

Thermal Oxidation and Photo-oxidation of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)

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Synopsis

The thermal oxidation and photo-oxidation of poly(2,6-dimethyl-1,4-phenylene oxide) have been examined. Oxidation of the plastic results in the evolution of carbon dioxide, nitrogen and traces of hydrogen, the introduction of considerable crosslinking, and increased absorption in the hydroxyl and carbonyl regions of the infrared spectrum. A free-radical oxidation mechanism is postulated.

INTRODUCTION

Polymerization of 2,6-dimethylphenol by oxidative coupling has been reported by Hay and others.¹ In 1964, the General Electric Company introduced this polymer under the trade name PPO. Its thermal degradation in vacuum² and nitrogen³ and in oxygen above 150°C.⁴ has been reported. The purpose of this work is to investigate the mechanism of thermal oxidation and photo-oxidation of PPO below 125°C.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide), free of antioxidants, obtained from the General Electric Company was used in this study. The structure was confirmed by nuclear magnetic resonance (lines at $\tau = 7.84$ and $\tau = 3.49$ with integration of 3:1). The base resin had an intrinsic viscosity of 0.52 dl./g. in chloroform at 25°C. Elemental analysis listed in Table I indicates that the resin as received from the manufacturer may contain some oxidation products.

Exposure Conditions

A series of 1- and 6-mil polymer films, cast from chloroform solution, was either heated in the dark at 125°C. in a forced-draft oven or exposed to ultraviolet light from either an S-1 (ASTM D620) or an RS sunlamp.

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TABLE I
Elemental Analysis of PPO Base Resin

	C, %	H, %	O, %	N, %
Calculated (unoxidized)	79.97	6.71	13.32	—
Found				
Unoxidized	79.98	6.73	13.51	0.14
Photo-oxidized 100 hr. (RS lamp)	79.41	6.79	14.16	—
Photo-oxidized 500 hr. (RS lamp)	79.15	6.73	14.30	—
Sol fraction of sample thermally oxidized 2000 hr. at 125°C.	76.01	6.15	17.84	—
Gel fraction of sample thermally oxidized 2000 hr. at 125°C.	75.96	6.09	17.95	—

Methods

The infrared absorption spectra of films 1 mil thick were obtained with a Perkin-Elmer Model 21 spectrometer. Gas-phase chromatography was carried out with an F and M Scientific Corp. Model 500 gas chromatograph with a 3 ft. type 5A Molecular Sieve-packed column, a helium flow of 30 ml./min. and temperature programmed from 50 to 250°C. at 11°C./min. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A60 spectrometer.

Gel content was obtained from the weight of dried polymer remaining after Soxhlet extraction with boiling chloroform. The change in weight was measured on powdered resin heated at 125°C. in open test tubes.

RESULTS

Thermal Oxidation

The infrared spectra of films heated at 125°C. (Fig. 1) show development of a broad absorption in the —OH region, gradual intensification of a C=O band at 1695 cm.⁻¹, probably due to carboxylic acid,⁵ and the appearance of a smaller band at 1660 cm.⁻¹.

Mass spectrometric analysis of the gaseous products evolved from the poly(phenylene oxide) sealed in oxygen and heated for 1 month at 125°C. reveals the presence of carbon dioxide, nitrogen and a trace of hydrogen.

The change in weight at 125°C. is shown in Figure 2. Volatiles are lost in the early stages of heating while, on prolonged heating, increases in weight are observed. Thermal oxidation produces appreciable amounts of gel (Fig. 3). Elemental analysis indicates that the gel and sol fractions absorb oxygen to the same degree (see Table I).

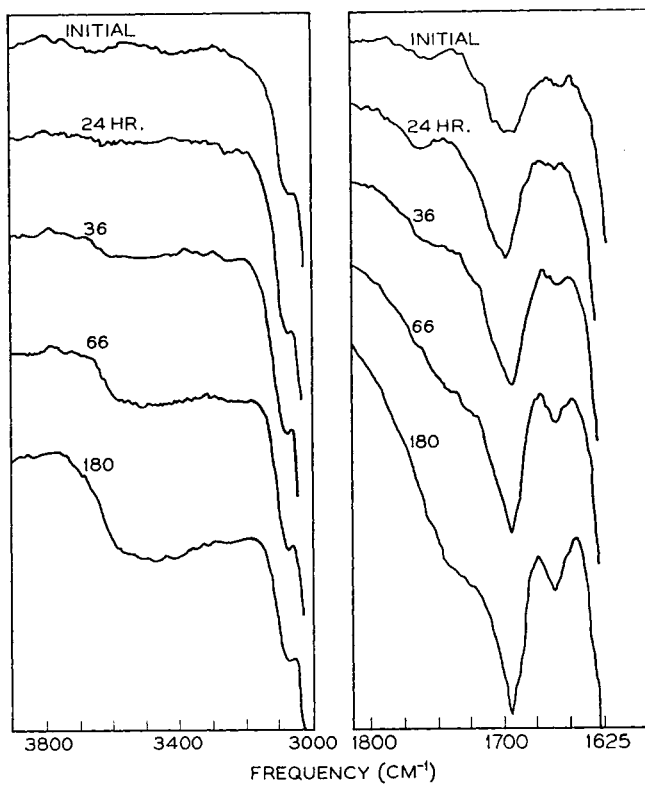


Fig. 1. Changes in the infrared absorption spectrum of poly(phenylene oxide) exposed at 125°C.

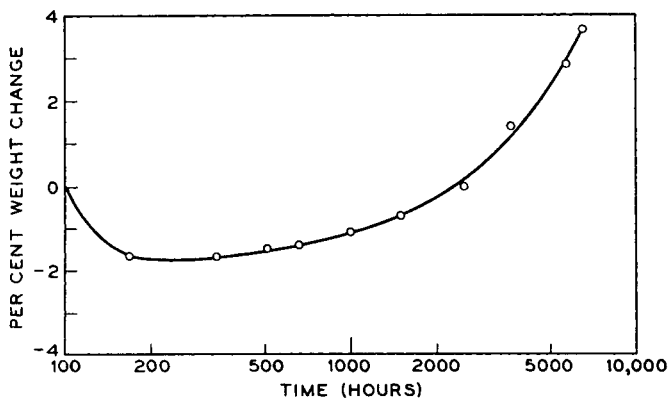


Fig. 2. Weight change in poly(phenylene oxide) in air at 125°C.

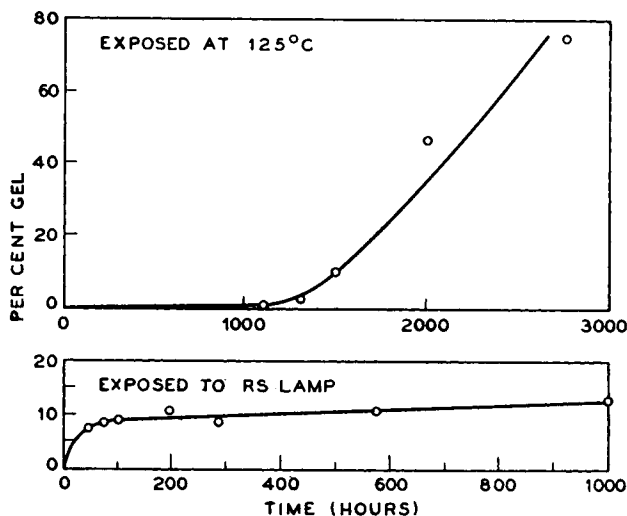


Fig. 3. Gel content of poly(phenylene oxide).

Photo-oxidation

Exposure to the S-1 sunlamp causes broad, poorly defined absorptions in both the OH and C=O regions of the infrared spectra (Fig. 4). Similar changes were also observed on a window-exposed sample. Mass spectrometric analysis of the gases evolved on RS lamp irradiation shows the development of carbon dioxide, nitrogen, and a trace of hydrogen. Gas-chromatographic data qualitatively confirm these results.

Electron spin resonance of a 6-mil film exposed to an RS sunlamp for 2 min. in air gives an absorption at $g = 2.0065$. The intensity of the line is doubled when the polymer is irradiated in vacuum.

The nuclear magnetic resonance spectrum of the chloroform extract of a photo-oxidized film shows no observable change from that of the original polymer. Infrared analysis of this soluble fraction shows the same increase in hydroxyl and carbonyl absorptions as the total polymer. The extract has an intrinsic viscosity of 0.49 dl./g. compared with a value of 0.52 dl./g. for the unexposed base polymer.

The gel content increases quite rapidly in the early stages of photo-oxidation but, as oxidation continues, follows on a less severe slope. Elemental analysis (Table I) shows a general increase of oxygen content with exposure time.

DISCUSSION

The comparison of results of thermal oxidation and photo-oxidation indicates that both processes proceed by the same general mechanism but that photo-oxidation initially has a faster rate. The infrared spectra (Figs. 1 and 4) of both the thermal and photo-oxidized polymer show a gradual increase in —OH and C=O absorption. The C=O bands of

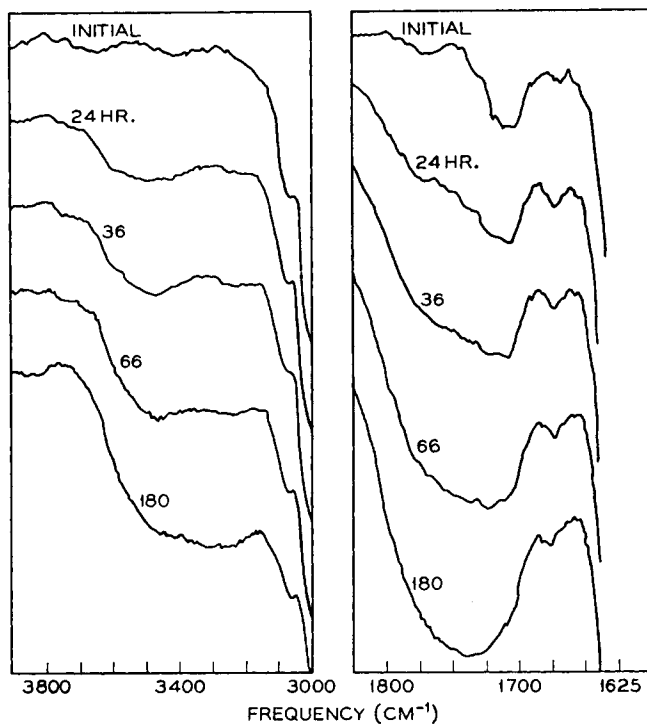


Fig. 4. Changes in the infrared absorption spectrum of poly(phenylene oxide) exposed to S-1 sunlamp.

the thermally oxidized plastic appear sharper throughout their term of exposure. This may indicate that even in the early stages, photo-oxidation gives rise to a greater variety of carbonyl-containing degradation products, which can be a consequence of a faster reaction rate or a less discriminate attack by reacting species.

The mass-spectrometric and gas-chromatographic analyses of the gases evolved in both processes show the production of carbon dioxide and nitrogen. The carbon dioxide can be generated by decarboxylation of acidic oxidation products. Nitrogen probably arises from the residual pyridine used in the preparation of the polymer.¹

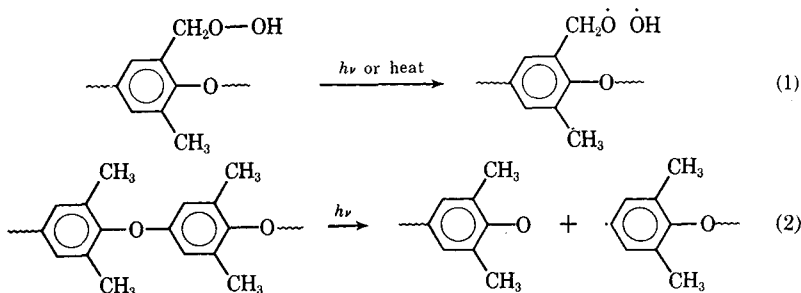
The gel content (Fig. 3) increases under both thermal and photo-oxidation conditions. Photolytically, gel increases rapidly but levels off with time; thermally, gel seems to increase by an autocatalytic process. The relatively large amounts of gel indicate that the predominant degradative mechanism is crosslinking. Furthermore, the close agreement of the viscosity-average molecular weight for the photo-oxidized sol and the unexposed base resin probably means that the change in sol structure is minimal and as a consequence should contribute little to the deterioration of physical properties in the plastic.

The elemental analysis (Table I) may suggest that the initial

material has a greater proportion of oxygen than can be explained by the monomeric unit alone. Since the polymer is prepared by oxidative coupling, it seems reasonable that the base resin might initially have finite concentrations of hydroperoxides and their acidic, aldehydic, and alcoholic degradation products. Such hydroperoxides may well be involved in the initiation reactions of the oxidative processes.

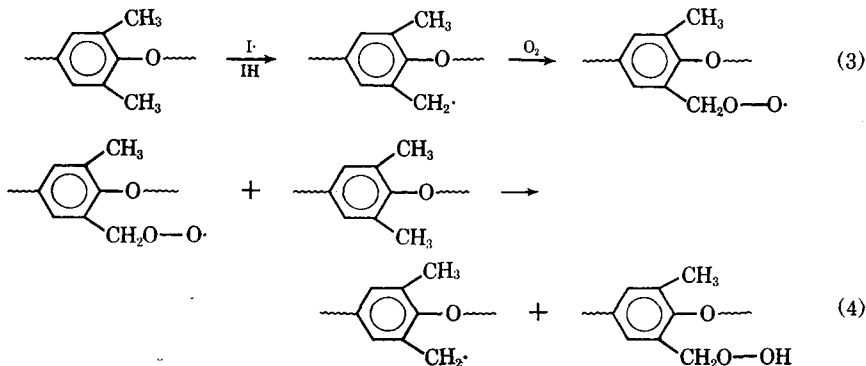
Electron spin measurements on photolyzed samples indicate that the radicals formed are closely associated with oxygen. The g value of 2.0065 obtained on the sample irradiated in air is in good agreement with that for phenoxy type radicals. Irradiation of the polymer in vacuum doubled the intensity of the line, indicating the relative instability of these radicals toward oxygen.

On the basis of the experimental results, initiation of the oxidative process can arise by thermal breakdown or photolysis of the hydroperoxides initially present or induced as shown in eqs. (1) and (2) or, in the case of photolysis, by carbon-oxygen bond scission.

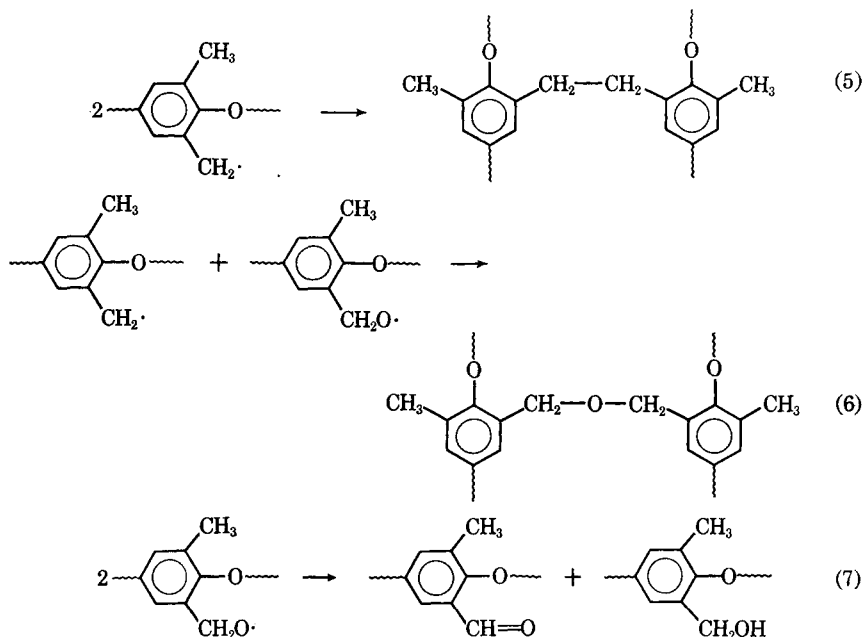


One might suspect that oxygen-induced formation of hydroperoxides, particularly in the thermal process, carried the bulk of the initiation process. However, no induction period was found in oxidations of poly(phenylene oxide), even at the lowest temperature of a previous study.⁶ This strengthens the premise that hydroperoxides are initially present in the polymer in sufficient quantity to catalyze the degradative process.

Propagation by initiator radicals can then proceed to the rest of the resin [eqs. (3) and (4)].



Both the newly formed hydroperoxide and the polymeric radicals can continue the chain process or terminate by crosslinking [eqs. (5) and (6)] or by disproportionation to inert degradation products [eq. (7)].



Further oxidation of the alcohol and aldehyde leads to acidic products which, in turn, can decarboxylate under drastic exposure conditions. The formation of these products is substantiated by the observed increases in the hydroxyl and carbonyl regions of the infrared spectra and the evolution of carbon dioxide.

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Résumé

L'oxydation thermique et photochimique de poly-2,6-oxide de diméthyl-1,4-phénylène a été examinée. L'oxydation du plastique résulte dans le dégagement d'anhydride carbonique, d'azote et de traces d'hydrogène. L'introduction d'un pontage considérable et une absorption accrue dans l'absorption infrarouge des régions hydroxylées et carbonylées. Un mécanisme d'oxydation par radicaux libres est postulé.

Zusammenfassung

Die thermische und photochemische Oxydation von Poly(2,6-dimethyl-1,4-phenylen)-oxyd wurden untersucht. Die Oxydation des Plastomeren führt zur Entwicklung von Kohlendioxyd, Stickstoff und Spuren von Wasserstoff, zum Auftreten einer beträchtlichen Vernetzung sowie zu einer erhöhten Absorption im Hydroxyl- und Carbonylbereich des Infrarotspektrums. Ein radikalischer Oxydations-mechanismus wird aufgestellt.

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