

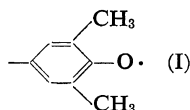
Electron Spin Resonance Study of Poly(2,6-dimethylphenylene oxide) Irradiated with Ultraviolet Light*

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ABSTRACT: The ESR spectra of poly(2,6-dimethylphenylene oxide) (PPO) were recorded before and after irradiation both in the solid state and in solution. The PPO powder sample gave an apparent eight-line spectrum with a separation of about 5.5 gauss, which is due to substituted phenoxy radical (I).



Signal intensity increased after irradiation at room temperature. Irradiation at -196°C gave an apparent singlet spectrum with some shoulders.

When a benzene solution of PPO was irradiated at room temperature in the presence of air, there was observed at an earlier stage an apparent seven-line spectrum with a coupling constant of 5.60 gauss, and after a longer time of irradiation a multi-component spectrum. Both spectra could be attributed to the free radical (I). On the other hand, irradiation in the presence of nitrogen or under vacuum gave only the multi-component spectrum.

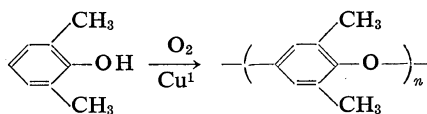
In all cases, the signal intensity was larger in the presence of air than under vacuum or in the presence of nitrogen.

ESR spectra observed at higher temperature showed line width alternation.

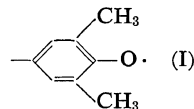
The mechanism of radical formation and the possible reactions during irradiation are discussed.

KEY WORDS Electron Spin Resonance / Poly(2,6-dimethylphenylene oxide) / Phenoxy Radicals / Ultraviolet Irradiation / Oxygen Effect / Line Width Alternation /

We are now carrying out a series of ESR studies on UV irradiated polymers, and have already reported the results on polyethylene,¹⁻⁶ polypropylene⁷⁻⁹ and poly 3,3 bis(chloromethyl) oxetane.^{10,11} In this paper we want to report the results on poly(2,6-dimethylphenylene oxide) (PPO), which is known as one of the engineering plastics. This polymer can be obtained by the oxidative coupling of 2,6-xylenol.



Synthesis of this polymer was reviewed by Hay.¹² Huysmans, *et al.*,¹³ reported that this polymer produces substituted phenoxy radicals (I) after oxidation by lead dioxide and



* This paper was read at 10th ESR Symposium, Osaka (1971) and preliminarily reported in Rept. Progr. Polym. Phys., Japan, **15**, 573 (1972).

that the same radicals were observed during the

polymerization of 2,6-dimethylphenol with lead dioxide. Kelleher, *et al.*,¹⁴ reported that photolysis of PPO in air gave an ESR spectrum with a g value of 2.0065 which is in good agreement with that for phenoxy type radicals. Very recently Symons, *et al.*,¹⁵ also reported ESR spectra of this polymer irradiated with ultraviolet light and high energy radiation. According to them, photolysis of this polymer in benzene solution produces the substituted phenoxy radical (I) and the coupling constants for the protons of the two methyl groups were unequal. This inequivalence of the coupling constants of two methyl groups was also reported by Huysmans, *et al.*,¹³ for the free radical (I) observed in the case of oxidation of the polymer. This inequivalence is caused by hindered rotation about the bridging O—C bonds, and results in the preferred asymmetric conformations. In this investigation an acceleration of radical formation was found in the presence of air, and we want to discuss the mechanism of radical formation from a detailed study of the wavelength dependence of radical formation.

EXPERIMENTAL

The purified polymer sample was dissolved in chloroform, benzene, xylene, or styrene. Photolysis in the ESR cavity was carried out at room temperature or higher with a Xe short arc lamp or a super-high pressure mercury lamp. The apparatus has already been described.^{1,3} A series of cut-off glass filters (Toshiba color glass filters) were applied for the examination of wavelength dependence of radical formation. ESR spectra were recorded with an X-band spectrometer with a 100 kc field modulation (Japan Electron Optics Lab. Co., model JES, 3BS-X) during and after irradiation. Absorption spectra were also recorded with chloroform solution using a Perkin Elmer 450 Spectrophotometer. The simulation of the ESR spectrum was carried out by using a spectrum accumulator (Japan Electron Optics Lab. Co., Ltd. model JRA-1).

RESULTS

Absorption Spectrum of Poly(2,6-dimethylphenylene oxide)

When PPO was dissolved in chloroform or

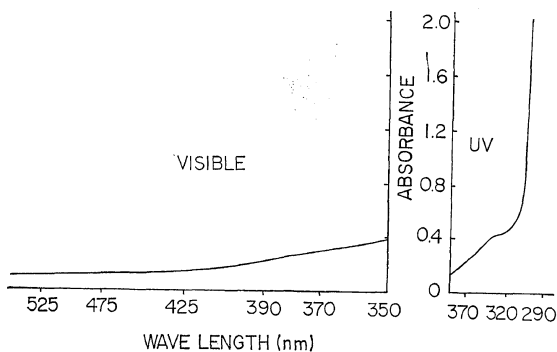
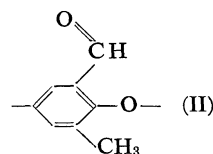


Figure 1. Absorption spectra of PPO in chloroform.

benzene, the solution was slightly yellow, and the absorption spectrum was as shown in Figure 1. The absorption begins at about 600 nm. Since phenoxy radicals were reported to show absorption over the visible region,^{16,17} this absorption can be thought to be due to the substituted phenoxy radicals which were detected by ESR in untreated PPO samples and their benzene solutions. These ESR results will be discussed in the next section.

Some absorption was also observed at about 330 nm. This absorption might be due to aldehyde groups on the benzene ring such as in structure (II), which can be produced by the oxidation of PPO. In fact benzaldehyde shows an absorption



at about 328 nm. Infrared spectrum of our PPO also supports this identification, that is, infrared bands were observed at 1700 (C=O) and 2750 cm^{-1} (—C=O).¹⁸⁻²⁰

ESR Spectra of Poly(2,6-dimethylphenylene oxide) Irradiated with Ultraviolet Light

Solid Polymer. Unirradiated solid polymer gave the ESR signal shown in Figure 2. It is an apparent eight-line spectrum with a separation of about 5.5 gauss at $g=2.005$. This spectrum has been identified as due to substituted phenoxy radicals (I) on the basis of ESR measurements

at X, S, and Q bands.¹⁵ It was shown that g anisotropy was quite large, $g_{\perp}=2.002$, $g_{\parallel}=2.006$.¹⁵ These phenoxy radicals would have been produced by autoxidation of polymers or during polymerization as propagating ends.¹²

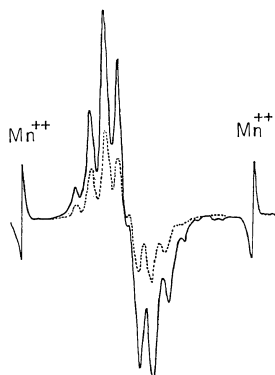


Figure 2. ESR spectra of PPO powder sample observed at room temperature in the presence of air before (dotted line) and after ultraviolet irradiation for 35 min (solid line). The separation between two Mn^{++} peaks is 86.7 gauss.

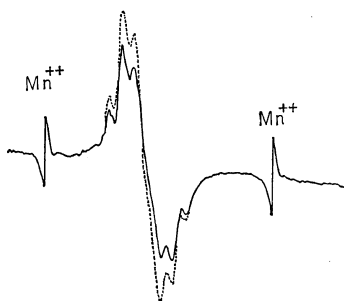


Figure 3. ESR spectra of PPO block sample under vacuum (solid line) and after introduction of air (dotted line).

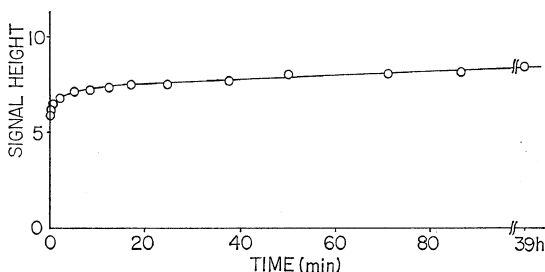


Figure 4. Increase of signal intensity of PPO block sample after introduction of air.

When the sample was evacuated, the signal intensity decreased to some extent. The subsequent introduction of air made the signal intensity larger as shown in Figures 3 and 4. At the same time, the spectral shape changed to some extent. Although the detailed mechanism is not known, a possible explanation for this strange behavior might be a change of relaxation time on the introduction of air or adsorption of oxygen.

At room temperature, both *in vacuo* and in the presence of air, when samples were irradiated in the sample cavity by using an unfiltered Xe short arc lamp, the signal intensity of the phenoxy radicals increased as shown in Figure 2.

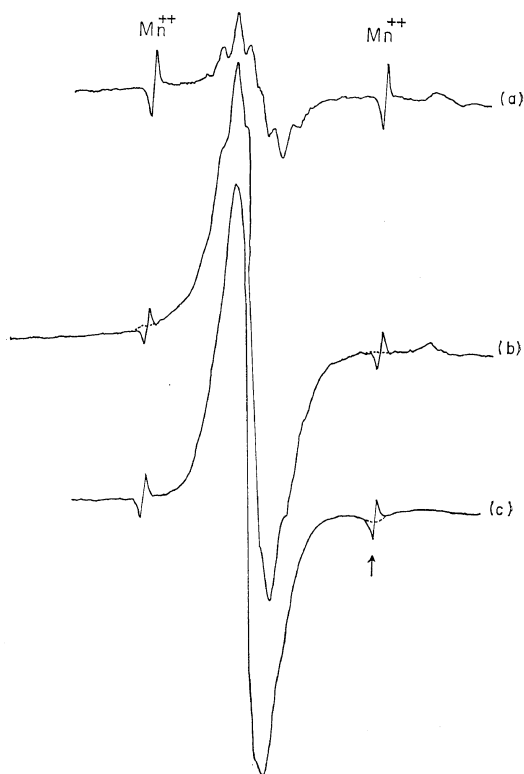


Figure 5. ESR spectra of a PPO powder sample irradiated at -196°C under vacuum: (a) before irradiation, $G=1000$; (b) after irradiation for 25 min, $G=710$; (c) overnight after introduction of air at -196°C . An arrow shows a hump at $g=2.032$. G represents an amplifier gain setting. The separation between two Mn^{++} peaks is 86.7 gauss.

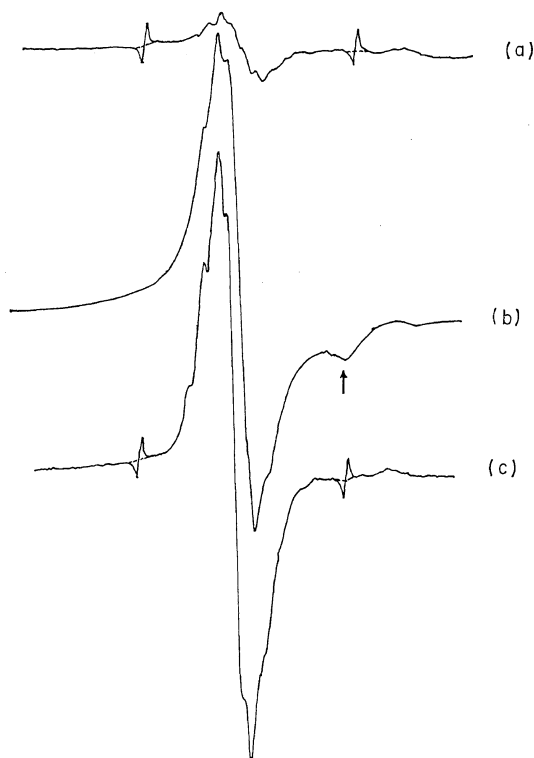


Figure 6. ESR spectra of PPO powder sample irradiated at -196°C in the presence of air: (a) before irradiation; (b) after irradiation for 24 min, an arrow mark shows a hump at $g=2.032$; (c) after keeping the irradiated sample at -78°C for about 3 hr. The separation between two Mn^{++} peaks is 86.7 gauss.

The irradiation effect at -196°C under vacuum is shown in Figure 5. When the solid sample was irradiated at -196°C under vacuum for 25 min, the spectrum became a relatively narrow singlet spectrum with some shoulders as shown in Figure 5b. The apparent g value is 2.004. No ESR spectrum due to hydrogen atoms was observed. The sample was subsequently maintained at -196°C overnight after introducing air and the spectrum shown in Figure 5c was obtained. This spectrum has a hump at $g=2.032$ (arrow mark), which was also observed after irradiation of the sample in the presence of air as shown in Figure 6(b) but the hump decayed away when the sample was maintained at -78°C for 3 hr as shown in Figure 6c. This hump is a part of the spectrum due to the peroxy radicals as described later.

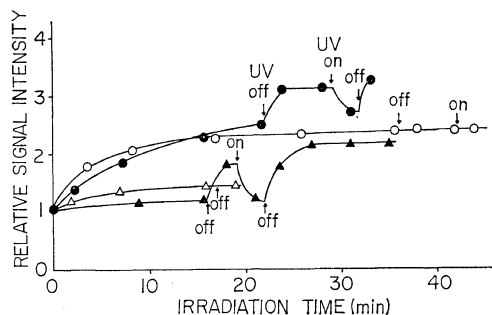


Figure 7. Dependence of signal intensity on irradiation time (PPO powder): \circ —, room temperature, in air; \triangle —, room temperature, under vacuum; \bullet —, -196°C , in air; \blacktriangle —, -196°C , under vacuum.

Intensity changes are shown in Figure 7 for the sample irradiated under vacuum and in the presence of air, at room temperature and at -196°C . It is clear that the increase in intensity is larger in the presence of air than under vacuum. However a heating effect during irradiation must be taken into consideration to some extent. The heating effect was clearly demonstrated by the intensity change observed when the irradiating light was turned on and off.³

It should be mentioned here that 2,6 xyleneol did not give any ESR signal even after irradiation.

Benzene Solution. When a high concentration of PPO was dissolved in benzene, a seven-line spectrum with a coupling constant of about 5.60 gauss was observed. The g value is about 2.005.

A benzene solution of the polymer (2 g polymer/1 cc benzene), which gave a negligible spectrum, was placed in the ESR cavity at room temperature and, in the presence of air, irradiated with the unfiltered light from the Xe short arc lamp. The yellow color was deepened by irradiation. The ESR spectrum recorded during irradiation for 2 min was a clear seven-line spectrum with a separation of about 5.60 gauss, and no observable substructures, Figure 8A. The intensity ratio is about 1 : 6 : 15 : 20 : 15 : 6 : 1, which is expected from six equal protons. This spectrum can be attributed readily to phenoxy radical (I). As is shown in Figure 8B, however, the spectrum after a 9 min irradiation showed some substructure. The detailed hyperfine structures were resolved, as shown in Figure 9,

ESR Study of Poly(2,6-dimethylphenylene oxide)

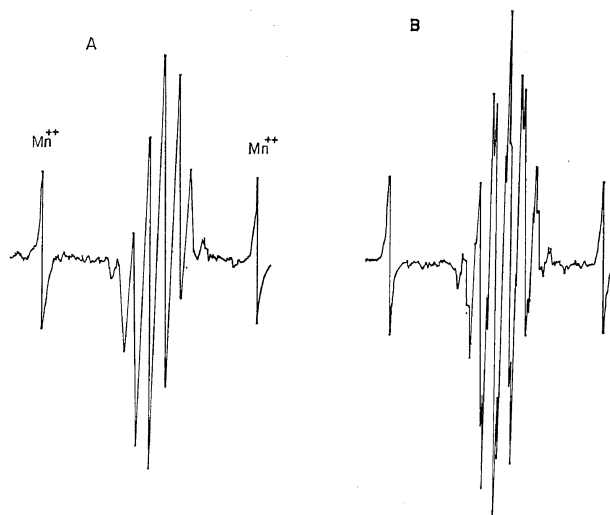


Figure 8. ESR spectra of PPO in benzene (2 g/cc) irradiated at room temperature in the presence of air: A, after irradiation for 2 min; B, after irradiation for 9 min.

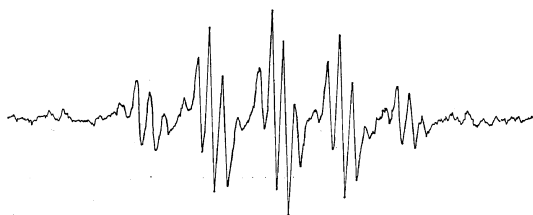


Figure 9. ESR spectrum of PPO in benzene (43 mg/cc) irradiated at room temperature for a relatively longer time; $a_{Me(I)}=5.13$, $a_{Me(II)}=6.20$, $a_{H(m)}=1.14$ gauss.

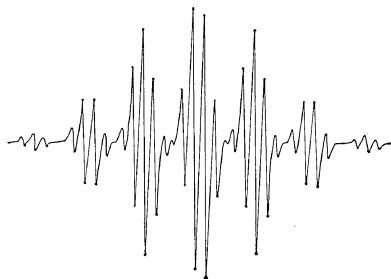


Figure 10. Simulated spectrum of poly(2,6-dimethylphenoxy) radical; $a_{Me(I)}=5.13$, $a_{Me(II)}=6.20$, $a_{H(m)}=1.14$ gauss; line width=0.6 gauss.

when the spectrum was recorded with a slow sweep rate and with a smaller modulation amplitude (0.5 gauss). This spectrum was similar to

that reported by Waters, *et al.*,¹³ and Symons, *et al.*,¹⁵ Therefore, this spectrum is attributed to phenoxy radical (I). The coupling constants obtained from our spectrum were $a_{Me(I)}=5.13$ gauss, $a_{Me(II)}=6.20$ gauss and $a_{H(meta)}=1.14$ gauss. These values are very close to the values reported in the literatures.^{13,15} The simulated spectrum shown in Figure 10 is almost identical with the observed spectrum. It should be pointed out here that irradiation in a nitrogen atmosphere gives the ESR spectrum with substructures as

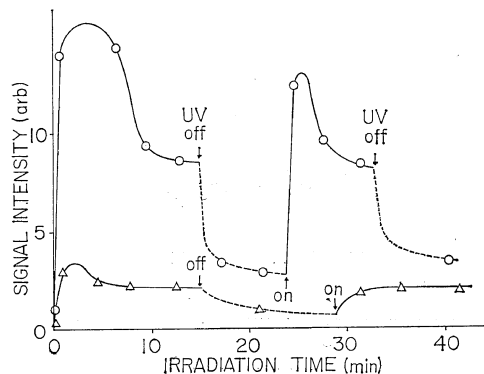


Figure 11. Dependence of signal intensity on irradiation time (PPO in benzene 50 mg/cc): —○—, in the presence of air; —△—, under vacuum or in the presence of nitrogen.

in Figure 8B immediately after irradiation.

The dependence of radical concentration on irradiation time is shown in Figure 11. In the presence of air, radical concentration increased rapidly at the beginning of the irradiation but gradually decreased from the maximum value with longer times of irradiation. When the irradiation light was cut off, the radical concentration dropped to a lower value at once. This decay was found to be neither a simple second order nor first order reaction. Subsequent irradiation caused a sudden increase of radical concentration similarly to the first irradiation. The maximum concentration in the second irradiation, however, was smaller than that in the first irradiation. The change of radical concentration observed after this irradiation was almost analogous to that observed after the first irradiation. Furthermore, the rate of radical formation was found to be proportional to the incident light intensity.

On the other hand, after irradiation in either an evacuated sample or in the presence of N_2 , the increase of radical concentration was very small compared with the value in the presence of air. Changes in radical concentration during irradiation were similar to those in the presence of air. These samples, however, gave larger radical yield when they were irradiated after introduction of air. On the other hand, when the solution was saturated with oxygen, no ESR signal was observed after irradiation. This may be caused by broadening of the line width due

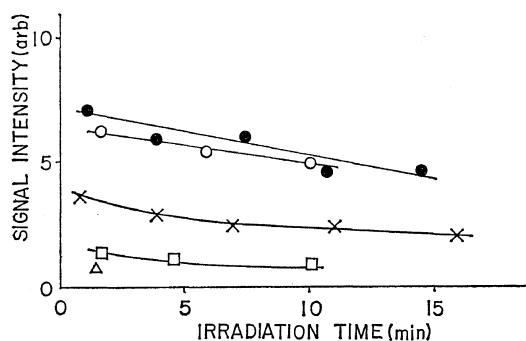


Figure 12. Dependence of signal intensity on irradiation time for various PPO concentration (PPO in $CHCl_3$): Δ , 0.0238 g/cc; \square , 0.0402 g/cc; \times , 0.0768 g/cc; \circ , 0.1833 g/cc; \bullet , 0.2663 g/cc.

to the paramagnetic effect of oxygen. Therefore, subsequent bubbling of nitrogen gas through the irradiated solution caused appearance of the ESR signal.

Figure 12 shows the dependence of radical concentration on irradiation time when chloroform was used as the solvent instead of benzene. In this case the radical concentration simply decreased after irradiation for 1 min. Therefore the maximum is expected to be reached immediately after irradiation. The dependence of radical concentration on polymer concentration is shown in Figure 13, where radical concentration was taken from the value at an irradiation

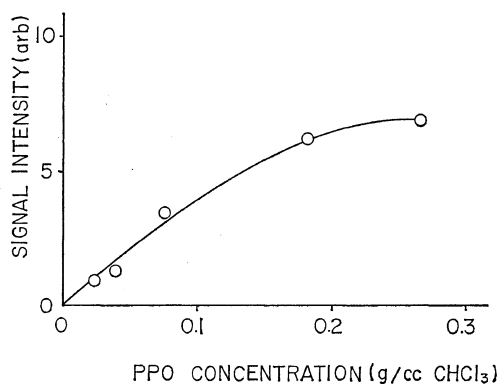


Figure 13. Concentration dependence of signal intensity after 1.5-min irradiation of PPO in $CHCl_3$.

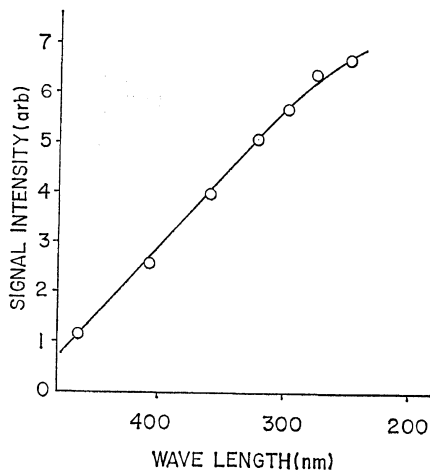


Figure 14. Wavelength dependence of signal intensity after 45-sec irradiation for PPO in $CHCl_3$, 5 mg/cc, irradiated in the presence of air.

time of 1.5 min. It is evident from Figure 13 that radical concentration increases with polymer concentration.

The dependence of radical concentration on the wavelength of irradiation light is shown in Figure 14. Radical concentration was taken from the value at an irradiation time of 45 sec. The radical concentration decreased with an increase in wavelength. However, free radicals were produced even after irradiation at the wavelength longer than 460 nm.

ESR spectra were not observed under the same experimental conditions for benzene solution of 2,6 xyleneol.

When styrene was used as a solvent for the polymer, the same ESR spectrum was observed as in benzene.

When a benzene solution of PPO was gradually warmed to about 80°C, the signal intensity increased as shown in Figure 15. Ultraviolet ir-

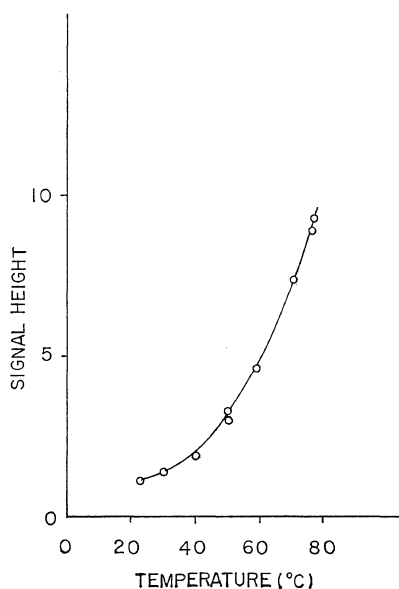


Figure 15. Temperature dependence of signal intensity of PPO in benzene (0.2912 g/5 cc).

radiation caused a further increase of signal intensity. ESR spectra observed at higher temperature were quite different from that observed at room temperature as shown in Figure 16. As is obvious from this figure, line width alternation was clearly observed at 100°C, and at

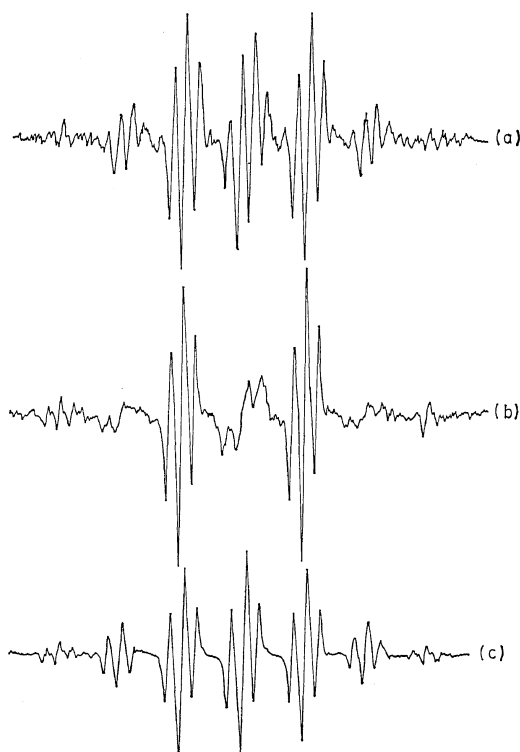


Figure 16. Temperature dependence of ESR spectrum of PPO in xylene: (a) 60°C; (b) 100°C; (c) 150°C.

150°C the spectrum which was observed is that expected from an almost equal coupling of the protons of two methyl groups. The coupling constant of the six methyl protons and the two *m*-protons are about 5.63 and 1.23 gauss, respectively. This coupling constant of the methyl protons is very close to an average of the two unequal coupling constants obtained at room temperature. These phenomena can be interpreted by the fact that the rotation frequency about the bridging C—O bonds becomes greater at higher temperature. The detailed discussion will be published in the near future.

DISCUSSIONS

Identification of Free Radicals

The apparent eight-line spectrum observed for the solid sample of PPO has been identified as due to substituted phenoxy radical (I) by Symons, *et al.*¹⁵

The solid PPO irradiated at -196°C under vacuum gave an apparent singlet spectrum with faint substructures. The g value of this spectrum ($g=2.004$) may indicate that this spectrum is mainly due to the phenoxy radicals, but some other spectrum must be superimposed, as peroxy radicals appeared after the introduction of air at -196°C . Phenyl radicals and alkoxy radicals might be involved as described below.

When the solid PPO was irradiated at -196°C in the presence of air, a hump was observed at $g\cong 2.032$ besides the central absorption at $g=2.004$. This hump can reasonably be attributed to a part of the spectrum due to peroxy radicals from both the g value and the fact that this hump was not observed in the sample irradiated *in vacuo* but appeared after maintaining the sample overnight at -196°C in the presence of air.

On the other hand the seven-line spectrum with a coupling constant of 5.60 gauss observed immediately after irradiation of the benzene solution of PPO in the presence of air may be attributed to the substituted phenoxy radical (I), as described before simply on the assumption that the coupling constants of six protons of two methyl groups are identical. The free radical (I), however, is expected to give different coupling constants for protons of the two methyl groups, since such coupling constants were obtained from the ESR spectra due to the free radical (I) observed during polymerization¹³ and the radical produced by ultraviolet irradiation of the polymer in benzene solution in the presence of nitrogen. Consequently, the apparent seven-line spectrum can reasonably be caused by the line broadening effect of oxygen on the well-resolved spectrum of the free radical (I). If this interpretation is correct, the oxygen concentration became smaller in the later stage of irradiation, as the well-resolved spectrum was observed after a longer time of irradiation even in the presence

of air. This mechanism will be discussed in the later section.

The coupling constants at room temperature for each methyl protons of the free radical (I) are 5.13 and 6.20 gauss. This is interpreted as a hindered rotation about the bridging O—C bonds and a preferred conformation rendering the radical asymmetric.¹⁵ Inequivalence of two methyl groups on the 2 and 6 positions of the phenyl ring has been found also in an ENDOR study²¹ and it resulted from a steric interaction which changed the spin densities in the ring. As described earlier, however, the coupling constants of the two methyl protons became equal at higher temperature on account of fast rotation.

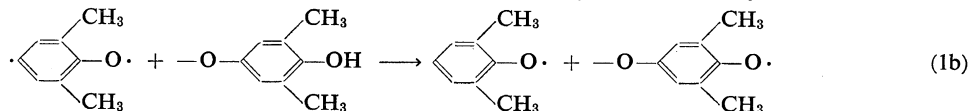
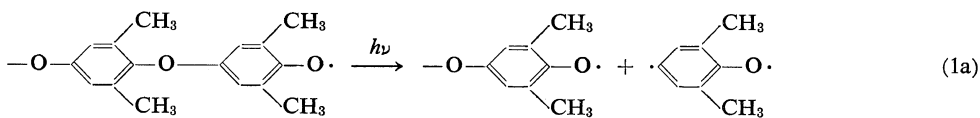
Mechanism of Radical Formation

From the molecular structure of PPO, absorption in the visible region can not be expected. Therefore the absorption in the visible region observed in the present investigation should be attributed to some other species. The most probable species responsible for this absorption is substituted phenoxy radical (I) which was detected by ESR spectroscopy and whose absorption spreads over the visible region.^{16,17} The deepening of the yellow color after irradiation supports this identification.

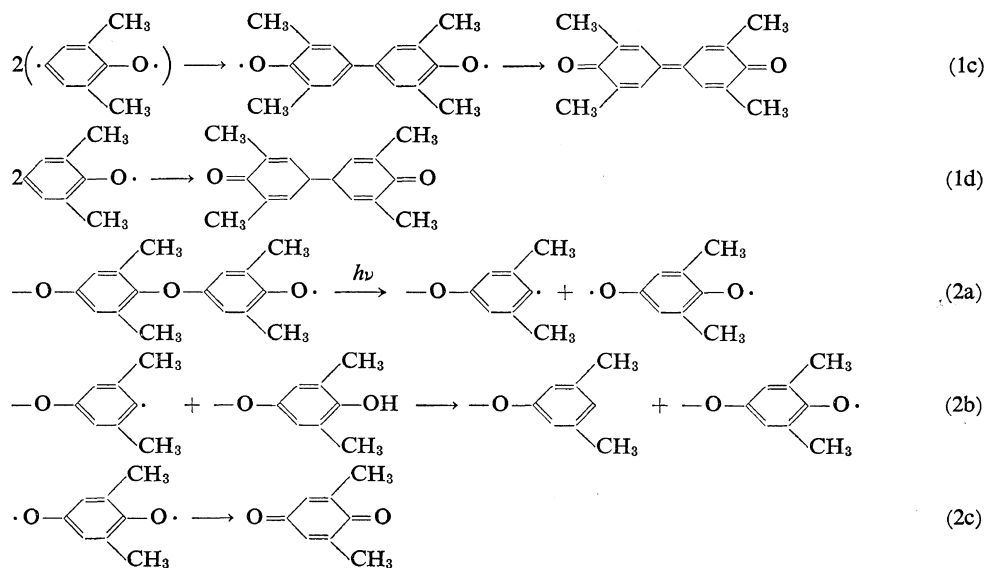
In the ultraviolet region, an absorption due to $\pi-\pi^*$ transition of benzene ring was observed.

Because the concentration of substituted phenoxy radicals increased after irradiation at wavelength longer than 400 nm, it seems reasonable to assume that the light energy absorbed by substituted phenoxy radical (I) is effective for radical formation when irradiations are carried out with light of longer wavelength.

Therefore the probable mechanism for the observed increase of phenoxy radical concentration after irradiation with visible light is as follows:

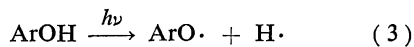


ESR Study of Poly(2,6-dimethylphenylene oxide)



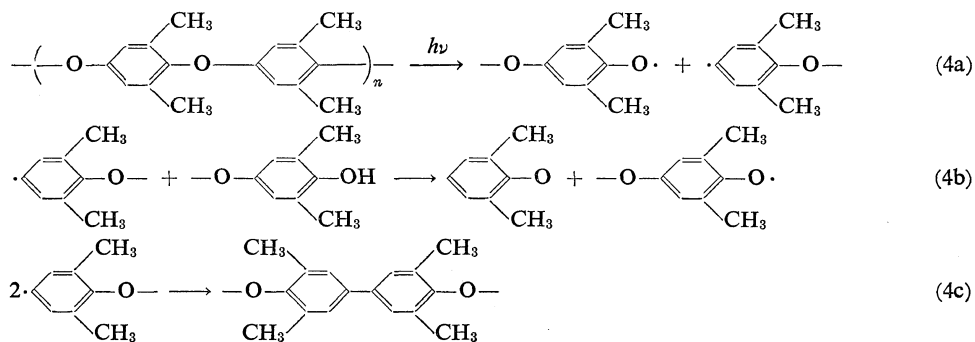
Among these schemes, the reactions (1a) and (1b) are thought to be predominant reactions for increase of phenoxy radical concentration.

In the case of ultraviolet irradiation of phenol, phenoxy radical formation has been reported for several cases in rigid matrixes, where dissociation of O—H bond takes place through the excited state of phenol.²²⁻²⁶

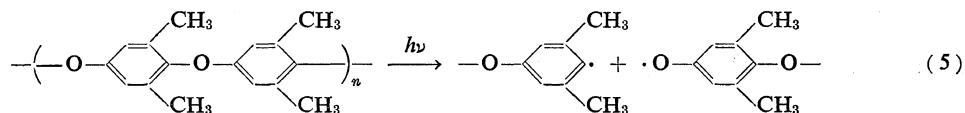


This mechanism may also be operative in the present case, where hydrogen atoms recombine

with each other. However no radicals were observed after irradiation of 2,6-xylenol under the same experimental conditions. This may indicate that, in the polymer, the C—O bond scission is more effective than O—H bond scission, although an efficient transfer of excitation energy through polymer chains is assumed for the reaction (3) by Symons, *et al.*¹⁵ Therefore, the radical formation mechanism for ultraviolet irradiation of the polymer can be described as follows: besides the reactions (1a) and (1b),



Instead of reaction (4a), the following reaction (5) may take place and 3,5-disubstituted phenoxy radicals may also be produced.



These phenoxy radicals, however, are expected to be unstable since they have no substituents on the 2 and 6 positions to stabilize the phenoxy radicals. Therefore, even though they are produced, they will decay away by recombination in a short time especially in the liquid state.

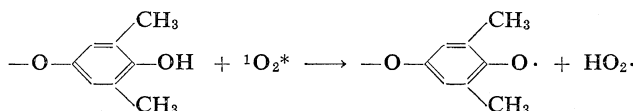
In the case of photolysis of solid PPO in air at -196°C , peroxy radicals were observed. Since phenoxy radicals are not expected to react with oxygen molecules so readily, it seems plausible that peroxy radicals are produced by the reaction of oxygen with phenyl type radicals produced by the reaction (4a). In the case of irradiation at -196°C under vacuum, phenyl type radicals were supposed to be trapped from the fact that the hump due to peroxy radical spectrum appeared after introduction of air at -196°C .

Kelleher, *et al.*,⁴ suggested the possibility of photolysis of hydroperoxides contained in the polymer besides the reaction (4a). The alkoxy radicals thus produced might partly be responsible for the singlet spectrum ($g=2.004^9$) observed after photolysis of solid PPO at -196°C .

PPO contains aldehyde groups on the side chain as mentioned before. However, the g value of the observed spectrum was $g=2.004$, so these groups do not seem to contribute to radical formation to a large extent as no benzoyl type radicals ($g\cong 2.001$, singlet)²⁷ were observed even after irradiation at -196°C .

Effect of Oxygen on Photo-Induced Radical Formation

The acceleration of radical formation in the



A similar mechanism has already been postulated for the photooxidation reaction.³⁵ Although the contribution of singlet oxygen to phenoxy radical formation is only speculative, it is also reported³⁶ that phenoxy radicals can be produced by using a sensitizer in the presence of oxygen.

Reactions of Phenoxy Radicals during Irradiation

The photolysis of PPO solution in the presence of air gave two different ESR spectra due to the substituted phenoxy radical (I). At the beginning of photolysis the ESR spectrum observed

presence of air observed in this investigation could be attributed to the following reasons:

- the formation of charge transfer complexes between PPO and oxygen molecules, with the complexes participating in energy absorption, or
- the contribution of singlet oxygen to radical formation.

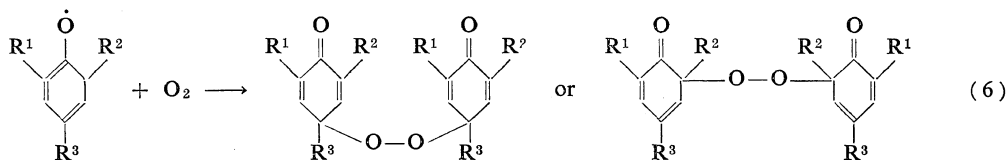
Formation of charge transfer complexes between PPO and oxygen molecules can readily be supposed since benzene,²⁸ ether,^{28,29} even polyethylene,^{2,8} polypropylene⁸ and poly 3,3 bis-(chloromethyl) oxetane^{8,11} form charge transfer complexes with oxygen. These charge transfer complexes are known to show an absorption in the ultraviolet region.^{8,28-30} In the case of latter three polymers, radical yield after ultraviolet irradiation was found to be greater in oxygen atmosphere than in nitrogen atmosphere. This was attributed to the extra absorption of light energy by the charge transfer complexes. If the same mechanism is applicable to PPO, the greater radical yield in air could be explained. However, detection of the absorption due to the charge transfer complexes was frustrated by experimental difficulty.

On the other hand, singlet oxygen molecules can be produced by energy transfer from excited benzene rings.³¹ The important role of singlet oxygen in photosensitized oxidation was pointed out by Kautsky, *et al.*,³²⁻³⁴ The reaction (3) may be facilitated in the presence of singlet oxygen as follows,

was an apparent seven-line spectrum with the separation of about 5.60 gauss. This spectrum could be attributed to the line broadening of the well-resolved ESR spectrum, since the well-resolved ESR spectrum was observed in the nitrogen atmosphere. The coupling constant, 5.60 gauss, is almost equal to an average of the proton coupling constants for two unequivalent methyl groups (5.13 and 6.20 gauss). Longer times of irradiation even in the presence of air, however, gave the well-resolved ESR spectrum

as shown in Figure 8B. This sample was mixed again to make the sample uniform and then reirradiated. A seven-line spectrum was observed initially after subsequent irradiation. From these results it can be supposed that oxygen concentration around the phenoxy radicals decreased

after longer irradiation times. This can be caused by the reaction of phenoxy radicals with oxygen molecules to form peroxides, as the concentration of the phenoxy radicals was large and the phenoxy radicals are known to form peroxides as follows,³⁷



The signal intensity increased as the temperature of the benzene solution of PPO was raised. This fact might be caused by the reverse reaction of eq 6, the thermal decomposition of the peroxides contained in the polymer,³⁷ or by the thermal dissociation of dimer forms of the phenoxy radicals.

Radical Growth Curve

When benzene solution of PPO was photolyzed, radical concentration increased quickly, reached the maximum and then decreased. This phenomenon indicates that the phenoxy radicals decayed when their concentration became large. Possible mechanisms responsible for this behavior may be the following:

- 1) Photo-induced radical decomposition,
- 2) Decay of phenoxy radicals by themselves.

Photolysis of phenoxy radicals trapped in a nitrogen matrix have been studied.²⁴ It was found that absorption of light quanta by phenoxy radicals breaks the bond between the 1 and 2 ring carbon atoms to produce an excited ring-opening radical. Therefore the substituted phenoxy radical studied here would be decomposed by a similar mechanism during irradiation.

When the irradiating light was shut off, the signal intensity due to the substituted phenoxy radicals dropped, although the decay rate is neither first order nor second order. This indicates that phenoxy radicals also decay by themselves during irradiation. This does not seem to be a simple bimolecular recombination.

Stability of Phenoxy Radicals

When chloroform was used as a solvent, the maximum in radical concentration was not observed, only a decreasing concentration after irradiation for 1 min. It can be supposed that

the maximum concentration is reached within 1 min, and that the phenoxy radicals are less stable in chloroform than in benzene.

In styrene, radical formation was almost the same as in benzene. In this system, thermal polymerization of styrene was retarded. This is due to the fact that phenoxy radicals act as an inhibitor of polymerization.³⁸

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REFERENCES

1. K. Tsuji and T. Seiki, *J. Polym. Sci., Part B* **7**, 839 (1969).
2. K. Tsuji and T. Seiki, *ibid., Part A-1*, **9**, 3063 (1971).
3. K. Tsuji and T. Seiki, *Polymer J.*, **2**, 606 (1971).
4. T. Takeshita, K. Tsuji, and T. Seiki, *J. Polym. Sci., Part A-1*, **10**, 2315 (1972).
5. K. Tsuji, T. Seiki, and T. Takeshita, *ibid., Part A-1*, **10**, 3119 (1972).
6. K. Tsuji and S. Okamura, Nobel Symposium No. 22, Stockholm, June 20–23, 1972.
7. K. Tsuji and T. Seiki, *Polymer J.*, **1**, 133 (1970).
8. K. Tsuji and T. Seiki, *J. Polym. Sci., Part B* **8**, 817 (1970).
9. K. Tsuji and T. Seiki, *ibid., Part B*, **10**, 139 (1972).
10. K. Tsuji, K. Hayashi, and S. Okamura, *ibid., Part A-1*, **8**, 583 (1970).
11. K. Tsuji and T. Seiki, *ibid., Part A-1*, **10**, 123 (1972).
12. A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967).
13. W. G. B. Huysmans and W. A. Water, *J. Chem.*

- Soc., Part B*, 1163 (1967).
14. P. G. Kelleher, L. B. Jassie, and B. D. Gasner, *J. Appl. Polym. Sci.*, **11**, 137 (1967).
 15. M. C. R. Symons and J. K. Yandell, *J. Chem. Soc., Part A*, 1995 (1970).
 16. E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967).
 17. A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London, 1968, p 287.
 18. R. T. Conley, *J. Macromol. Sci. (Chem.)*, **A1**, 81 (1967).
 19. A. Factor, *J. Polym. Sci., Part A-1*, **7**, 363 (1969).
 20. R. A. Jerussi, *ibid.*, *Part A-1*, **9**, 2009 (1971).
 21. C. Steelink, J. D. Fitzpatrick, L. D. Kispert, and J. S. Hyde, *J. Amer. Chem. Soc.*, **90**, 4354 (1968).
 22. E. J. Land, G. Porter, and E. Strachen, *Trans. Faraday Soc.*, **57**, 1885 (1961).
 23. G. Porter and E. Strachen, *ibid.*, **54**, 1595 (1958).
 24. J. L. Roebber, *J. Chem. Phys.*, **37**, 1974 (1962).
 25. H. Tsubomura, K. Kimura, H. Yamada, and M. Kato, *Tetrahedron Lett.*, No. 47, 4217 (1965).
 26. K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).
 27. J. E. Bennett and B. Mile, *Trans. Faraday Soc.*, **67**, 1587 (1971).
 28. H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).
 29. A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).
 30. V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1968).
 31. D. R. Snelling, *Chem. Phys. Lett.*, **2**, 346 (1968).
 32. H. Kautsky and H. de Bruijn, *Naturwissenschaften*, **19**, 1043 (1931).
 33. H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, *Ber. deut. Chem. Ges.*, **66**, 1588 (1933).
 34. H. Kautsky, *Biochem. Z.*, **291**, 271 (1937).
 35. D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, **10**, 193 (1969).
 36. T. Matsuura, K. Omura, and R. Nakashima, *Bull. Chem. Soc., Japan*, **38**, 1358 (1965).
 37. ref 17, p 294.
 38. R. G. Caldwell and J. L. Ihring, *J. Amer. Chem. Soc.*, **84**, 2878 (1962).