

Photo-oxidation of Phenoxy Resin

P. G. KELLEHER and B. D. GESNER, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974*

Synopsis

A study has been made of the photolysis and photo-oxidation of phenoxy resin. Photolysis results in the evolution of hydrogen, methane, ethane, propene, propane, toluene, and the oxides of carbon. Also observed are increased yellowing, a rapid rise in gel content, and a decrease in intrinsic viscosity and elongation. Photo-oxidation causes similar changes, but produces oxidized chain fragments, more gel, and less yellowing as well as broad absorptions in the hydroxyl and carbonyl regions of the infrared spectrum. A free-radical mechanism is proposed in which both chain scission and cross-linking occur.

INTRODUCTION

It has previously been reported that the sulfone group in polysulfone plays an important role in its photo-oxidative reactions.¹ Phenoxy resin is structurally related to polysulfone. The syntheses of both polymers are based on 2,2-bis(4-hydroxyphenyl)propane: polysulfone, by reaction with 4,4'-dichlorodiphenyl sulfone; phenoxy resin, by condensation with epichlorohydrin. Differences in the photo-oxidative behavior of these two polymers should be related to the latter portions of the molecular chain. A study of the mechanism of photo-oxidation of phenoxy resin is therefore of interest and is the subject of this report.

EXPERIMENTAL

The material studied is a commercial polymer with a molecular weight of approximately 30000.² Extraction by either boiling methanol or water produced no evidence of antioxidants. Traces of silicon, magnesium, aluminum, copper, and calcium were found by spectrographic analysis.

An RS sunlamp was used as an ultraviolet light source. Tensile property measurements were made on 0.125 in. thick injection-molded type L (ASTM D1822) tensile impact specimens by use of a table model Instron tester. One mil films, cast from chloroform solution, were used for infrared analysis and 6 mil films for gel content and gas analysis. Infrared spectra were taken on a Beckman IR-8 spectrometer, and ultraviolet spectra on a Cary model 15 spectrometer. Samples for gas analyses were sealed in quartz break-seal tubes under a vacuum of 1 μ or in a 50 vol.-% oxygen atmosphere. Mass spectrometric analyses of volatiles were done by Gollob

Analytical Service, Inc. Elemental analyses were conducted by Midwest Microanalytical Laboratory; yellowing measurements were made according to ASTM D1925.

RESULTS AND DISCUSSION

Photolysis

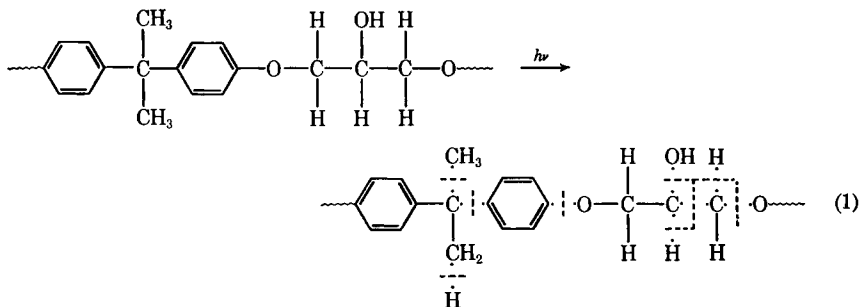
It is not surprising that unstabilized phenoxy resin, which absorbs at 3000 Å, will degrade in ultraviolet light. The intrinsic viscosity decreased 16% after 120 hr RS lamp exposure. This decrease and the gas analysis data (Table I) can be explained by postulating that random bond scission

TABLE I
Gases Found after Ultraviolet Irradiation of Phenoxy Resin

Constituents	Concentration, vol-%	
	Photolyzed 1000 hr <i>in vacuo</i>	Photolyzed 1000 hr in 50 vol-% oxygen
Hydrogen	8.7	0.35
Oxygen	0.21	13.3
Nitrogen	2.9	49
Argon	0.043	0.60
Methane	7.5	0.24
Ethane	4.2	0.14
C ₃ hydrocarbon	1.3	0.024
Acetone	—	0.31
Toluene	0.40	0.032
Organic ^a	—	0.19
Carbon monoxide	67	6.2
Carbon dioxide	7.8	30
Total amount of gas, cc (STP)	0.31	11

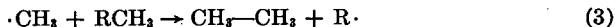
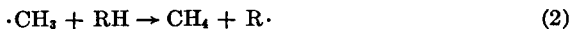
^a Oxygenated low molecular weight hydrocarbon.

[eq. (1)] occurs with the apparent exception of the aromatic carbon-carbon and carbon-hydrogen bonds:

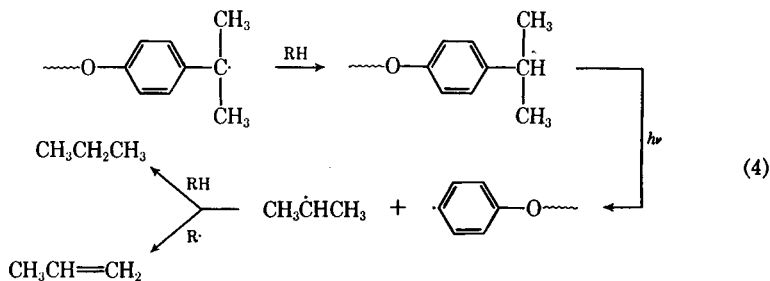


Hydrogen radicals can be formed by carbon-hydrogen bond scission either in the isopropylidene group or in the aliphatic ether portion of the

chain. Subsequent hydrogen abstraction can produce molecular hydrogen. $\text{CH}_3\text{—C}$ cleavage followed by hydrogen and methyl abstraction may generate methane and ethane, respectively [eqs. (2) and (3)].



Chain scission at the aromatic isopropylidene link can lead eventually to a mixture of what appears from mass spectral analysis to be propane and propene [eq. (4)].



Carbon-oxygen scission is supported by the electron spin resonance results which gave a signal with a g value of 2.004₂, indicating oxygen radicals.

Of the other gaseous products detected after photolysis (Table I), nitrogen, oxygen and argon are present as absorbed gases in the system. Even though carbon monoxide and carbon dioxide account for approximately 75% of the gases found, the total amount of gas is so small (0.31 cc) that we believe the oxides of carbon owe their presence to acidic and aldehydic oxidation products generated during polymer preparation or processing.

The fact that no benzene was found leads us to believe that toluene may be present as a trace contaminant from the polymerization reaction.³

The gel observed under photolytic conditions (Fig. 1) must result from

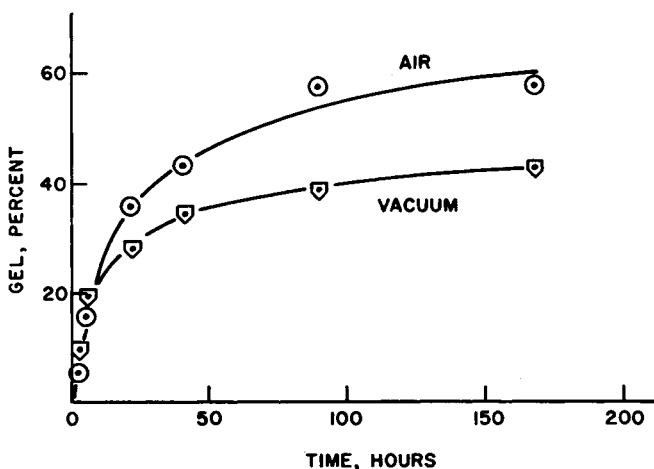
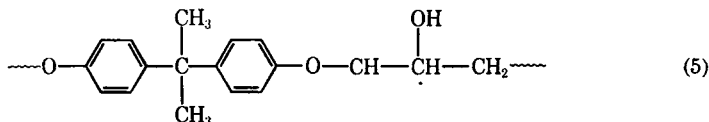


Fig. 1. Gel formation on exposure of phenoxy resin to ultraviolet light.

recombination of radicals formed in the aliphatic ether portion of the polymer chain [eq. (5)].



During the first 120 hr of exposure, we observe a decrease in intrinsic viscosity as well as gel formation, indicating that chain scission and cross-linking are occurring simultaneously.

Photo-oxidation

The gases found after irradiation in air (Table I) are generally the same as those found after photolysis in vacuum. Nitrogen, oxygen, and argon are present initially. Hydrogen, methane, ethane, and the C₃ hydrocarbon are most likely generated by random bond scission in the manner outlined in the discussion on vacuum photolysis. It is interesting that the absolute volumes of nonoxidized gaseous products are the same in both the vacuum and oxygen experiments. The fact that acetone is formed on photo-oxidation further indicates chain scission at the isopropylidene-aromatic bond [eq. (6)].

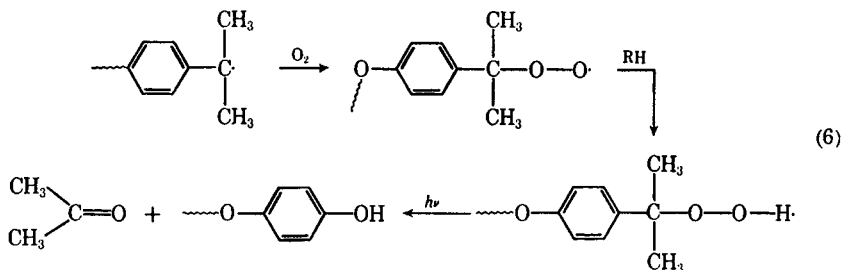
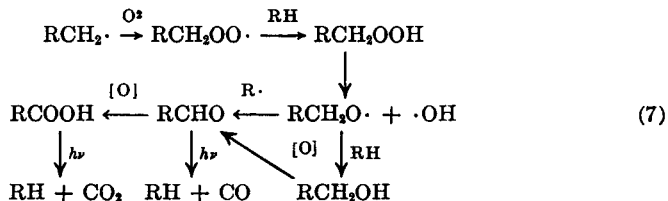


Photo-oxidation also leads to evolution of the oxides of carbon [eq. (7)].



The structure of the oxygenated low molecular weight hydrocarbon has not been unequivocally determined. Mass spectrometry showed lines at mass 60, 45, and 31. Mass 60 is presumably a parent peak and masses 45 and 31 are fragments. Normal propanol is a possibility from the mass spectral data but not from the structure of the polymer chain. At present we believe that acetic acid and glycol aldehyde (both mass 60) are the two oxygenated low molecular weight organic products. Work is in progress to

determine the exact identity of these materials. It is noteworthy that products of this type were not formed during irradiation *in vacuo*.

The results in Figure 1 indicate that more cross-linking occurs in oxygen than in vacuum. In oxygen the following recombinations are possible:



This would explain the greater crosslinking in oxygen, since some relief of steric crowding would be realized in these reactions. Elemental analyses (Table II) of samples photooxidized for 90 hr in air reveal that both sol and

TABLE II
Elemental Analysis of Phenoxy Resin

	C, %	H, %	O, %
Phenoxy resin			
Calculated	76.0	7.1	16.9
Found	75.9	7.3	17.1
Samples photo-oxidized 90 hr in air using RS Sunlamp			
Total polymer	74.9	6.9	18.3
Sol fraction	74.3	7.1	18.7
Gel fraction	75.2	6.9	17.9
Samples photolyzed 90 hr <i>in vacuo</i> using RS Sunlamp			
Total polymer	75.7	7.4	17.0
Sol fraction	75.5	7.3	17.2
Gel fraction	75.8	7.4	16.8

gel do contain more oxygen than the unoxidized polymer and the polymer exposed *in vacuo*. This confirms the role of oxygen in the crosslinking reaction during photo-oxidation. In addition, the sol in the photo-oxidized polymer contains the greater amount of oxygen. Apparently the chain scission reactions require more oxygen than those involving crosslinking. Perhaps the decreased mobility of the cross-linked chains lowers their reaction rate with oxygen. This behavior is somewhat similar to that of polysulfone¹ in which the low molecular weight fragments carry the bulk of the oxygen consumed. The fact that no gel was found in polysulfone under photo-oxidative conditions or in polycarbonate under thermo-oxidative conditions⁴ supports the assumption that the rapid crosslinking observed (Fig. 1) in the phenoxy resin involves a reaction of the aliphatic ether portion of the chain.

Bulk Effects

In the infrared spectrum, photo-oxidation produced a broadening of the hydroxyl band along with an intensification of the carbonyl band, indicative of a variety of oxygenated products. No such changes were observed on photolysis where oxygen is not involved in the reaction.

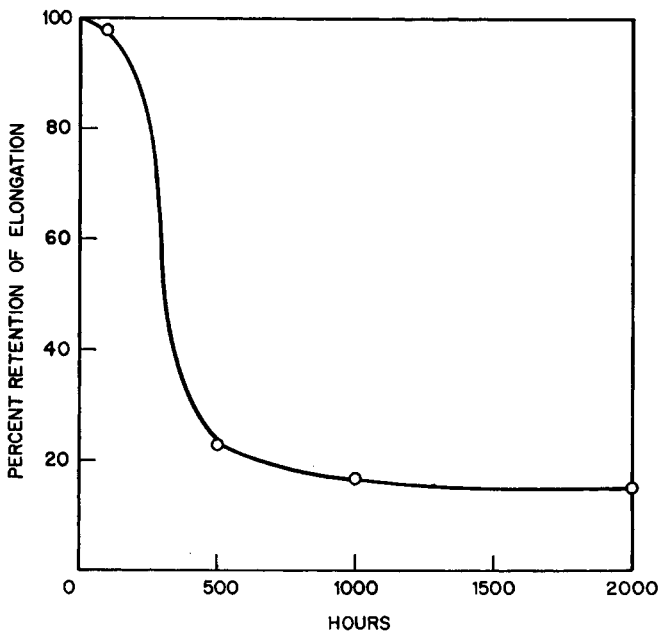


Fig. 2. Effect of RS lamp exposure on elongation of phenoxy resin.

A marked decrease in elongation occurs on exposure to ultraviolet light in air (Fig. 2). This is due to the rapid crosslinking reaction indicated by gel formation (Fig. 1). The retention of elongation is greater during photolysis (55% in 570 hr) since less crosslinking takes place. Both curves level off as oxidation progresses. This could mean that an oxidized, protective layer is formed on the surface, thus preventing further degradation. Removal of the irradiated tensile specimen surface results in a three fold increase in elongation retention, indicating that the elongation loss is indeed a surface effect.

RS lamp exposure causes a gradual shift in the ultraviolet absorption spectrum of the phenoxy resin from 3000 Å to approximately 3800 Å after 1000 hr. The yellowing of the polymer (Fig. 3) probably results from the formation of a conjugated structure in the bisphenol A units similar to that proposed by Lee for polycarbonate.⁴ The polymer yellows more *in vacuo* than in air. The radicals *in vacuo* are not quenched by oxygen and therefore can more readily give rise to conjugated structures which are highly colored.

On prolonged photo-oxidation, the yellowness index curve levels off. When the oxidized layer is removed by solvent, the color of the aged sample is the same as that of the unaged polymer. Evidently, the protective, oxidized layer functions as a barrier to oxygen diffusion because of its cross-linked nature and also as a light screen because of its intense yellow color.

It is interesting to compare the photo-oxidative behavior of phenoxy resin with that of polysulfone.¹ Irradiation of both polymers is similar in that it

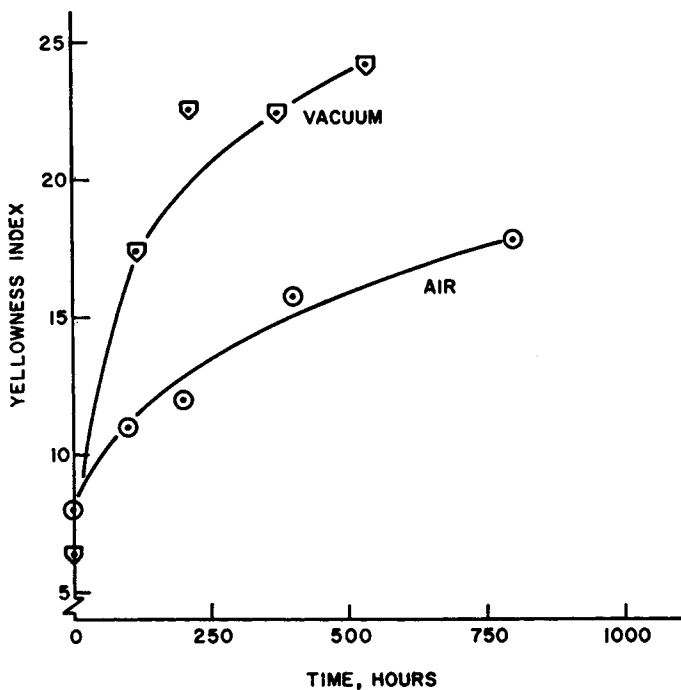


Fig. 3. Yellowing of phenoxy resin on exposure to ultraviolet light.

causes random chain scission, oxygen consumption by the low molecular weight fragments and evolution of hydrogen, methane and ethane. The photo-oxidative characteristics are also analogous in that the sulfone group gives rise to sulfur dioxide, whereas the alkyl hydroxy group generates low molecular weight oxygenated products.

Irradiation of phenoxy resin produces propane, propene, and acetone. The absence of acetone in polysulfone oxidation could be due either to quenching of the ketone precursor by sulfur dioxide or to reaction of the acetone with oxy sulfur acids. Another dissimilarity is the fact that phenoxy resin gels rapidly, indicating a crosslinking reaction involving the alkyl hydroxy portion of the polymer. The sulfur dioxide group in polysulfone is incapable of crosslinking. Hence, polysulfone does not form a gel fraction, even after extensive photo-oxidation.

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