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A reappraisal of the photo-oxidation mechanism at short and long wavelengths for poly(2,6-dimethyl-1,4-phenylene oxide)

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A detailed re-examination of the photo-oxidation mechanism of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) at both long and short irradiation wavelengths under accelerated conditions is reported. The formation rate of polydimethylphenoxy (PDMP) radicals is observed both in the presence and in the absence of ultra-violet (u.v.) light by using electron spin resonance spectroscopy. In order to explain the great stability of PDMP radicals, the bimolecular decay observed in the dark is discussed. In addition, spin-trapping experiments using nitrosodurene reveal the existence of benzylic-type radicals under u.v. irradiation conditions. Under mild oxidative conditions, i.e. thermo-oxidation at 80°C, the changes in the Fourier-transform infra-red spectra after 1215 h show the formation of two main absorption bands at 1694 and 1658 cm^{-1}, assigned to aromatic aldehydes and quinonic groups, respectively. The poor photo-stability of these two primary oxidation products generates, by fast photolytic conversion to benzoic acids and esters, a broad band centred at 1734 cm^{-1} under accelerated photo-oxidative conditions. Furthermore, the cyclic voltammetry of PPO solution in the dark indicates both the existence of superoxide radical anions in the absence of u.v. light and the electro-catalytic effect possibly induced by quinonic groups. In this work direct formation of radical cations and superoxide anions by a photo-induced electron-transfer reaction is suggested under photo-oxidative conditions. The catalytic role of quinonic groups on the further generation of superoxide anions and PDMP radicals at long irradiation wavelengths and in the dark is also considered on the overall PPO photodegradation.

(Keywords: poly(phenylene oxide); photo-oxidation; electron transfer)

INTRODUCTION

In past years the photochemical and thermal oxidation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been extensively studied[1–5]. These previous studies report two primary competitive photochemical processes to explain the photo-oxidative degradation of this polymer (see *Scheme 1*). One photochemical process (a) has been attributed to chain scission of the polymer backbone by direct absorption of u.v. light (290–350 nm). Flash photolysis and e.s.r. spectroscopy provided experimental evidence about the formation of the poly(2,6-dimethylphenoxy) (PDMP) radical **1** (see *Scheme 1*)[4]. In addition, Tsuji observed that the apparent eight-line e.s.r. spectrum, detected in the solid state, increased significantly in the presence of oxygen under u.v. irradiation; radical **1** was also revealed by irradiation above 400 nm[6–9].

The other photochemical process, i.e. (b) in *Scheme 1*, has been attributed to the formation of benzylic-type radicals **2** by the photolytic elimination of a hydrogen atom belonging to methyl substituents of the aromatic ring[3,5]. Benzylic-type radicals have also been proposed as the main precursors for the formation of hydroperoxides generating aromatic acids and esters.

Later, Pickett suggested a self-sensitized photo-induced electron transfer leading to oxidation of the polymer backbone generating chain scissions and a large number of yellowish products[9]. In this case, the excited states of the PPO backbone can undergo a photo-induced electron transfer with another unexcited aromatic unit in the polymer matrix, forming a radical cation and anion pair as reported in *Scheme 2*[9]. The radical anion could rapidly transfer an electron to oxygen, yielding superoxide radical anions, $O_2^{-\cdot}$. In this mechanism, the superoxide and radical cations can then lead to photo-labile primary oxidation products, which can undergo further oxidation, ultimately leading to final stable carbonylic products[1–3,9]. Some experimental evidence supporting this mechanism has been obtained by using both some compounds acting as selective electron-transfer quenchers and the spin-trapping technique. The formation of superoxide has been suggested in *Scheme 2* using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and observing the e.s.r. spectrum of the corresponding nitroxy radical, in agreement with previous studies[10]. Thus, the proposed mechanism is

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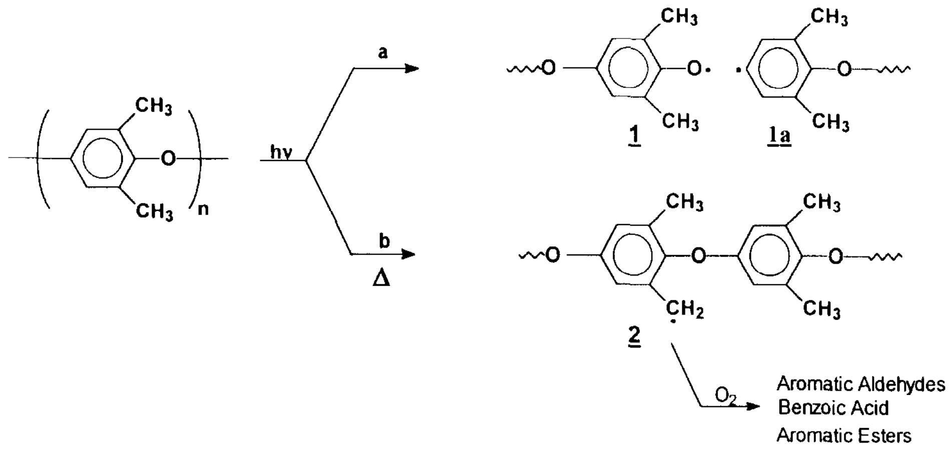
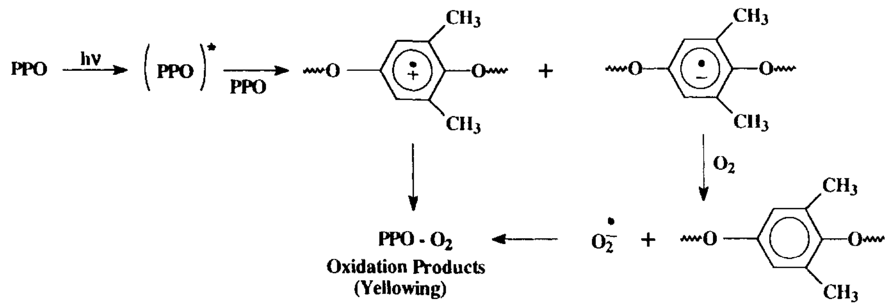
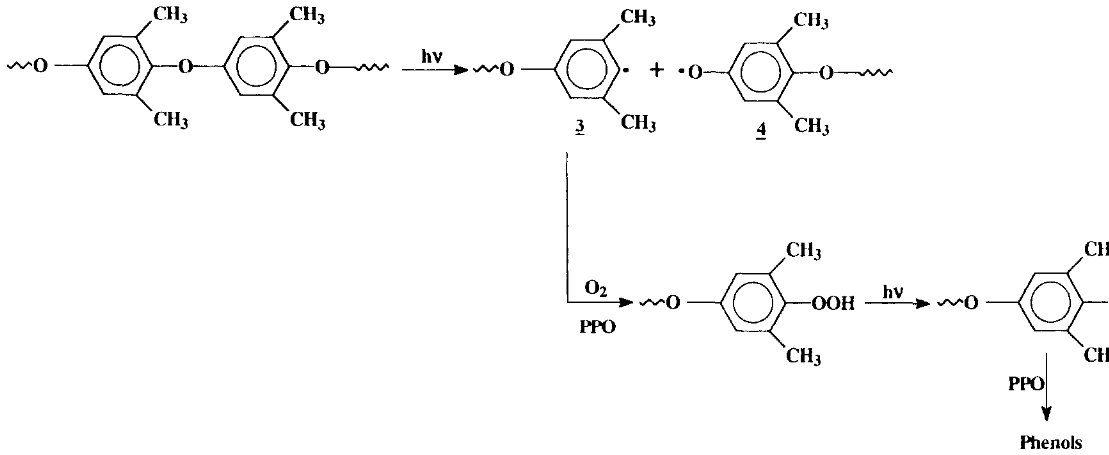


Scheme 1



Scheme 2



Scheme 3

consistent with oxidation by photo-induced electron transfer without invoking the existence of the photo-induced free-radical formations as previously reported in *Scheme 1*.

Recently Rivaton and Morel have reinvestigated the photo-oxidation mechanism under accelerated conditions at both short and long wavelengths, suggesting an alternative mechanism reported in *Scheme 3*[11]. To explain a faster decrease of the absorbance at 1021 cm^{-1} of ether groups in the *FT*i.r. spectra in the presence of air, the authors suggest an alternative photolytic process (see *Scheme 3*) instead of reaction (b) in the previously reported *Scheme 1*. In this case, the radicals **1** and **3**, indicated in *Schemes 1* and *3* respectively, have been assumed to be formed separately. The hydroperoxides generated by radicals **3** have been suggested as the intermediates responsible for the high yields of oxidation products observed in *FT*i.r. spectra in the presence of air. Furthermore, the benzylic-type radicals can originate from a hydrogen abstraction process by phenoxy radicals, which leads to both phenolic and quinone-methide groups. In contrast with the mechanism reported in *Scheme 1*[11], the formation of benzylic-type radicals has been ruled out for the direct photolysis.

To our knowledge, the enhancement in the formation rate of radical **1** in the presence of air under long- and short-wavelength irradiation has not been fully explained in previous work. Since DMPO is an efficient spin trap for both tertiary carbon and oxygen centred short-lived radicals giving identical spectral pattern[12,13], we believe that further e.s.r. measurements using another spin trap such as 1,2,4,5-tetramethyl-3-nitrosobenzene, i.e. nitrosodurene (ND), could reveal the existence of other free radicals in the absence of air during the photodegradation of PPO. Besides, some cyclic voltammetry measurements in the absence of light can provide conclusive experimental evidence of the existence of superoxide radical anion formation. Finally, a re-examination of degradation products under mild oxidation conditions could be very important to identify some photo-labile species to gain insight into the photo-oxidation mechanism for PPO.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in powder form was purchased from Aldrich ($M_w \approx 244\,000$ and $M_w/M_n = 7.62$). The polymer was purified by dissolving it in chloroform (20 ml) and then adding the solution to a large volume of methanol. This procedure was repeated at least three times. The precipitated polymer was then filtered and dried under vacuum for 36 h at room temperature. The traces of solvent were checked by infra-red spectrosocopy. The ^1H spectrum recorded at 200.13 MHz in $CDCl_3$ confirmed the chemical structure, showing only two resonances at 2.09 and 6.47 ppm with intensity ratios of 3 to 1, respectively.

All the solvents used were purchased from Aldrich and were spectroscopic grade.

Preparation of films

Thin PPO films (5–20 μm) were made by casting from a chloroform solution (15% w/v) and then the traces of solvent were removed under vacuum overnight. Thick PPO films (120–300 μm) were made by compression moulding of purified polymer powder at 210°C for 1 min using a Specac hydraulic press equipped with heatable plates and temperature controller unit.

FT*i.r. spectra*

*FT*i.r. spectra of the photo- and thermo-oxidized films were carried out with a Bruker IFS88 spectrometer, which was continuously purged with dry air without carbon dioxide by using Balston FT-50 equipment. Each spectrum was measured with a DTGS (deuterated triglycine sulfate) detector, 2 cm^{-1} resolution and at least 256 scans.

U.v.-visible spectra

U.v.-vis. spectra of photo- and thermo-oxidized films were recorded by a Perkin-Elmer Lambda 6 spectrophotometer equipped with an integrating sphere to avoid scattered light detection. The resolution was set at 1 nm.

Photo-oxidation at short and long wavelengths under accelerated conditions

Films were irradiated at 60°C under accelerated weathering conditions in a Sairem-Sepap 12.24 apparatus (Material Physico-Chimique, France) equipped with four mercury medium-pressure lamps (400 W) filtered by a borosilicate glass bulb ($\lambda > 300$ nm) simulating outdoor exposure[14]. Irradiation at long wavelengths ($\lambda > 400$ nm) was conducted using a cut-off in front of the film in the same experimental conditions. The transmittance of the used cut-off remained unchanged during the whole experiment. The oxidation degrees formed under thermo- and photo-oxidation conditions were obtained by calculating the carbonyl areas from the difference *FT*i.r. spectra at the different oxidation times using the spectrum of the starting unoxidized polymer as reference. All calculated areas were normalized by the film thickness.

Oven ageing procedures

Thermo-oxidation was carried out in an oven at 80°C with forced air ventilation. A thermo-oxidized film for 1215 h at 80°c was treated with an acetonitrile solution (5 wt%) of 2,4-dinitrophenylhydrazine (DNPH) following the procedure reported elsewhere[15] to identify carbonyl groups. The chemical modifications due to the different treatments were followed by *FT*i.r. spectroscopy.

E.s.r. spectra

All the e.s.r. spectra were recorded by a Bruker ER200D X-band spectrometer equipped with a temperature controller unit and employing 100 kHz modulation. The *g*-values were calculated by comparison with the spectrum of 2,2-diphenyl-1-picrylhydratyl hydrate, free radical (Aldrich) (DPPH) ($g = 2.0037$). The microwave incident power on the cavity was of the order of 5 mW (10 dB), a level at which saturation of the resonance did not occur.

E.s.r. spectra of photo-oxidized films under accelerated conditions in Sepap 12.24 were carried out with a Wilmad quartz flat tissue cell. In the case of photo-oxidation experiments directly into the e.s.r. cavity, Wilmad quartz Taperlock tubes having a glass joint for vacuum line were used. Tubes containing freshly prepared PPO film by casting were degassed by five freeze–pump–thaw cycles (10^{-5} mmHg) and then irradiated by a conventional Hg medium-pressure Oriel lamp (250 W) equipped with WG-320 and GG-400 Ealing Electro-optics cut-off filters used for the photo-oxidation at short and long wavelengths, respectively. Under those experimental conditions, the effect of oxygen on the e.s.r. signal intensity was obtained by introducing air into the tube under continuous irradiation. All recorded e.s.r. signals carried out during photo-oxidation experiments were compensated by normalization with the fixed signal intensity of a ruby chip used as external standard[16].

The spin-trap technique was used under u.v. irradiation for 20 min ($\lambda > 300$ nm) of a quartz tube containing a PPO film freshly prepared by casting immersed in an ethanol solution (1×10^{-3} M) of 1,2,4,5-tetramethyl-3-nitrosobenzene (nitrosodurene) (ND)[9,17]. ND was purchased from Aldrich and used as received. The solution was deaerated by five freeze–pump–thaw cycles ($\sim 10^{-5}$ mmHg). Under the same experimental conditions the ND solution did not show any e.s.r. signal in the absence of polymer film after 20 min of u.v. irradiation ($\lambda > 300$ nm). The spectrum simulation was carried out on an Epson 486 personal computer using slightly modified software reported elsewhere[18].

The e.s.r. spectra of thermo-oxidized film inside the cavity were carried out using both a Bruker temperature controller unit and a dry air flow to heat the quartz tube containing unoxidized PPO film.

Electrochemical measurements

Electrochemical measurements were carried out using a computer-driven EG&G model 273 potentiostat with M270 electrochemical software. Cyclic voltammetry measurements were carried out using a glassy carbon rotating-disc electrode (RDE) (Metrohm). A silver wire

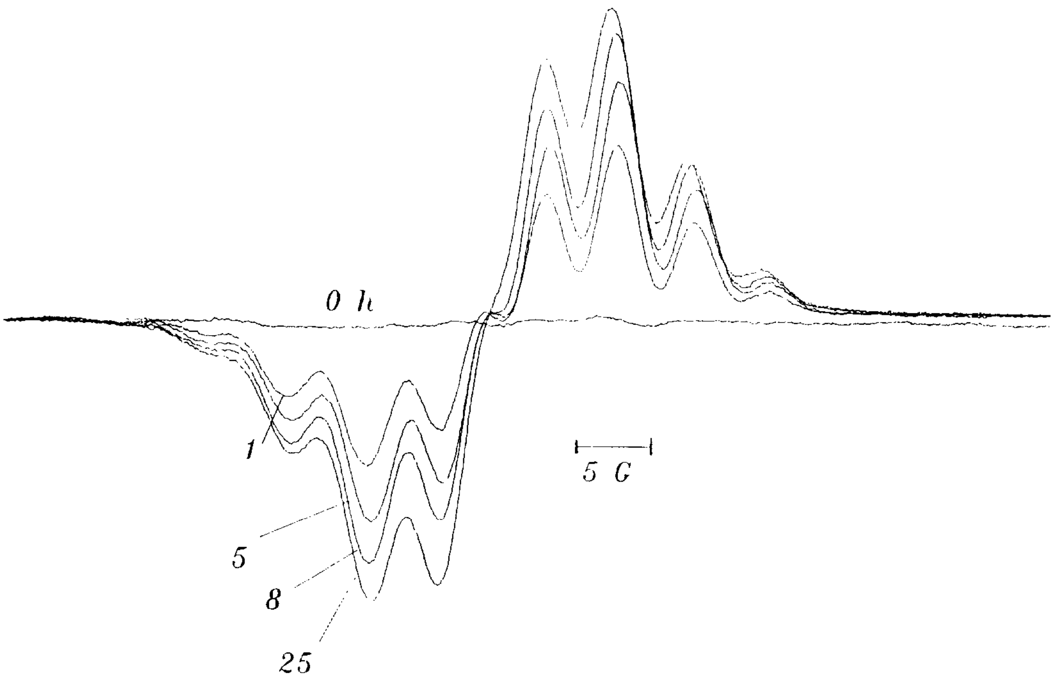


Figure 1 E.s.r. spectra of PDMP radicals under accelerated conditions recorded after irradiation at short wavelength (times in hours)

has been used as a quasi-reference electrode ($E_{\text{ref}} = -0.20\,\text{V}$ *versus* NHE). The supporting electrolyte was tetrabutylammonium perchlorate (Fluka) and the solvent, CH_2Cl_2 (Fluka), was purified according to standard methods.

RESULTS AND DISCUSSION

E.s.r. spectra of PPO films under accelerated oxidative conditions

The photo-oxidative degradation of this polymer simulating outdoor exposure ($\lambda > 300\,\text{nm}$) can be easily followed by e.s.r. spectroscopy at room temperature. Typical e.s.r. spectra obtained for a thick PPO film as a function of irradiation times under accelerated photo-oxidative conditions are reported in *Figure 1*. According to previous papers[6–8], the spectra have been assigned to PDMP radicals ($g = 2.0049$) consisting of an apparent eight-line spectrum due to inequivalent *ortho* methyl couplings with the aromatic ring protons. In addition, a comparative study of a series of both polymeric and monomeric 2,6-dialkylphenoxyl radicals demonstrated that at higher temperatures (> 100°C) both methyl groups become equivalent[19]. These data indicate that PDMP radicals can be formed in agreement with pathway (a) reported in *Scheme 1* under accelerated photo-oxidative conditions.

The stability of PDMP radicals generated in the solid state after 15 h of irradiation under accelerated photodegradation conditions is also investigated. The great stability of these radicals is in good agreement with previous studies on hindered phenolic polymeric stabilizers[20] having two alkyl substituents in *ortho* positions such as methyl or butyl groups, while the short-lived phenoxy radicals derived from unhindered phenols can be observed only by the spin-trap technique. In addition, some authors have suggested that an important contribution can be due to both (i) the presence of an oxygen atom in *para* position, which permits spin delocalization as in the case of some thermal stabilizers, e.g. Santonox having sulphur atoms in that position, and (ii) a direct overlap of two π orbitals. In the case of two methyl substituents, the mechanism (ii) seems to play an important role. Some bimolecular reactions, i.e. recombination, disproportionation or electron-transfer processes, consisting of a second-order reaction such as[21]:

$$\text{PDMP} + \text{PDMP} \rightarrow \text{Products} \qquad (1)$$

are expected to be present at $T < T_g$ for glassy polymers in the dark. This can explain the second-order decay in the absence of light as shown in *Figure 2*, where the reciprocal e.s.r. signal intensity *versus* post-irradiation time gives a straight line. The calculated half-life time for reaction (**1**) is about 120 h by using the well known equation $t_{1/2} = (I_0 k)^{-1}$, where I_0 is the initial e.s.r. signal intensity in arbitrary units after 15 h of accelerated irradiation and k is the slope of the straight line derived from *Figure 2*[22].

The formation rate of PDMP radicals is very high and reaches a limiting value after 30 h or irradiation under accelerated photo-oxidative conditions ($\lambda > 300\,\text{nm}$) (see *Figure 2*). A different kinetic behaviour can be observed for irradiation at longer wavelength ($\lambda > 400\,\text{nm}$), where the low amount of PDMP radicals rapidly levels off and remains constant for long irradiation times. The e.s.r. signal intensities reported in *Figure 2* can be correlated to the efficiency of main-chain scissions photo-induced by either short or long-wavelength irradiation. The formation of PDMP radicals is found to be dependent on the film thickness under accelerated long-wavelength irradiation. This is probably because the weak absorption at 320 nm has an additional tail above 400 nm probably due to the presence of contaminants and/or oxidation products[9,23]. However, the e.s.r. signal intensity obtained in those conditions, in the presence of oxygen, confirms that the photolysis of these products does not bring about a significant generation of PDMP radicals.

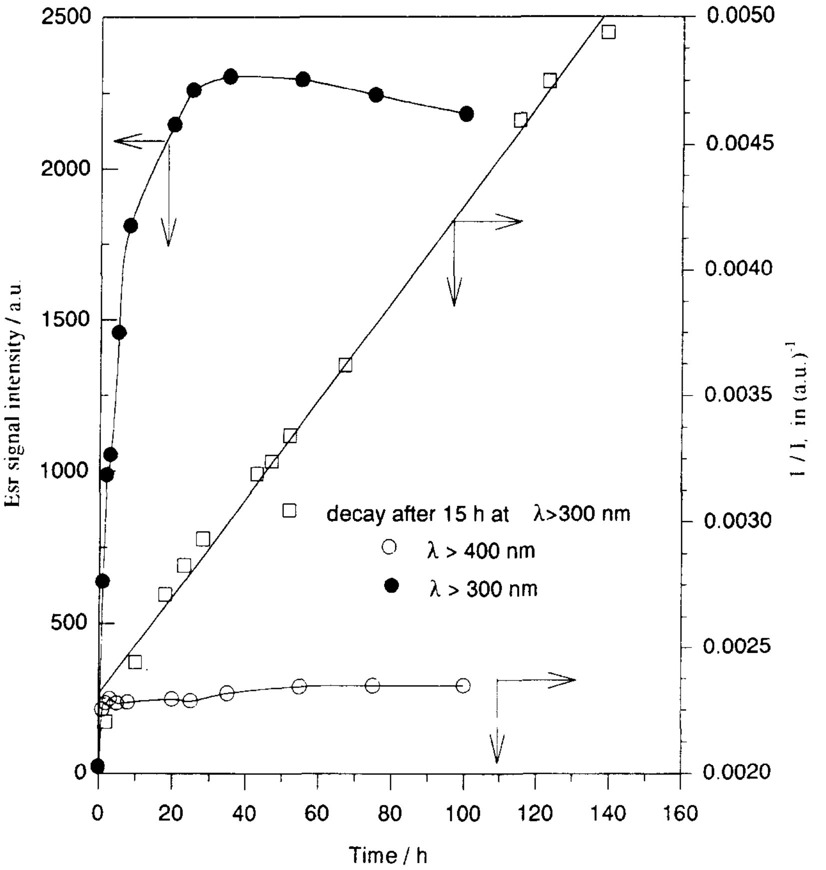


Figure 2 Formation rate of PDMP radicals under accelerated short ($\lambda > 300$ nm) and long ($\lambda > 400$ nm) wavelength irradiation. The reciprocal e.s.r. signal decay $(I_t)^{-1}$ recorded in PDMP spectra for a photo-oxidized PPO film after 15 h under accelerated short-wavelength irradiation shows a straight line against post-irradiation times

E.s.r. spectra of photo-oxidized PPO film into the e.s.r. cavity

A detailed investigation on the formation rate of PDMP radicals in deaerated PPO film has been carried out with a Hg medium-pressure lamp at short and long wavelengths in the e.s.r. cavity. The e.s.r. spectra detected in PPO film under u.v. irradiation into the cavity show both the same spectroscopic pattern and *g*-value as those previously assigned to PDMP radicals obtained under accelerated photo-oxidative conditions (see *Figure 1*). The effect of oxygen on the formation rate of PDMP radicals obtained under u.v. irradiation into the e.s.r. cavity is shown in *Figure 3*. This figure shows that, in the absence of air, the PDMP radical concentration reaches a maximum after 6 h for irradiation above 300 nm; but in the presence of air, the observed e.s.r. signal intensity rapidly increases by 50% after just 2 h in the same photo-oxidative conditions. A similar kinetic behaviour, showing a lower final PDMP radical concentration, is also observed at longer wavelengths ($\lambda > 400$ nm) both in vacuum and in air. It is worth noting that the final concentrations of PDMP radicals remain quite stable under long-wavelength irradiation, but above $\lambda > 300$ nm after 25 h they decay smoothly. These findings are in agreement with the above results obtained under accelerated photo-oxidative conditions. In addition to the results discussed above, *Figure 3* shows that both the film thickness and the presence of oxygen can influence the final concentration of PDMP radicals under long-wavelength irradiation conditions. Some previous experimental data based on model compounds, e.g. dimers and trimers of PPO, showed that no electronic absorption bands have been attributed to phenolic end-groups above 300 nm[9,23]. Besides, it has been demonstrated that the band usually detected at 320 nm in PPO films[11] gave a long absorption tail, giving a yellow coloration in the presence of a strong base solution. A reversible bleaching has also been observed when an acidic solution is added in the absence of oxygen[23]. Both for these spectroscopic changes and for the suggested oxidation products of 2,4,6-trisubstituted phenolic antioxidants[24], this 'anomalous' band is tentatively assigned to some quinonic groups probably formed by radical addition, e.g. peroxy radicals, in either *ortho* or *para* positions. Since air-saturated PPO film can rapidly undergo oxidation processes forming these groups both in the dark and during the polymerization reaction[25], we believe that the light absorption of those quinonic groups can explain the photolytic behaviour of PDMP radical generation as a function of both the film thickness and of the presence of air above $\lambda > 400$ nm. The existence of quinones (Q) can easily photo-induce electron-transfer processes, generating quinone radical anions ($Q^{-\cdot}$), which can also react rapidly with oxygen, giving superoxide radical anions with a typical reaction such as[21]:

$$Q^{-\cdot} + O_2 \rightarrow Q + O_2^{-\cdot} \quad (2)$$

where the position of the equilibrium is dependent on the redox potentials of $Q/Q^{-\cdot}$. Thus, the light absorption of

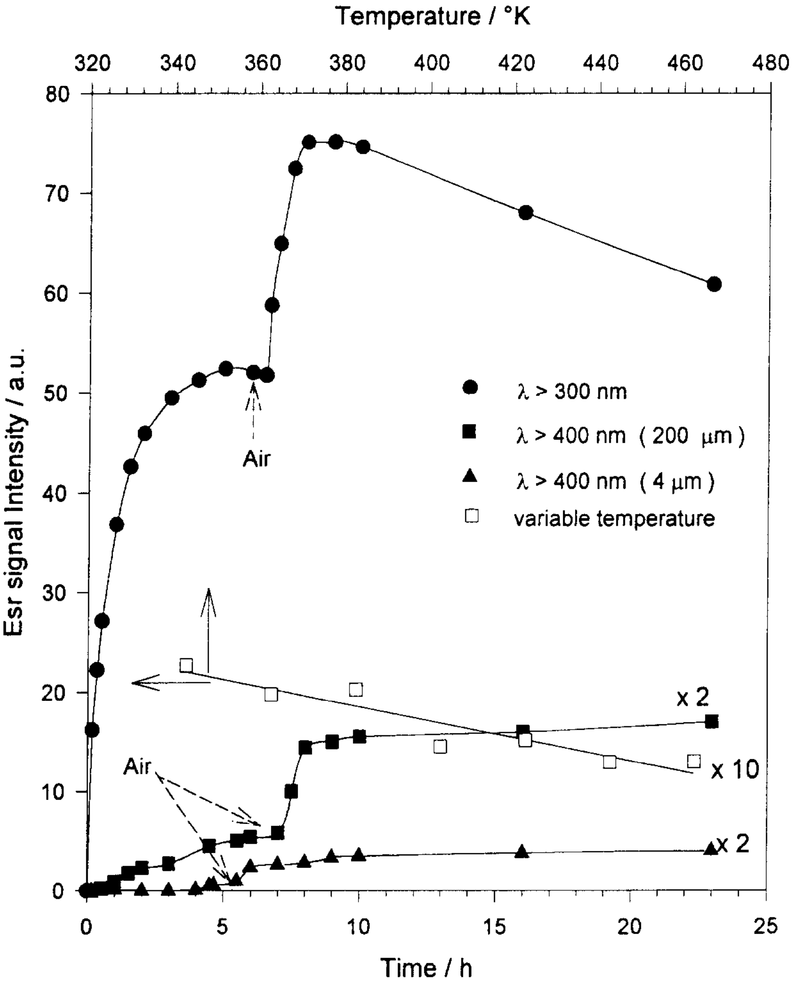


Figure 3 E.s.r. signal changes showing both the enhancement in the presence of air and the effect of temperature and film thickness on the final PDMP radical concentration. (The arrows indicate the introduction of air into the glass tube under continuous irradiation)

some previously formed quinonic groups in the polymer suggests that under long-wavelength irradiation these oxidation products can act as photosensitizers of further oxidation processes involving the formation of PDMP radicals and superoxide radical anions by electron-transfer reaction. The extent of this photosensitization effect can be correlated with the film thickness, i.e. with the amount of absorbed visible light, under photo-oxidative conditions as shown in *Figure 3*.

Finally, the thermo-oxidation of a thin PPO film carried out into the e.s.r. cavity at variable temperature shows that the PDMP radical concentration has a similar order of magnitude as that of the corresponding experiment conducted in photo-oxidative conditions under long-wavelength irradiation ($\lambda > 400$ nm). Upon heating the unoxidized film rapidly at 70°C, a small amount of PDMP radicals can be formed, but these radicals slowly decrease on increasing the temperature. As previously reported for a solution of PPO gradually warmed up to 100°C[8,19], the rate of decomposition increases with increasing temperature and is probably affected by recombination or addition reactions favoured by the minor glassy state of the polymer matrix.

Spin-trapping e.s.r. spectra of u.v.-irradiated PPO film

Under u.v. irradiation of PPO film in the absence of air, two expected radicals could be trapped in agreement with the mechanism of *Scheme 1*. The spin adducts generated by superoxide radical anions, $O_2^{-\cdot}$, or PDMP radicals, using DMPO as spin trap, can give a spectrum with a similar multiplicity of the splitting pattern, i.e. a triplet of doublets. We believe that the detection of these expected radicals requires two separate investigations to demonstrate their formation under the same irradiation conditions. For these reasons, it is convenient to use a spin trap such as ND to identify, in the absence of air, the presence of other radicals in the PPO film, while evidence of the superoxide radical anions should be sought by another analytical method, e.g. electrochemical measurement[26]. There are two main advantages in the use of ND as spin trap instead of DMPO: (i) information concerning the chemical structure of the trapped radical is more easily extracted from the spectrum; and (ii) the lifetime of the stabilized radicals, i.e. spin adducts, is usually greater than that of the corresponding nitrone compounds under the same irradiation conditions[27].

In our case the spectrum of the observed spin adduct after 20 min of irradiation ($\lambda > 300$ nm) into the e.s.r. cavity of PPO film immersed in a deaerated ethanol solution of ND is shown in *Figure 4A*. The simulated spectrum (*Figure 4B*), which is in fair agreement with the corresponding experimental one (*Figure 4A*), is calculated from the superposition of both (C) and (D) components (see *Figure 4*)[18]. Since the magnitude of the nitrogen hyperfine coupling constant (a_N) varies from

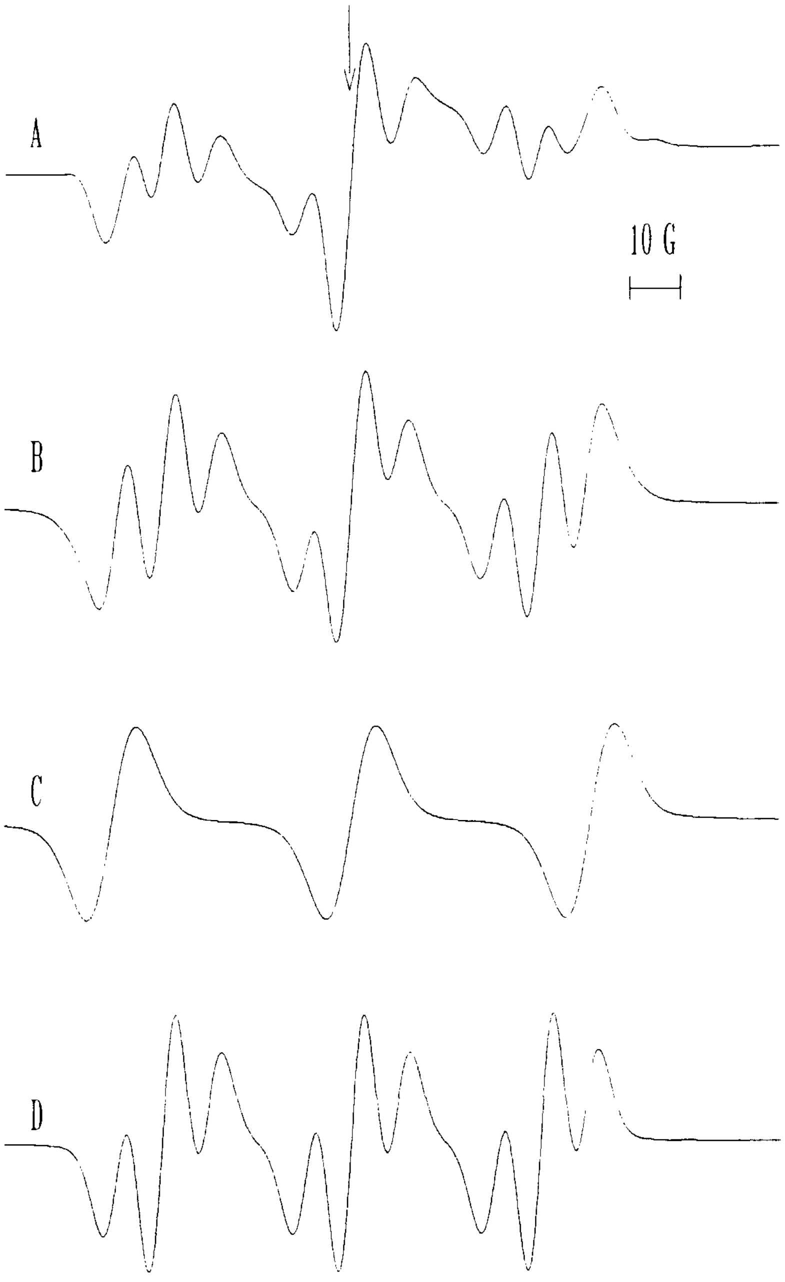
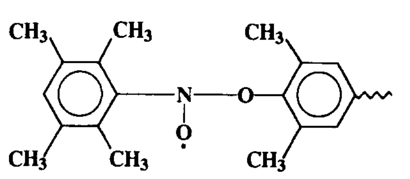


Figure 4 The observed e.s.r. spectrum of the spin adduct (A) formed by PPO film irradiation in the presence of a deaerated ethanol solution of ND is compared with (B) a simulated e.s.r. spectrum obtained by superposition of the calculated spectra of the (C) and (D) components

13 G for carbon-atom-centred radicals to 24 G for alkoxy alkyl nitroxides[26–28], the component (C) is assigned to spin adduct I (SA–I):

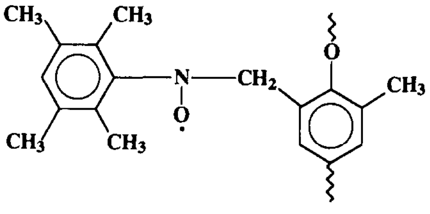


Triplet : $a_N \doteq 17.5$ G $g = 2.0060$

(see component C in fig. 4)

SA - I

In fact, the spectrum (C) is characterized by both an $a_N = 17.5$ G and the absence of further splittings due to β-H couplings. On the other hand, the component (D), showing a triplet of triplets, is attributed to spin adduct II (SA–II), which is due to reaction of ND with benzylic-type radicals generated by u.v. irradiation:



Triplet of triplets : $a_N = 13.8$ G $a_{H\beta} = 3.2$ G $g = 2.0058$

(see component D in fig. 4)

SA - II

Since the calculated (D) component shows (i) an a_N value (13.8 G) typical of a carbon-atom-centred radical,

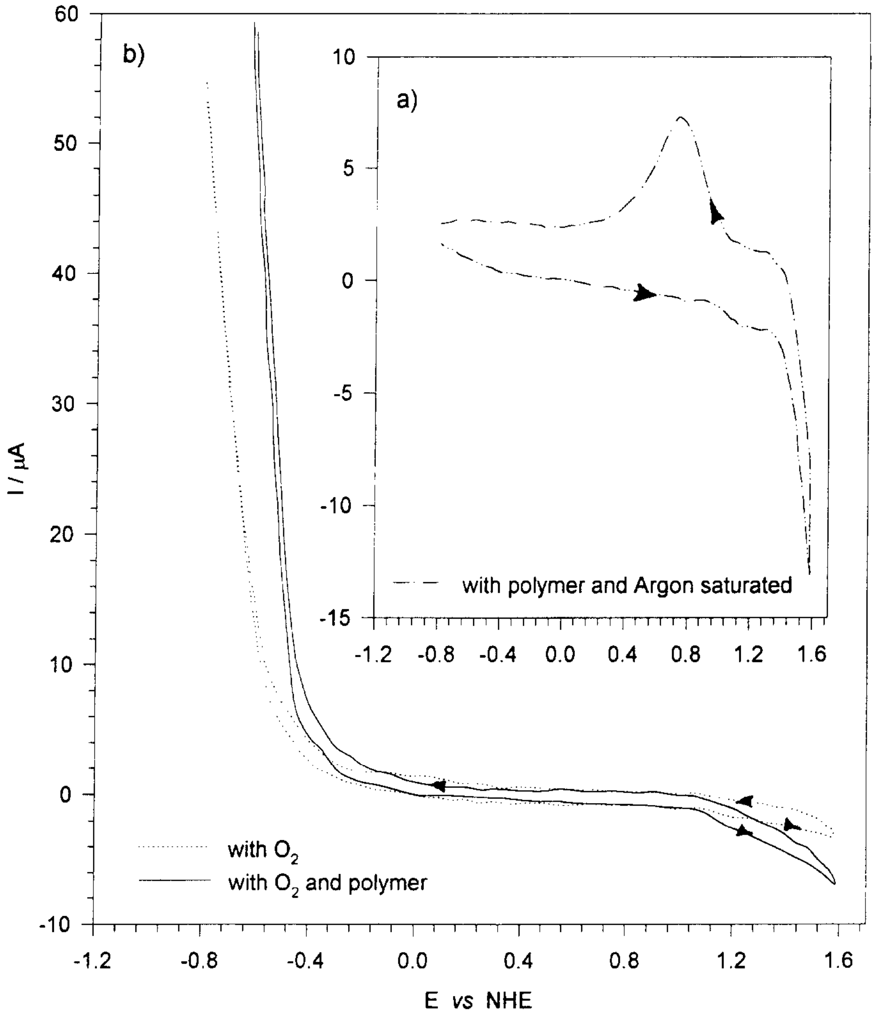


Figure 5 Cyclic voltammetry curves for glassy carbon electrode in CH_2Cl_2 and tetrabutylammonium perchlorate (see text): (a) argon deaerated solution containing PPO after potential holding at 1.25 V for 3 min and (b) oxygen saturated solution with and without PPO

(ii) $a_{H-\beta}$ constant splitting of 3.2 G, leading to discrimination with alkyl radicals giving greater $a_{H-\beta}$ values than the corresponding aromatic ones, and (iii) two equivalent β-hydrogen couplings in agreement with some previous studies[29], we are in favour of a benzylic-type chemical structure of trapped radicals. No radicals were trapped at long-wavelength irradiation under the same irradiation conditions.

However, the formation of the benzylic-type radicals under u.v. irradiation into the e.s.r. cavity in the absence of oxygen cannot be unequivocally explained by the spin-trapping experimental results. The benzylic-type radicals can be formed both by a C–H bond photolysis and by some possible hydrogen abstraction reactions on the methyl substituents. In fact, other primary radicals, e.g. radicals **1** and **1a** (see *Scheme 1*), originated by a photolytic chain scission process can induce hydrogen abstraction reactions under the same irradiation conditions. The great stability of e.s.r. signal intensity assigned to PDMP radicals clearly suggests that these radicals are not involved in further radical processes, while a possible hydrogen abstraction reaction due to radical **1a** could originate benzylic-type radicals in the absence of oxygen. This radical process can explain why in PPO film under u.v. irradiation the radical **1a** has not been trapped, but in the same conditions the radical **1a** could alternatively dimerize or induce a rearrangement of the aromatic ring by the cage effect. Tsuji[7,8] observed the e.s.r. signal of peroxy radicals under u.v. irradiation at −196°C of PPO powder in the presence of oxygen, but the possible formation of peroxy radicals and the corresponding unhindered phenols by oxygen attack of radical **1a**, as previously reported under accelerated photo-oxidative conditions (see *Scheme 3*)[11], could also promote hydrogen abstraction reactions forming benzylic-type radicals. Usually, the hydrogen abstraction reaction does not take place or is of no importance with sterically hindered phenols, but its probability increases with decreasing phenoxyl radical stability[20]. The existence of benzylic-type radicals is proved by the spin-trapping results, but their formation mechanism cannot be unequivocally explained under u.v. irradiation.

Electrochemical measurements

In *Figure 5* are shown the current–potential curves obtained for a glassy carbon RDE in the presence of the polymer in CH_2Cl_2. *Figure 5a* shows the cyclic voltammetry in the argon deaerated solution; the increase in the anodic current above 1.2 V is attributed to the oxidation of the polymer. This current is not diffusion-controlled, as indicated by the lack of dependence on stirring. In effect, an examination of the electrode revealed that a thin film of the polymer covered the surface.

When the electrode potential is held at the upper limit

(~1.4 V), a reduction peak appears at 0.52 V during the reverse scan. The formation of reducible species upon oxidation is in keeping with the data reported above in this work, which provide evidence of long-lived radicals and quinonic compounds.

In *Figure 5b* are shown the current–potential curves obtained in O_2 saturated solutions in the absence and in the presence of the polymer. In the latter case, one observes a noticeable catalytic effect on the electroreduction of O_2. In the non-aqueous solvent used in this experiment, the reduction of O_2 leads to O_2^-; and the observed catalytic effect can be reasonably attributed to an increase in the rate of the first electron transfer.

A possible reason for the catalytic effect on the electroreduction of O_2 is the introduction, on the electrode surface, of quinonic species produced by the oxidation of the polymer. In this respect, it is interesting to note that quinones are reported to play a major role in the electron-reduction of oxygen on carbon electrodes[30]. An increase in the concentration of these species can account for the observed catalysis.

The results of the electrochemical experiments are in fair agreement with the conclusions drawn from the other investigation discussed in this work. A separate, deeper electrochemical study on this system is worth while and is presently being considered in our laboratories.

FT*i.r. spectra of PPO film under accelerated oxidative conditions*

The formation of oxidation products of PPO has been followed by *FT*i.r. and u.v.-vis. spectroscopies. The main spectral changes in the *FT*i.r. spectra have been detected in the regions of hydroxyl, carbonyl and ether stretching vibrations and below 1050 cm^{-1}.

In the hydroxyl region, a broad band absorption centred at 3450 cm^{-1} is observed at short- and long-wavelength irradiation under accelerated conditions. According to some previous results[3,11], this band has been attributed to bonded hydroperoxides identified by titration with SO_2.

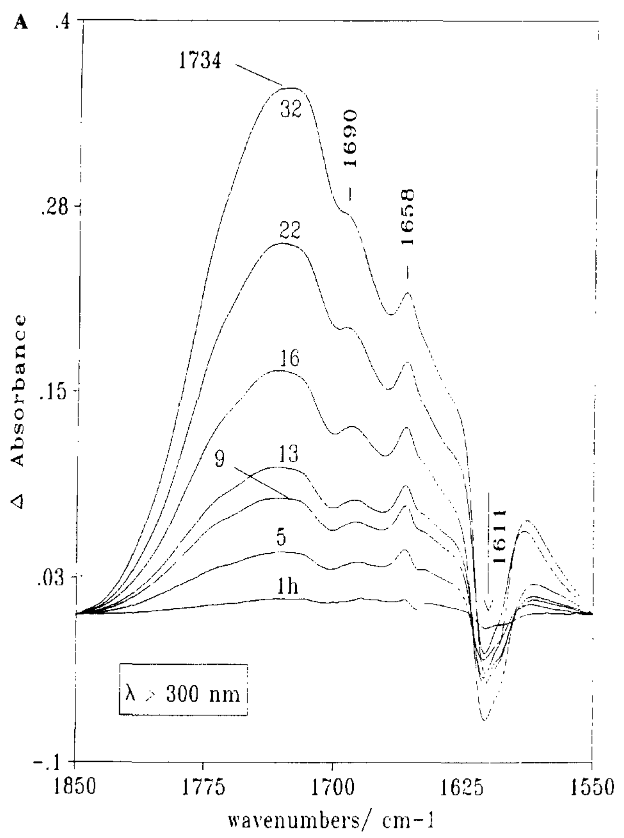
In the carbonyl region, the difference spectra shows the existence of both a broad band centred at 1734 cm^{-1} and two sharp absorptions at 1690 and 1658 cm^{-1} under short-wavelength irradiation as reported in *Figure 6A*. In the case of long-wavelength irradiation ($\lambda > 400$ nm), these two sharp bands exhibit stronger intensities than the corresponding ones shown in *Figure 6A*. After 1215 h under thermo-oxidative conditions at 80°C, the observed spectral changes in the carbonyl region are quite different. In fact, *Figure 6B* shows significant absorption bands at 1694 and 1658 cm^{-1} and only two weak ones at 1715 and 1735 cm^{-1}. These results confirm that the assignment of the band at 1734 cm^{-1} in *Figure 6A* has to be attributed to photolysis of two primary products associated with the main absorption bands at 1694 and 1658 cm^{-1} in the absence of light. These primary oxidation products decrease significantly after treatment with DNPH, while the other bands remain essentially unchanged. It is worth noting in *Figure 6B* that the comparison of *FT*i.r. spectra before (curve a) and after (curve b and c) the DNPH treatment allows detection of two bands that contribute to the strong absorption band at 1694 cm^{-1}; a strong band centred at 1694 cm^{-1} undergoes a significant decrease with DNPH and after two subsequent treatments (curves b and c) a pronounced shoulder is observed at 1684 cm^{-1}. Under thermo-oxidation conditions, the band at 1694 cm^{-1} in *Figure 6B* can probably be assigned to aromatic aldehydes in agreement with some previous results[11,31], while the uninfluenced shoulder with DNPH treatment at 1684 cm^{-1} can be assigned to a dimeric form of benzoic acid whose existence has been confirmed by SF_4 derivatization[11]. Furthermore, the band at 1735 cm^{-1} is mainly attributed to aromatic esters generated by further oxidation of aromatic aldehydes at 1694 cm^{-1} in these oxidation conditions. The weak bands at 1715 and 1775 cm^{-1} shown in *Figure 6B* are reasonably assigned to unbounded benzoic acid and peracids, respectively[11,32]. Unfortunately, the presence of other strong absorption bands in the *FT*i.r. spectra in the C–H stretching region (2850–2720 cm^{-1}) for PPO cannot give further evidence supporting the assignment of the band at 1694 cm^{-1} to aromatic aldehydes.

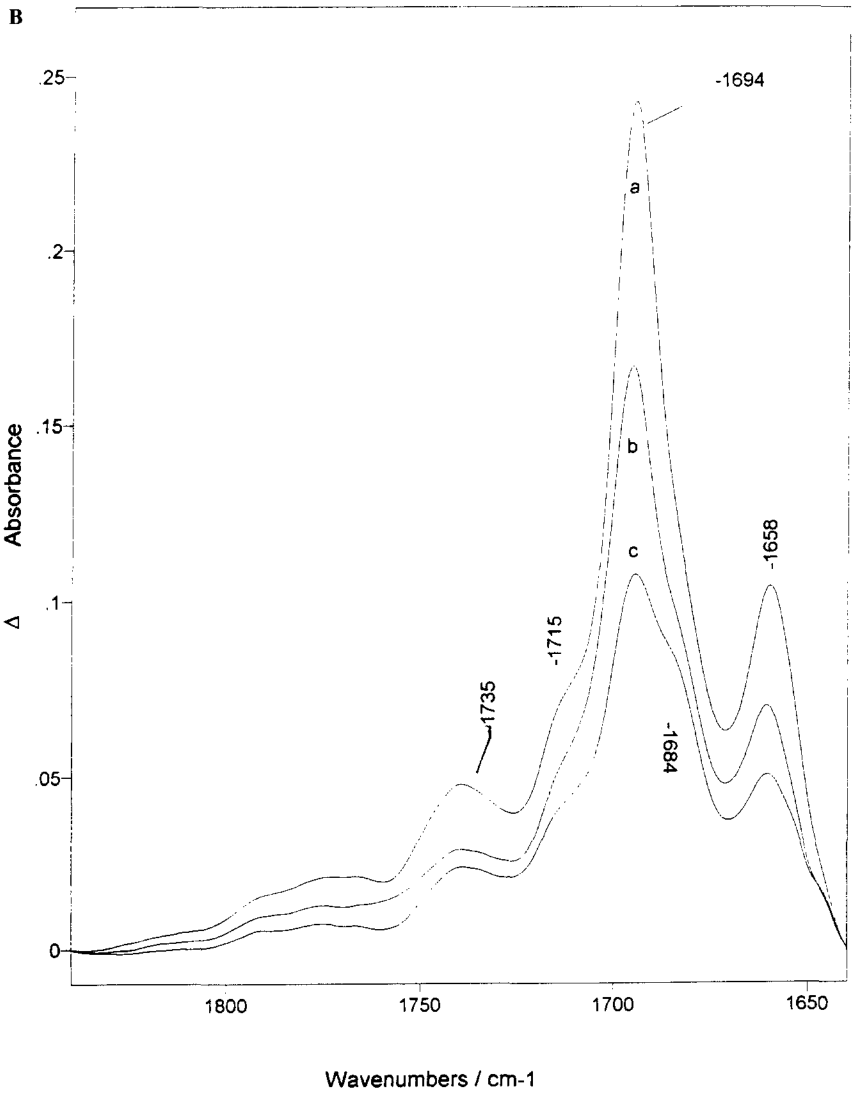
The other primary oxidation product associated with the band at 1658 cm^{-1}, which is still observed at the early stages of thermo-oxidation, is assigned to the formation of some quinonic compounds in agreement with the above-mentioned e.s.r. results (*Figure 3*).

The assignments of the observed bands under mild oxidation conditions are of great importance for the explanation of the complex band envelope reported in *Figure 6A*. In fact, under short- and long-wavelength irradiation, the changes in the *FT*i.r. spectra emphasize mainly the secondary photo-oxidation products which give rise to a broad band centred at 1734 cm^{-1} by the photolytic reactions of the primary oxidation products occurring at 1690 and 1658 cm^{-1} in the early stage of the accelerated photo-oxidation. For these reasons, we believe that the very broad band at 1734 cm^{-1} shown in *Figure 6A* is mainly due both to unbounded benzoic acids and to aromatic esters and saturated acids as the final photostable products originating from the above-mentioned photolabile intermediates. The aromatic aldehydes, detected in the mild oxidation conditions, are rapidly converted into the corresponding acids and esters under photo-oxidative conditions as indicated in *Scheme 1*[31]. This free-radical chain pathway for the degradation of PPO forming those oxidation products is also supported by the existence of the trapped benzylic-type radicals detected by e.s.r. spectroscopy.

The normalized area of the whole carbonyl complex band indicating the oxidation degree obtained under different oxidation conditions is shown in *Figure 7*. The yellowing of the thermo- and photo-oxidized films giving a long absorption tail up to 460 nm in u.v.-vis. spectra can be fairly well correlated with the carbonyl group content in agreement with some results reported elsewhere[3–11]. After 500 h under long-wavelength irradiation, the observed carbonyl group content is similar to the corresponding ones obtained under short-wavelength irradiation. In contrast, thermo-oxidation at 80°C reveals a low amount of carbonylic compounds also for long times indicating the important role of u.v. light in the degradation of PPO as shown in *Figures 2* and *3*. Since the kinetic behaviour of PDMP radicals derived from e.s.r. results both in the absence and in the presence of light can be correlated with the absorption band at 1658 cm^{-1}, we believe that these radicals are the precursors of quinonic compounds detected in *FT*i.r. spectra. Some additional infra-red spectral changes in the ether stretching vibrations are shown in *Figure 8A*. The band occurring at 1389 cm^{-1} increases and simultaneously two other ones at 1306 and 1379 cm^{-1} smoothly disappear during the photo-oxidation. According to some previous authors[33], the bands occurring at 1306 and 1186 cm^{-1} are assigned to backbone ether stretching vibrations, but only the former one, showing a medium intensity, can be adopted for reliable kinetic investigations. The other two bands at 1379 and 1389 cm^{-1} are reasonably attributed to in-phase deformation of methyl substituents and to ring stretching of some final stable oxidation products, respectively[34]. Aromatic acids are probably responsible for the absorption of 1389 cm^{-1}, because they typically show a strong band in that region. Some experimental absorbance changes involving both the methyl substituents or the ether vibrations are not clearly observed in other spectral regions for thin films.

Finally, *Figure 8B* shows that all observed bands below 1050 cm^{-1} decrease smoothly during accelerated photo-oxidation. In contrast with previous results[11], we assign the band at 1021 cm^{-1} to in-plane CH bending vibration of the aromatic ring sometimes interacting with carbon–carbon ring stretching[34], while the remaining decreasing absorption (see *Figure 8B*) is assigned to CH out-of-plane bending vibrations of aromatic rings sensitive to ring substitution. All these bands indicate a loss of aromaticity of the polymer backbone, as also





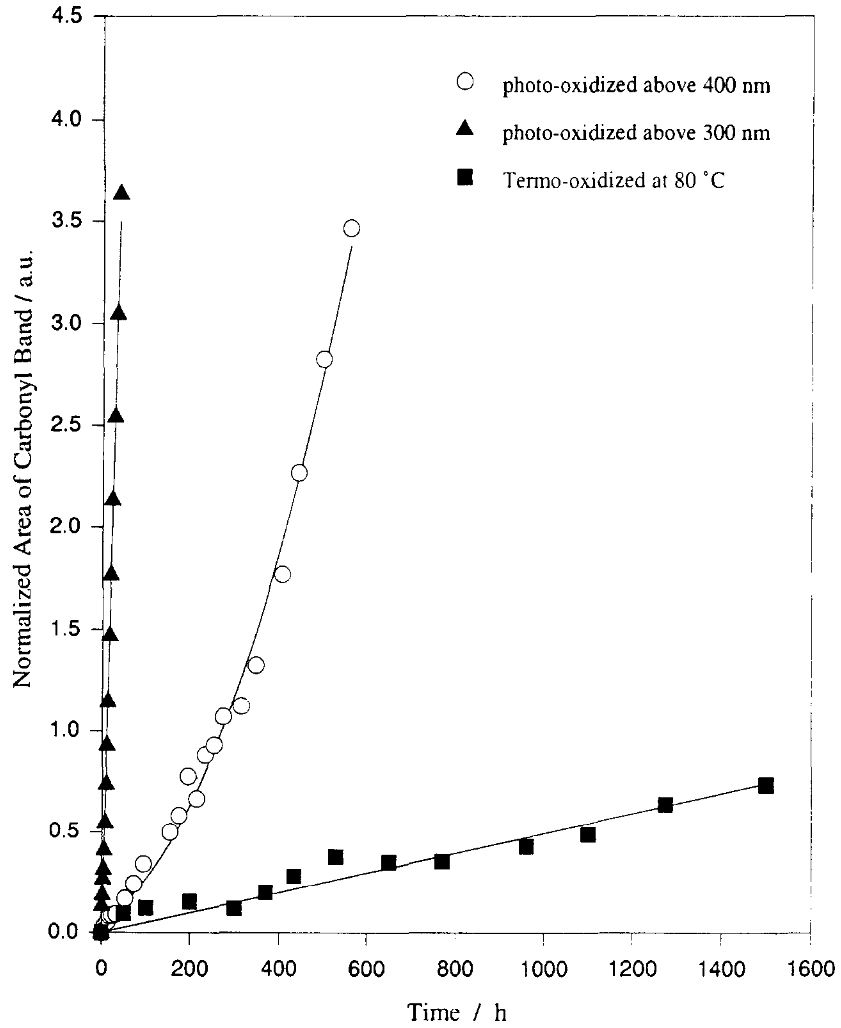


Figure 7 The oxidation degree calculated from the normalized area of the carbonyl band (1840–1625 cm^{-1}) detected by *FT*i.r. is reported as a function of different oxidative conditions (see text)

found for the disappearance of the band at 1611 cm^{-1} (see *Figure 6A*). In fact, superoxide radical anions can then attack the aromatic rings of the backbone giving rise to some photolabile products, e.g. peroxides and endoperoxides, which when illuminated by U.V. light undergo a further reaction via the ring-opening oxidation reactions of phenyl rings. These photo-labile products can generate some unstable products such as α,β-unsaturated carbonyl compounds and quinones, as recently proposed by Pickett[35]. Accordingly the disappearance rate of all aromatic bands of *Figure 8B* can be correlated with the formation of carbonylic compounds in the different oxidation conditions. Unfortunately, their formation cannot be definitely ascertained by *FT*i.r. spectroscopy because of the presence of other oxidation products due to the benzylic-type oxidation radicals, which give rise to absorption bands at similar wavenumbers[32].

Degradation mechanism of PPO under photo-oxidative conditions

In order to suggest a mechanism for the photodegradation of PPO, we have to consider the existence of four main pathways due to (a) the presence of benzylic-type radicals as intermediates for further oxidation reactions by a free-radical chain mechanism, (b) the formation of PDMP radicals by direct photolysis of polymer backbone, (c) $O_2^{-\cdot}$ generation by photo-induced electron transfer and (d) a photo-catalytic role of quinones under long-wavelength photo-oxidative conditions.

The former degradative pathway involving the methyl substituents is supported by the detection of the trapped benzylic-type radicals in the solid state (see *Figure 4*) produced both by highly probable hydrogen abstraction reactions or by the C–H bond photolysis on the methyl substituents[3]. The free-radical chain oxidation of the methyl substituents has also been demonstrated under mild oxidation conditions, i.e. thermo-oxidation at 80°C, where some final stable oxidation products are reasonably attributed to benzoic acids and aromatic aldehydes using a DNPH treatment. Accordingly, a modification reaction of PPO by using radical initiators, such as organic peroxides or brominating agents, can represent a

Figure 6 *FT*i.r. spectral changes of carbonyl region: (A) under accelerated short-wavelength irradiation; and (B) after thermo-oxidation at 80°C for 1215 h (curve a) and two subsequent treatments with a DNPH solution of the previous thermo-oxidized film (curves b and c)

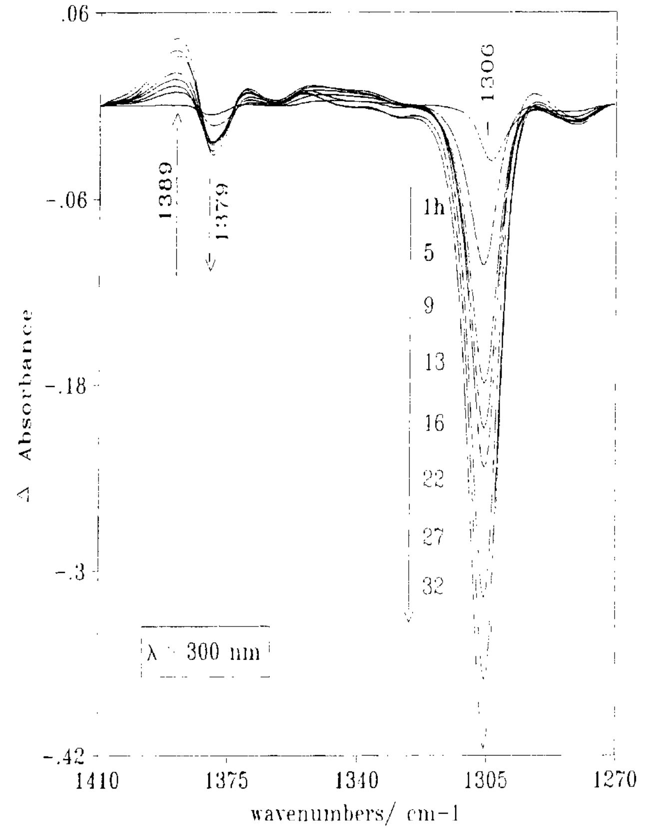


Figure 8A *FT*i.r. spectral changes in the region of ether stretchings and in plane-deformation vibrations under given photo-oxidative conditions

well known efficient method to prepare bromomethylated PPO[36] by hydrogen abstraction reactions induced by peroxy or halide radicals. Since a low amount of PDMP radicals can be formed by the cleavage of ether bonds also in the absence of u.v. light (see *Figure 2*), the generation of superoxide radical anions can play a negligible role under these oxidation conditions. In fact, the slight infra-red spectral changes below 1050 cm^{-1} for long times, showing a low degree of aromaticity loss of polymer matrix, are in favour of no involvement of $O_2^{-\cdot}$ under thermo-oxidative conditions. Thus, we believe that the pathway (a) shown in *Scheme 4* is prevailing both under thermo-oxidative conditions ($T \geqslant 80°C$) and in the presence of high contents of unhindered and peroxy radicals in polymer matrix as shown by some modification reactions of PPO.

The second pathway (b) is attributed to the direct photolyis of polymer backbone in agreement with the e.s.r. results in the absence of oxygen as shown in *Figures 3* and *4*. Much experimental evidence has been reported in the literature on the formation of these radicals under photo-oxidative conditions[1-9]. On the other hand, the pathway (c) has to be considered as an additional process originating PDMP radicals in the presence of oxygen. In contrast with the previous mechanism suggested by Pickett (see *Scheme 2*), we believe that superoxide radical anions can be directly generated by a photo-induced electron-transfer process, since the excited state of the polymer backbone can show higher reducing properties than the corresponding ground state.

There are two considerations in favour of this hypothesis. The former is based on electrochemical results in dichloromethane solution, where the determined oxidation potential of the PPO ground state is 1.2 V. The calculated oxidation potential* of the excited state of PPO can be approximately estimated to be ~3 V[37], assuming that no electronic differences exist between the polymer solution and film. The strong reducing nature of the excited state is fairly well correlated with the high ability of the formation of $O_2^{-\cdot}$ under photo-oxidative conditions. These results argue against a self-sensitized electron-transfer oxidation, since the best candidate, thermodynamically speaking, for the reduction process is oxygen under those photo-oxidative conditions[37,38]. The second consideration is based on the fluorescence quenching of PPO (up to 50%) in oxygen saturated solution also observed in the presence of an electron-transfer quencher as reported elsewhere[9,38]. Thus, the excited state of PPO polymer backbone can efficiently originate with oxygen, either by energy- or electron-transfer processes, an excited complex (exciplex)[37]. Accordingly, Foote[38] has demonstrated that the photo-oxidation of some 2,4,6-trisubstituted phenols undergoes a photo-induced electron-transfer process forming superoxide radical anion and phenol radical cation pair via the intermediacy of singlet oxygen. Under those conditions, the formation of phenoxy radicals, detected spectroscopically, has been attributed to the cleavage of O–H bonds of the initial phenol radical cations.

On this basis, we suggest that a reappraisal of PDMP radical generation mechanism during PPO photo-oxidation can be summarized in *Scheme 4*. This mechanism explains that the formation rate of PDMP radicals (see *Figure 3*) can proceed both by a direct photolysis of polymer backbone in the absence of air (pathway (b)) and by an additional process generated by a photo-induced electron-transfer process from the electron-rich compound, i.e. polymer backbone, to oxygen to give a radical cation and superoxide anion pair ($D^{+\cdot}O_2^{-\cdot}$) under photo-oxidative conditions as shown in pathway (c) of *Scheme 4*. According to the mechanism suggested by Foote for trisubstituted phenols, those radical cation and anion pairs can be rapidly converted into stable PDMP radicals and superoxide anions by chain scission and electron-transfer reactions, respectively. Under our conditions, the involvement of singlet oxygen in the radical cation and anion pair generation cannot be ruled out during the photodegradation of PPO.

Furthermore, our electrochemical results show that quinone groups could be reduced instead of oxygen in CH_2Cl_2 solution. The lack of quinone-free PPO films, reasonably expected for the conventional oxidative

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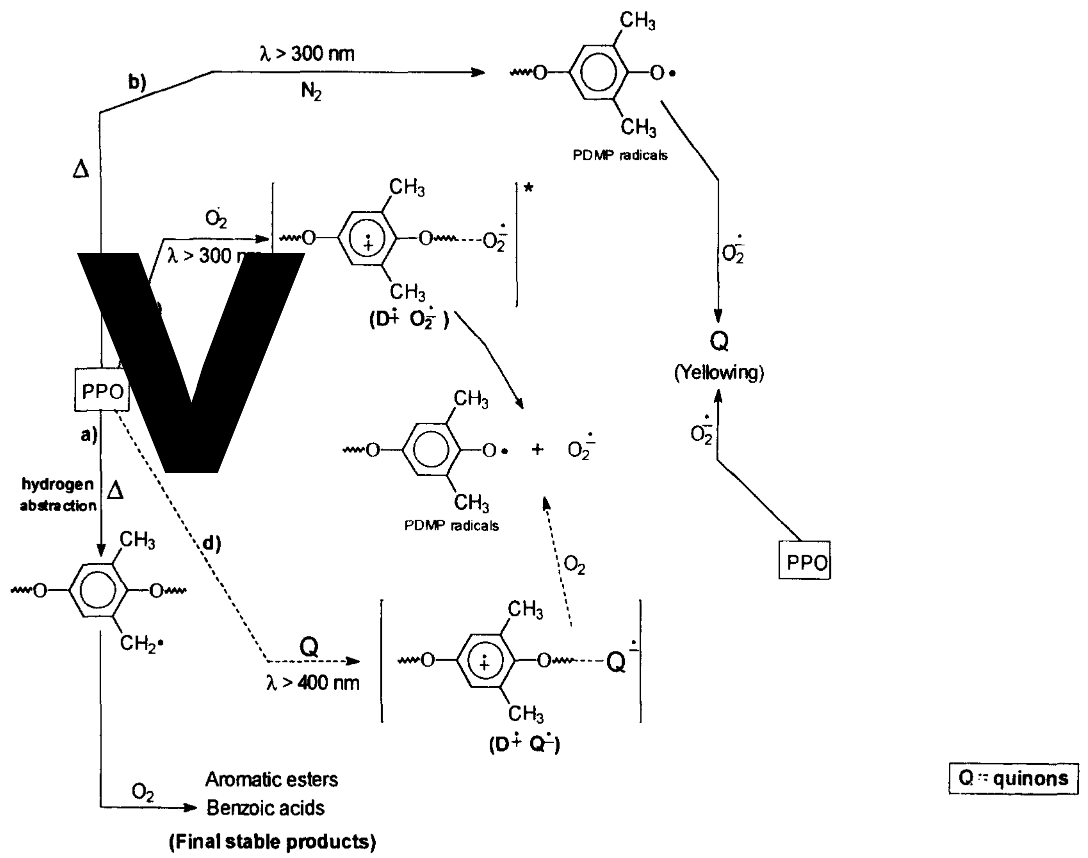
* It should be noted that the oxidation potential in the excited state can be readily calculated by the following equation:

$$E(PPO^{+}/PPO*) = E(PPO^{+}/PPO) - E^{00}$$

where PPO* is the polymer in the excited state, $E(PPO^{+}/PPO)$ is the oxidation potential of the ground state, estimated as ~ 1.2 V (see *Figure 5*), and E^{00} is the one-elecron potential corresponding to zero–zero spectroscopy energy derived from the difference energy between the ground and excited states. This energy can be experimentally determined by fluorescence and absorption spectra in dichloromethane solutions giving the energy of E^{00} vibronic transition, which for PPO is assumed at 295 nm, corresponding to $E^{00} \approx 4.2$ eV



Scheme 4

coupling polymerization of 2,6-dimethlyphenol[25], can probably generate a photo-induced electron-transfer reaction between PPO polymer backbone and some oxidation products, i.e. quinones (Q), forming a complex ($PPO^{+}Q^{-}$) as tentatively shown with dashed pathway (d) in *Scheme 4*. The subsequent reaction between quinone radical anions and oxygen, mentioned above in equation (2), could induce a possible photocatalytic effect of quinone groups giving rise to both further formation of superoxide radical anions and PDMP radicals in the presence of oxygen under long-wavelength irradiation[39–42]. This suggested mechanism could explain both the formation rate of carbonyl groups (see *Figure 7*) reaching high values after long photo-oxidation times and the enhancement of the e.s.r. signal intensity in the presence of oxygen under long-wavelength irradiation as

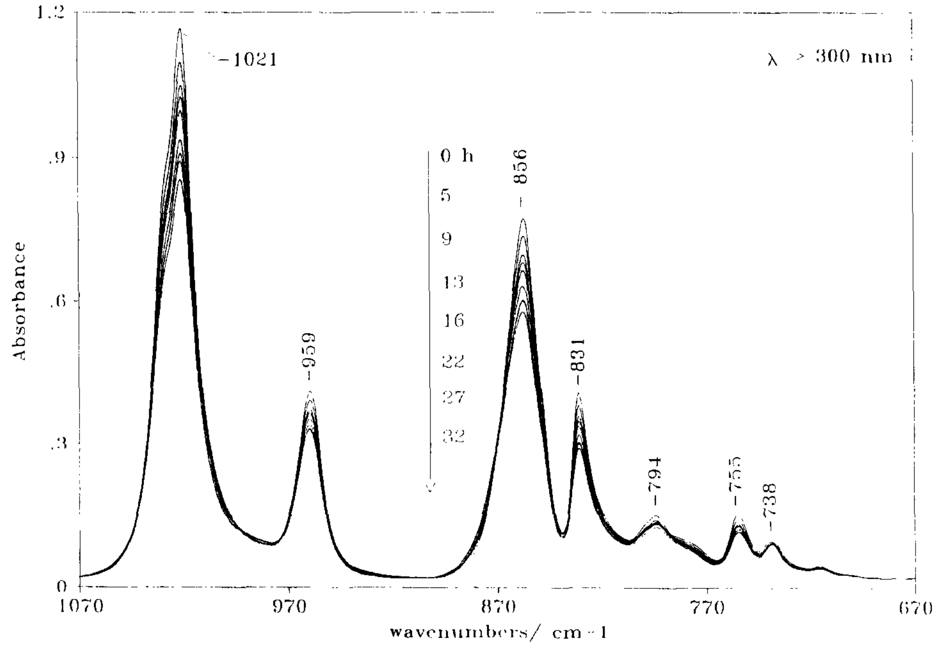


Figure 8B *FT*i.r. spectral changes in the region of in-plane and out-of-plane deformations of aromatic rings during the accelerated photo-oxidation under short-wavelength irradiation conditions due to a sensitized photo-oxidation of quinones previously formed in the early stage. However, a further and detailed investigation will be necessary to demonstrate the role of those oxidation products on the overall photodegradation of PPO.

CONCLUSIONS

The combination of e.s.r. and *FT*i.r. spectroscopies shows that two main processes forming PDMP radicals can take place during the photo-oxidation of PPO. The former process explains the enhancement of e.s.r. signal intensity in the presence of oxygen forming simultaneously superoxide radical anions and PDMP radicals by a photo-induced electron-transfer reaction. The subsequent photodegradation process occurs because the superoxide radical anion can efficiently react both with PDMP radicals and polymer backbone forming quinones and/or unsaturated carbonyl compounds by ring-opening reactions. These e.s.r. results are in fair agreement with *FT*i.r. spectral changes. The second process is tentatively attributed to the existence of a photocatalytic effect of quinone groups, as suggested by cyclic voltammetry measurements, which provide a further process to generate superoxide anions and PDMP radicals in the solid state under long-wavelength irradiation. Besides, a concomitant free-radical chain mechanism involving the methyl substituents by most probably hydrogen abstraction reactions cannot be ruled out in the photo-oxidation of PPO. Conclusively, the glassy nature of PPO should probably restrict both superoxide and other oxidation product generation on film surfaces under photo-oxidative conditions.

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