heating at temperatures below 140°C. causes only slight changes in the properties of polysulfone. Exposure to ultraviolet light, however, results in substantial changes as evidenced by broad absorption in both the hydroxyl and carbonyl regions of the infrared spectrum, evolution of carbon monoxide and dioxide, decrease in polymer elongation and intrinsic viscosity, and pronounced yellowing. A free-radical mechanism is proposed in which chain scission occurs with the formation of low molecular weight, oxidized fragments as the predominant oxidation products.

INTRODUCTION

Several reports[1-4] on the thermal stability of polysulfones have shown that these materials are relatively stable at high temperatures. This paper reports the results of prolonged exposure at temperatures below 140°C. as well as the photo-oxidation of the polymer.

EXPERIMENTAL

The material studied is a commercial polysulfone produced from 2,2-bis-(4-hydroxyphenyl)propane and 4,4'-dichlorodiphenyl sulfone.[4] Antioxidants were not detected in methanol or water extracts of the polymer. An inorganic salt, presumably sodium chloride, was found in the water extract. Sodium, magnesium, and lithium were detected by atomic absorption spectroscopy and chlorine by x-ray fluorescence. The polymer had an amorphous x-ray diffraction pattern and an intrinsic viscosity of 0.56 dl./g. in chloroform at 25°C.

Samples were either heated in the dark at 110, 125, or 140°C., or exposed to ultraviolet light from an RS sunlamp. For heat aging, tensile property measurements were made on ASTM D 1822, Type L tensile-impact specimens by using a table model Instron. Ultraviolet light exposure studies were done on 1-mil chloroform-cast films for infrared analysis, 6-mil chloroform-cast films for gel content and 10-mil compression-molded films for tensile properties. Thermal oxidation was conducted at 140°C. as previously described.[5] Infrared spectra were taken on a Beckman IR8 spectrometer. Elemental analyses were conducted by the Midwest Microanalytical Laboratory; yellowing measurements were made according to ASTM D 1925.

Samples for gas analyses were sealed in breakseal quartz tubes under a vacuum of 1 μ or in oxygen-enriched air (approximately 50% oxygen) at atmospheric pressure. After 500 hr. irradiation with an RS sunlamp, the gaseous products were analyzed by mass spectrometry (Gollob Analytical Service, Inc.). Droplets were observed on the surface of polymer photolyzed in oxygen. This photo-oxidized polymer was washed with cold distilled water. The addition of 0.5 cc. of 5% w/v barium chloride solution to the aqueous washings gave a white precipitate which persisted after the addition of 0.5 cc. concentrated hydrochloric acid. The same treatment on the sample photolyzed in vacuum gave no precipitate. The infrared spectrum of the photo-oxidized sample after washing and drying showed appreciable absorption in the hydroxyl and carbonyl regions; that of the vacuum photolyzed sample showed slight changes in the hydroxyl region.

The material remaining in aged samples after chloroform extraction was originally considered gelled or crosslinked polymer. However, the elemental analysis of this fraction led us to suspect that this "gel" was actually a highly oxidized fragment, perhaps a disulfonic acid. The solubility of this material in dimethyl sulfoxide, dilute aqueous alkali, and hot water confirmed our suspicion. In this paper we will refer to this material as the polar extract.

RESULTS AND DISCUSSION

Thermal Oxidation

Although they do not preclude some form of oxidation not revealed by the measurements made, the experimental observations indicate that polysulfone is essentially inert to both air and oxygen up to 140°C. Less than 3 cc. of oxygen per gram of polymer was absorbed in 9000 hr. at 140°C. After 5000 hr. in air at 125°C., no gel or polar extract was found in the polymer and after an additional 3000 hr., the infrared spectrum of the aged sample was unchanged from that of the original polymer. The weight loss of polymer in air at 125°C. for 7000 hr. was less than 0.2%. Aging at 110°C. does not affect the tensile properties to any appreciable extent. After 6 months at 110°C. in air the tensile break strength changes by less than 10% and the elongation by less than 5%. When these data are compared with those of previous studies,[6,7] polysulfone ranks as one of the most stable thermoplastics under thermal oxidative conditions.

Photo-oxidation

Unstabilized polysulfone would be expected to degrade under suitable irradiation, because it absorbs light in the region of 3200 A. It is not surprising, then, that exposure of this polysulfone to ultraviolet light causes chemical changes as evidenced by broad absorptions in both the hydroxyl and carbonyl regions of the infrared spectrum (Fig. 1), indicative of a variety of oxidation products. A simultaneous decrease in the methyl absorption band at 1385 cm.$^{-1}$ (Fig. 2) denotes that the methyl groups are

attacked during photo-oxidation. Electron spin resonance spectroscopy of a film irradiated in oxygen gave a signal with a g value of 2.003_4. On irradiation in vacuum a g value of 2.004_1 was observed. These results are not significantly different and both suggest the presence of an oxygen radical. This merely means that oxygen radicals are stable in this system.
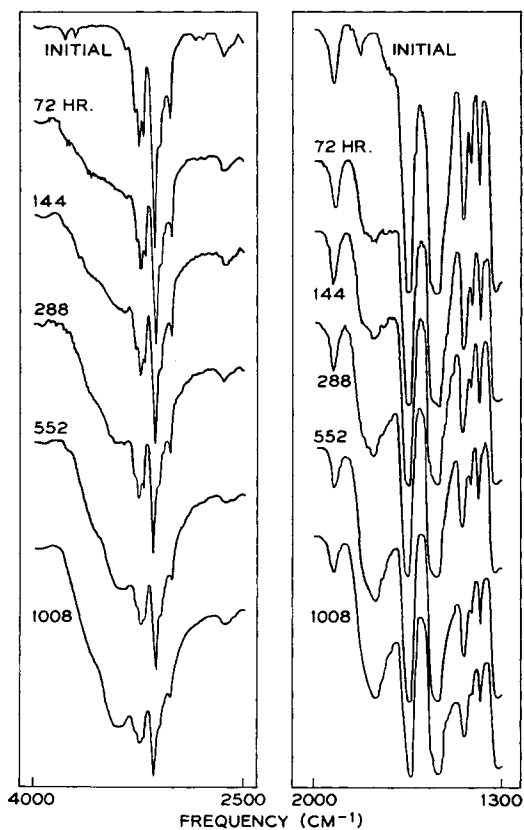

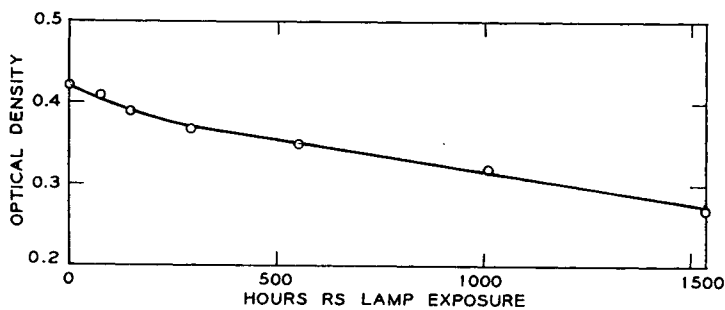Fig. 1. Changes in the infrared absorption spectrum of polysulfone exposed to RS sunlamp.

Fig. 2. Effect of photo-oxidation of polysulfone on 1385 cm.$^{-1}$ infrared band.

TABLE I
Gases Found After Ultraviolet Irradiation of Polysulfone[a]

| Constituents	Composition, vol.-%	
	Photolyzed in vacuum	Photolyzed in oxygen-enriched air
Hydrogen	22.9	0.03
Water	Not detected	Not detected
Methane	1.9	0.14
Ethane	Trace	Not detected
Benzene	0.1	Trace
Carbon monoxide	41.9	9.6
Carbon dioxide	25.9	32.2
Nitrogen	2.0	57.4
Oxygen	2.3	0.02
Carbonyl sulfide	2.6	0.01
Sulfur dioxide	0.5	0.001
Carbon disulfide	Not detected	Trace
PV, mm.-cc.	40	10,000

[a] Exposure time of 500 hr.

It does not exclude sulfur or carbon radicals as participators in the degradative scheme.
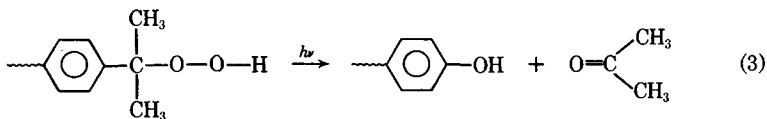
The products of photolysis in vacuum (Table I) indicate that random scission occurs. In the initiation process, scission apparently takes place at every bond except the aromatic C—C and C—H bonds [eq. (1)].

$$(1)$$
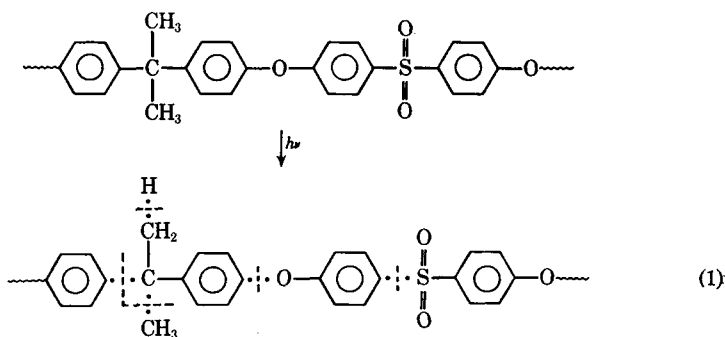
If isopropylidene radicals formed in this polymer decomposed by normal pathways, scission at the aromatic–isopropylidene single bond would appear to be quite infrequent. The isopropylidene radical should undergo both disproportionation and oxidation reactions. One product of the disproportionation reaction would contain a methylene endgroup [eq. (2)].

$$(2)$$
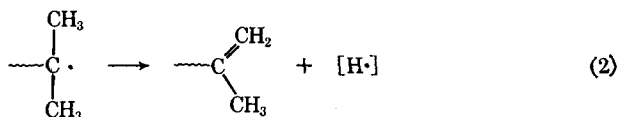
Oxidation would lead to cumene hydroperoxide endgroups, which typically undergo decomposition to acetone and phenols, as shown in eq. (3).

$$
\text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\text{---}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\text{---}C\text{---}}}\!\!\text{---O---O---H} \xrightarrow{h\nu} \text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\text{---OH} \;+\; O\!\!=\!\!C\!\!\underset{CH_3}{\overset{CH_3}{<}} \tag{3}
$$

Acetone was not detected in the evolved gases, and methylene bonds were not observed in the infrared spectrum of aged polymer. We cannot discount, however, the possibility that both of these materials may have reacted with the oxy sulfur acids and esters formed by other processes [eqs. (14)–(17)].
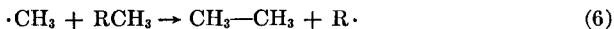
Hydrogen most likely arises after C—H bond scission by quenching through aliphatic groups [eq. (4)].
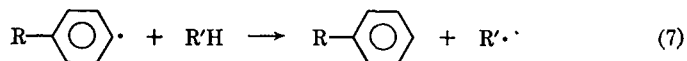
$$
H\cdot \;+\; RH \rightarrow H_2 \;+\; R\cdot \tag{4}
$$

Methane can be formed after C—CH_3 bond scission by hydrogen abstraction [eq. (5)].

$$
\cdot CH_3 \;+\; RH \rightarrow CH_4 \;+\; R\cdot \tag{5}
$$
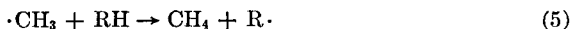
Traces of ethane can be explained by methyl abstraction, as shown in eq. (6).

$$
\cdot CH_3 \;+\; RCH_3 \rightarrow CH_3\text{---}CH_3 \;+\; R\cdot \tag{6}
$$

The formation of benzene requires bond scission at both sides of an aromatic ring. The process probably involves a hydrogen abstraction leading to a phenyl endgroup [eq. (7)].

$$
R\text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\cdot \;+\; R'H \longrightarrow R\text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle \;+\; R'\cdot\cdot \tag{7}
$$

Photolytic scission at the terminal phenyl–polymer C—C bond and quenching of the radical would give rise to benzene [eqs. (8) and (9)]

$$
R\text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle \xrightarrow{h\nu} R\cdot \;+\; \left\langle\!\!\bigcirc\!\!\right\rangle\!\!\cdot \tag{8}
$$

$$
\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\cdot \;+\; R'H \longrightarrow \left\langle\!\!\bigcirc\!\!\right\rangle \;+\; R'\cdot \tag{9}
$$
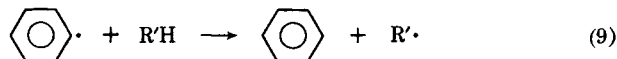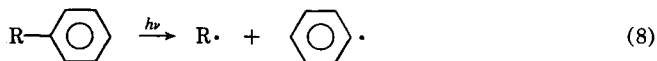
For any appreciable amount of benzene to be formed the secondary bond-breaking reaction must be at least as favorable as the initial scission processes.

Sulfur dioxide undoubtedly arises after scission at the carbon sulfur linkage by expulsion of SO_2, as shown in eq. (10).

$$
\text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\text{---}SO_2\cdot \xrightarrow{h\nu} \text{---}\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\cdot \;+\; SO_2 \tag{10}
$$

Carbonyl sulfide and carbon disulfide can be formed by the interaction of carbon monoxide and sulfur dioxide[8] [eqs. (11), (12)].

$$CO + SO_2 \rightarrow COS + O_2 \tag{11}$$
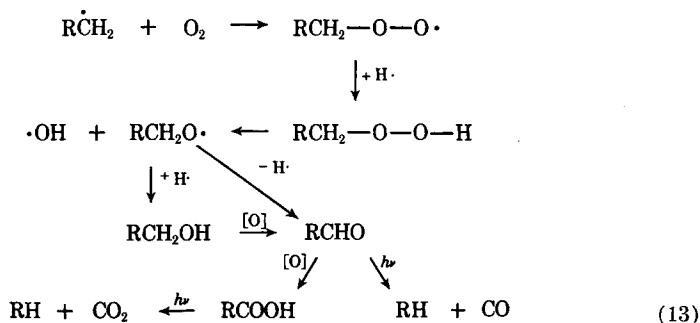
$$6CO + 2SO_2 \rightarrow CS_2 + 5CO_2 \tag{12}$$
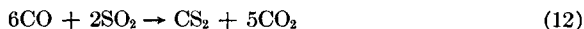
Small quantities of oxygen can be explained by the reactions of CO with SO_2. In the vacuum photolysis, the amount of oxygen necessary to account reasonably for the oxides of carbon must evolve from polymer. The expulsion of molecular oxygen from polymer under these photolytic conditions would have to proceed by unreasonable mechanisms. The facts that sulfate is not detected on the surface of the vacuum photolyzed polymer and that SO_2, a notorious hydroperoxide scavenger,[9] is present in the evolved gases in greater amount than in the case of photo-oxidation indicate that the precursors to the oxides of carbon—aldehydes and carboxylic acids—were initially present in the polymer and did not arise because of oxidation during photolysis [see eq. (13)].

No estimate of the extent of C—O or isopropylidene C—C bond breaking can be made, but from the gases isolated the order of other bond breakage can be approximated. C—H bond cleavage statistically corrected is of the same order of magnitude as C—S and C—CH₃ bond scission. It seems reasonable to assume that C—O and isopropylidene C—C bond breaking would also be of this order of magnitude. As would be expected, secondary breakage leading to benzene is the lowest in the order of scission.

The important difference between vacuum photolysis and photo-oxidation is the overwhelming oxygen quenching reaction. During photo-oxidation the oxygen initially present is almost completely consumed. The principal gases formed are carbon monoxide and dioxide.

As with benzene, secondary reactions must be responsible for the oxides of carbon. In the presence of excess oxygen, these secondary reactions are predominant. The presence of carbon monoxide and dioxide is due, then, to the oxidation of the methyl groups in the polymer leading first to aldehydes and carboxylic acids and then by decarboxylation and decarbonylation to carbon dioxide and monoxide [eq. (13)].

$$
\begin{array}{l}
R\dot{C}H_2 \; + \; O_2 \;\; \longrightarrow \;\; RCH_2{-}O{-}O\cdot \\[4pt]
\qquad\qquad\qquad\qquad\qquad \downarrow {\scriptstyle +\,H\cdot} \\[4pt]
\cdot OH \; + \; RCH_2O\cdot \;\; \longleftarrow \;\; RCH_2{-}O{-}O{-}H \\[4pt]
\qquad \downarrow {\scriptstyle +\,H\cdot} \quad\; {\scriptstyle -\,H\cdot} \\[4pt]
\qquad RCH_2OH \;\; \xrightarrow{\;[O]\;} \;\; RCHO \\[4pt]
\qquad\qquad\qquad {\scriptstyle [O]}\!\!\nearrow \quad\; \searrow {\scriptstyle h\nu} \\[4pt]
RH \; + \; CO_2 \;\; \xleftarrow{\;h\nu\;} \;\; RCOOH \qquad\quad RH \; + \; CO
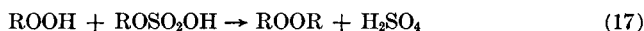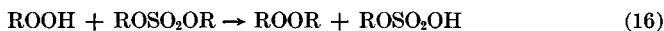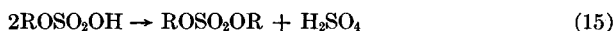\end{array}
\tag{13}
$$

With the exception of methane, there is surprisingly little difference between the absolute amount of the remaining gases from photo-oxidation

and from vacuum photolysis. Carbon disulfide, benzene, and oxygen are approximately a factor of two greater in the photo-oxidation experiment; hydrogen and sulfur dioxide are approximately a factor of two lower; carbonyl sulfide is present in nearly the same amount in both experiments. The twentyfold increase in the amount of methane for the photo-oxidation is completely opposite to what one would expect. The situation is the same for benzene, but the difference is much less. The only reasonable explanation is that photo-oxidation takes place rapidly, oxygen is consumed in the early stages, and the process becomes essentially the same as vacuum photolysis except that the predominant gaseous products act as diluents. In order to explain the sharp increase in the production of methane, one must assume that photo-oxidation products are able to increase the rate of homolysis and the existing conditions favor the methane-forming reaction.

The lower amount of SO_2 in the photo-oxidation points to its role as a hydroperoxide decomposer. The fact that water was not isolated in the gaseous oxidation products does not necessarily mean that the SO_2-catalyzed decomposition of hydroperoxide proceeds by a concerted mechanism. It is true that if hydroperoxide decomposition leads to free hydroxy radicals, subsequent reactions should lead to the formation of water. However, water could be consumed by the reactive sulfur compounds [eqs. (14)–(17)] and escape detection.

Polymeric hydroperoxides would decompose in the presence of sulfur dioxide to peroxides and/or esters of sulfuric acid [eqs. (14)–(17)].

$$ROOH + SO_2 \rightarrow ROSO_2OH \qquad (14)$$

$$2ROSO_2OH \rightarrow ROSO_2OR + H_2SO_4 \qquad (15)$$

$$ROOH + ROSO_2OR \rightarrow ROOR + ROSO_2OH \qquad (16)$$

$$ROOH + ROSO_2OH \rightarrow ROOR + H_2SO_4 \qquad (17)$$

The qualitative identification of sulfate on photo-oxidized polymer surface supports this mechanism.

During the first 500 hr., light exposure causes little change in tensile break strength and modulus but reduces the ultimate elongation to 9% of its original value. Further exposure causes no additional change. The intrinsic viscosities of the sol fractions parallel this behavior, showing a reduction of 25% after 500 hr. with no subsequent change after an additional 1500 hr. Since the polar extract content formed during 2000 hr. of photo-oxidation is nearly 1%, chain scission must be the predominant degradative process. Crosslinking is not observed.

Elemental analysis (Table II) reveals, understandably, that the polymer combines with oxygen on irradiation. Fractionation shows quite surprisingly that the combined oxygen is present only in the polar extract. Furthermore, examination of the sol fractions by infrared analysis discloses that the groups in the total polymer which absorb strongly in the hydroxyl and carbonyl regions are no longer present but appear only in the polar

TABLE II
Elemental Analysis of Polysulfone Photo-oxidized by RS Sunlamp

	Analysis			
	C, %	H, %	O, %	S, %
Calculated	73.28	5.01	14.46	7.25
Total polymer, 1000 hr.	71.20	4.91	17.00	6.89
Sol fraction				
500 hr.	73.03	4.99	14.84	7.14
1000 hr.	73.19	5.15	14.68	6.98
1500 hr.	72.89	5.11	14.96	7.04
Gel fraction, 1000 hr.	46.19	4.95	38.55	10.31

extract. Since a yellow solution resulted when photo-oxidized films were extracted either with dilute aqueous alkali or hot water and the extracted films were less yellow, it seems quite reasonable that the polar extract contributes substantially to the yellowing observed in the total polymer
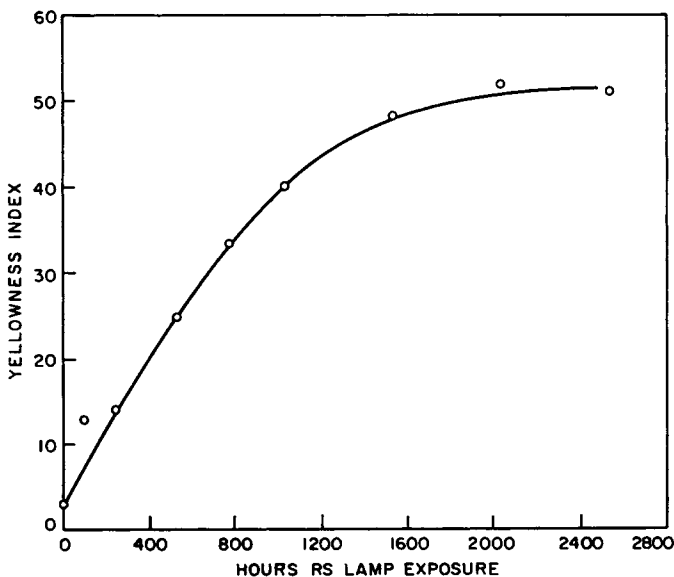

Fig. 3. Effect of RS lamp exposure on yellowing index of polysulfone.

(Fig. 3). The solubility behavior of the polar extract coupled with its infrared spectrum and relatively high oxygen and sulfur contents lead to the conclusion that the polar extract consists of low molecular weight highly oxidized sulfonic acids. Carbon and sulfur analysis indicate that the polar extract consist mainly of disulfonic acids of type I.

$$HOSO_2-\langle\bigcirc\rangle-O-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-O-\langle\bigcirc\rangle-SO_2OH$$
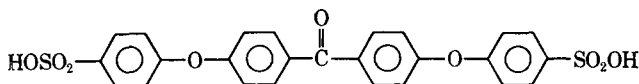
I

The formation of these oligomeric sulfonic acids is one of the most interesting reactions in the degradative scheme. The experimental evidence indicates that these compounds play a significant role in the photo-oxidative process. Two pathways are open for the formation of these acids. The sulfonyl radicals formed by C—S bond cleavage can be quenched by oxygen [eq. (18)]:

$$RSO_2\cdot + O_2 \rightarrow RSO_2OO\cdot \tag{18}$$

Attack of the peroxy radical on polymer would lead to hydroperoxide. Decomposition of this hydroperoxide would end in a sulfonic acid [eq. (19)].

$$RSO_2OOH \rightarrow \cdot OH + RSO_2O\cdot$$

$$\tag{19}$$

$$RSO_2O\cdot + R'H \rightarrow R'\cdot + RSO_2OH$$
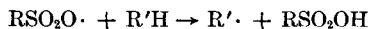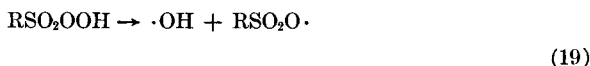
Since in this process a secondary cleavage would be necessary to give rise to disulfonic acids, the large amount of polar extract must arise by an alternate pathway, depending on the direct decomposition of hydroperoxides by polymer sulfone groups [eq. (20)].

$$R'OOH + RSO_2R \rightarrow RSO_2OH + [R'OR] \tag{20}$$
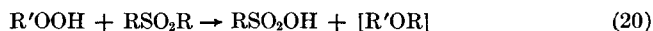
A similar reaction was reported by Denison and Condit,[10] where hydroperoxidized hydrocarbons were the substrate and their decomposition, induced by aliphatic sulfones, led to sulfonic acids. Elemental analysis of polar extract and sol (Table II) show that the bulk of oxidation is localized in the low molecular weight fragments. It seems reasonable to assume that reactions leading to these fragments or reactions of the fragments themselves are responsible for retarding the oxidative breakdown of the remaining polymer.

References

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