

## Photosensitized Degradation of Polyolefins

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### Synopsis

The effect of aromatically substituted dienes such as 1,1,4,4-tetraphenylbutadiene (TPB) as sensitizers of the accelerated oxidative photodegradation of polyethylene has been studied. The mechanism of photosensitization has been investigated by ESR and IR spectroscopy, while the degradation rate has been monitored by following the change of the mechanical properties during accelerated indoor and outdoor weathering tests. It was found that TPB is an efficient sensitizer for the oxidative degradation of polyethylene. The degradation of the polymer takes place via  $^1\text{O}_2$  formation, and it was interpreted on the basis of two simultaneous processes. In the first, excited singlet oxygen ( $^1\text{O}_2$ ) is produced by TPB itself or by ketonic impurities present in the polymer. In the second,  $^1\text{O}_2$  reacts with TPB giving benzophenone, peroxides, and other oxygenated products which in turn can promote the degradation of polyethylene. Irradiation carried out in the absence of air seems to rule out the possibility of a photodegradation mechanism via excitation of TPB to an upper excited state capable of hydrogen abstraction from the polymer.

### INTRODUCTION

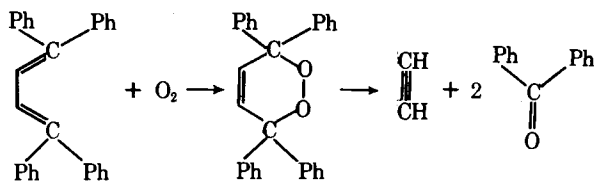
The photo-oxidative degradation of polyolefins, induced by photoactive groups such as aromatic or ketonic derivatives, has been intensively studied during the last few years, also in connection with the problem of combating environmental pollution by plastic waste.<sup>1-6</sup>

The mechanism of sensitization of these compounds used as additives or covalently bound to the polymer via grafting<sup>7</sup> or copolymerization<sup>8</sup> has been interpreted in terms of a direct hydrogen atom abstraction process and/or in terms of the well-known Norrish type I and type II reactions. The photosensitized formation of excited singlet oxygen ( $^1\text{O}_2$ ) induced by aromatic ketones,<sup>9</sup> dyes,<sup>10</sup> or aromatic hydrocarbons<sup>11</sup> has also been postulated as further factor in the photodegradation of the polymer.

However, for aromatic derivatives, besides the possibility of singlet oxygen sensitization as a way of inducing photo-oxidative degradation, a further mechanism of sensitization has been suggested. In fact, the induced photodegradation of polyethylene activated by phenanthrene or quinoxaline<sup>6</sup> has been attributed to a mechanism of biphotonic excitation of the additive to an upper excited triplet state capable of inducing allylic hydrogen abstraction followed by the formation of peroxy radicals.

In connection with the problem of the induced photodegradation of polyolefins by aromatic derivatives, we report here a study on the photooxidative behavior of polyethylene activated by aromatically substituted dienes such as 1,1,4,4-tetraphenylbutadiene (TPB).

We have found that TPB indeed sensitizes the photodegradation of polyethylene, and we have tried to establish whether this compound can act as sensitizer of singlet oxygen formation ( $^1\text{O}_2$ ) or can react directly with the polymer by a process of hydrogen atom abstraction via an upper excited state. Moreover, we have also tried to establish whether the real sensitizer of the photodegradation of polyethylene is the benzophenone formed by the reaction of TBP with singlet oxygen, according to the scheme reported by Rio and Berthelot<sup>12</sup>:



## EXPERIMENTAL

The polymers used were samples of both low-density, LDPE (Riblene B 24 ANIC), and high-density, HDPE (A 1050 Solway; SS 538 ANIC), polyethylene.

1,1,4,4-Tetraphenylbutadiene of very high purity supplied by Koch-Light Lab. was used without any further purification. The additive was introduced in the polymers by use of a mixing roll at about 160°C. The effective concentration of the additive was determined from IR spectra of thin film making use of a calibration curve and reading the absorbance of the maximum at 761  $\text{cm}^{-1}$ , characteristic of TPB. Rods and thin films (0.1–0.2 mm thick) of the polymers were obtained by hot press.

Both thin films and rods were irradiated with an Osram 6000-W xenon arc lamp, fitted with water-cooling Pyrex glass jacket (effective wavelength above 290 nm) and placed at a distance of 47 cm according to ASTM E 239. The effective sample temperature was 30° ± 2°C.

The outdoor weathering tests were carried out in Sicily during the period February–May, exposing samples of activated polyethylene at a 45° angle facing south. The films were exposed in stepwise fashion, and changes in IR spectra, carbonyl absorbances, ESR spectra, and per cent elongation (%El) were measured at each interval.

Per cent elongation was measured on microtensile specimens according to ASTM D-1708. Carbonyl absorbances referred to sample thickness were measured at 1715  $\text{cm}^{-1}$  on a P. E. Model 325 spectrometer.

ESR measurements were carried out with samples previously purified by dissolution in boiling xylene, reprecipitation in methanol, and washing with *n*-hexane. ESR spectra were recorded on a Varian E-4 spectrometer

equipped with ancillary temperature control unit. Irradiation in the ESR cavity was carried out with superhigh-pressure xenon-short arc lamp (Illumination Industries Inc., 100 W). Pyrex glass filters kept the effective wavelength above 290 nm.

ESR measurements were carried out at  $-196^{\circ}\text{C}$  under irradiation both in the absence and in presence of air. For ESR measurements in the absence of air, the samples were first kept at  $60^{\circ}\text{C}$  under a vacuum of  $10^{-5}$  torr for 24 hr, sealed in a quartz tube under  $\text{N}_2$  pressure, and then irradiated. Viscosity measurements were carried out in decaline (concn. 0.1 g/100 ml) at  $135^{\circ}\text{C}$  with a Scott Viscotimer, and the intrinsic viscosities were calculated according to the equation<sup>13</sup>

$$[\eta] = \frac{1}{C} [2(\eta_{\text{spec}} - \ln \eta/\eta)]^{1/2}.$$

The average molecular weights were obtained by intrinsic viscosity measurements.

The extraction of irradiated polyethylene was carried out by dissolution in boiling toluene and reprecipitation with methanol. The solution was evaporated to dryness and the residue dissolved again in chloroform to be analyzed by gas chromatography-mass spectroscopy or TLC. The TLC experiments were carried out by applying the chloroformic solution on silica gel F<sub>254</sub> (Merck) using benzene-*n*-hexane (83:20) as developing system. The gas-chromatographic-mass-spectrophotometric determinations were carried out on a Varian MAT III GC-MS spectrometer.

## RESULTS AND DISCUSSION

The accelerating effects of TPB on the rate of photodegradation of polyethylene, both in indoor and outdoor weathering tests, are shown in Figures 1, 2, 3, and 4 where the rate of carbonyl formation and the loss of elongation are reported. From the experimental data, it is evident that the rate of carbonyl formation, though useful, is not always a good screening tool for polymer degradation. This is emphasized by the fact that although LDPE shows a carbonyl index higher than HDPE after the same time of irradiation ( $\sim 200$  hr), in the case of HDPE the per cent elongation is already reduced to zero, while this is not the case of LDPE, which still retains most of its plastic properties. From intrinsic viscosity measurements, a reduction of about 50% of molecular weight can be calculated when % El = 0. The absence of any gel when the polymer is dissolved for measurements of intrinsic viscosity seems to indicate a prevalence of chain scission versus termination by radical combination followed by cross-linking.

Chromatographic separation of the products obtained from toluene extraction at different stages of irradiation of polyethylene activated by TPB leads to the identification of several compounds via gas chromatography-mass spectroscopy and TLC.

TPB was always found in all the extracts, its concentration decreasing with progress of the irradiation. Besides TPB, benzophenone, benzpinacol, and benzaldehyde were unequivocally identified. Another compound, having a molecular weight of 208, was identified as a diphenyl oxetene,

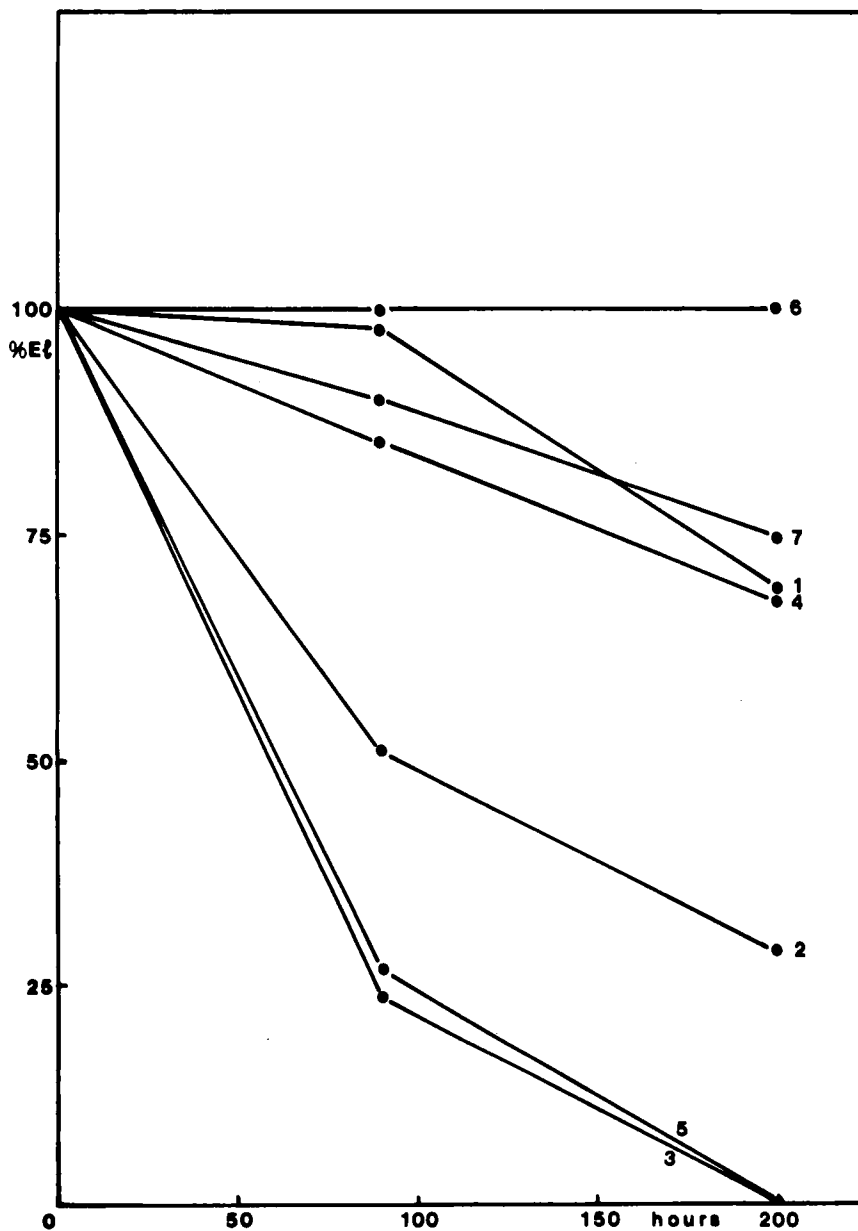


Fig. 1. Per cent elongation loss as function of irradiation time during indoor aging tests (xenon lamp): (1) HDPE SS 538 F<sub>1</sub> as reference; (2) HDPE SS 538 F<sub>1</sub> plus benzophenone 0.3%; (3) HDPE SS 538 F<sub>1</sub> plus TPB, 0.3%; (4) HDPE ELTEX A 1050 as reference; (5) HDPE ELTEX A 1050 plus TPB, 0.3%; (6) LDPE B 24/2 as reference; (7) LDPE B 24/2 plus TPB, 0.3%.

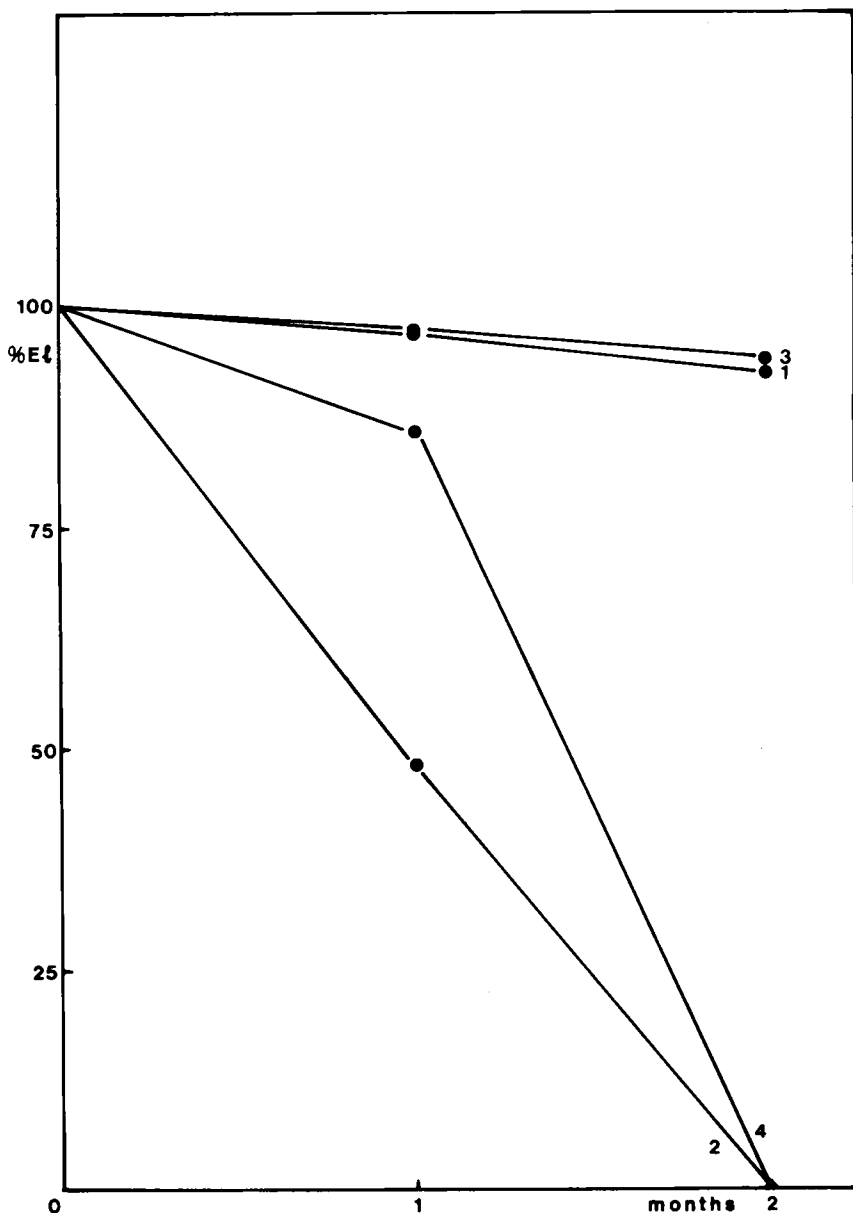


Fig. 2. Per cent elongation loss as function of irradiation time during outdoor aging tests: (1) HDPE SS 538 F<sub>1</sub> as reference; (2) HDPE SS 538 F<sub>1</sub> plus TPB, 0.3%; (3) HDPE ELTEX A 1050 as reference; (4) HDPE ELTEX A 1050 plus TPB, 0.3%.

probably obtained from the photochemical addition between benzophenone and acetylene.

When the irradiation of pure TPB was carried out in air and without photosensitizers ( $\lambda > 290$  nm), both in a solution of *n*-heptane or as a dispersion on neutral silica or alumina, the same compounds were obtained. These results could be explained on the basis of a primary photochemical

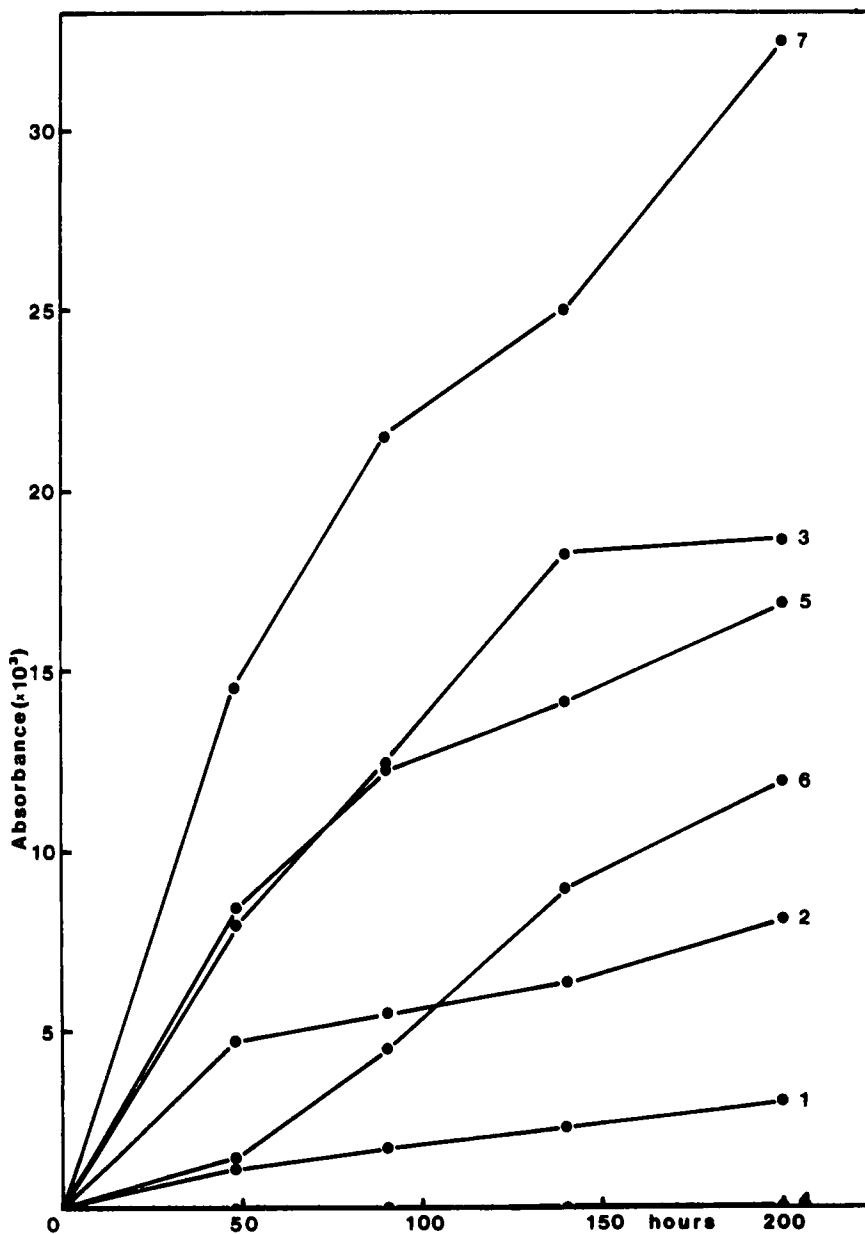


Fig. 3. Carbonyl absorption as function of irradiation time during indoor aging tests (xenon lamp) (all data are corrected for background absorption): (1) HDPE SS 538 F<sub>1</sub> as reference; (2) HDPE SS 538 F<sub>1</sub> plus benzophenone, 0.3%; (3) HDPE SS 538 F<sub>1</sub> plus TPB, 0.3%; (4) HDPE ELTEX A 1050 as reference; (5) HDPE ELTEX A 1050 plus TPB, 0.3%; (6) LDPE B 24/2 as reference; (7) LDPE B 24/2 plus TPB, 0.3%.

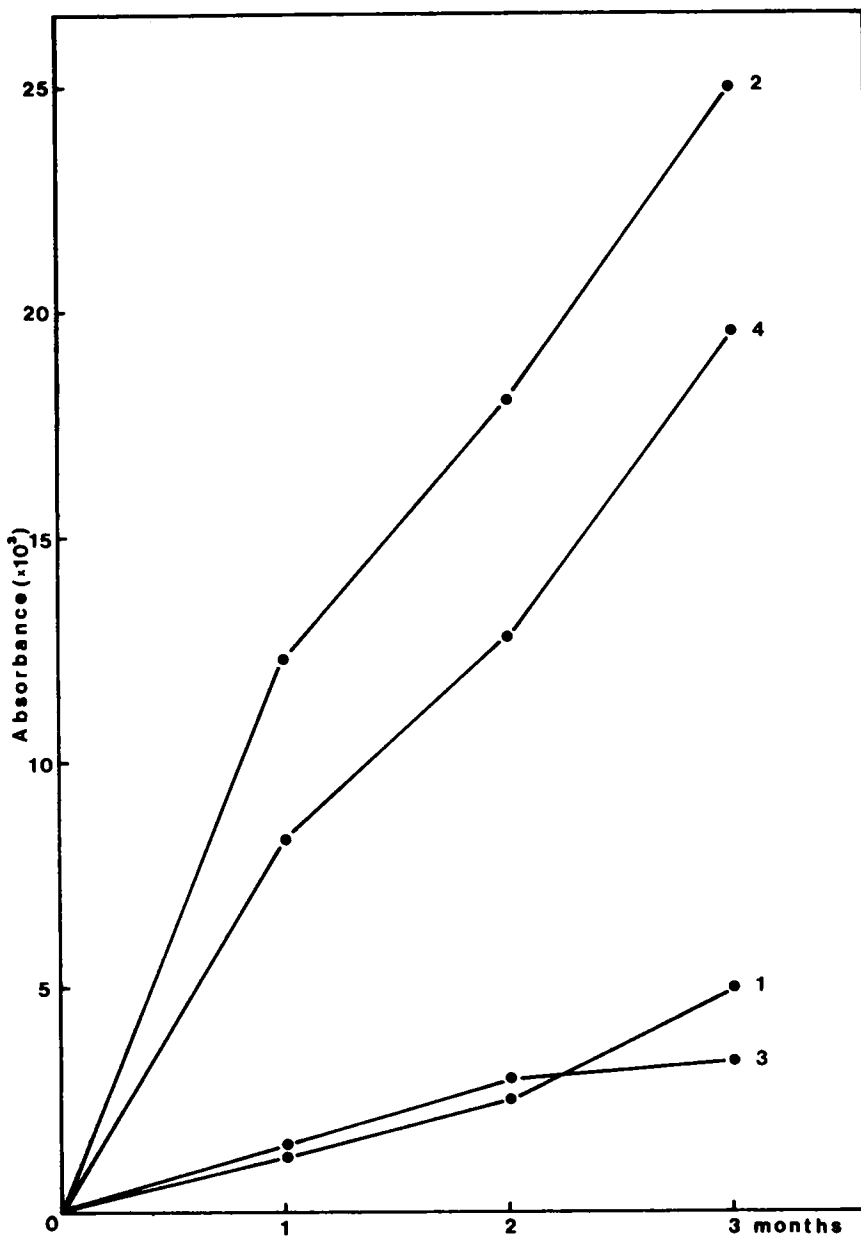


Fig. 4. Carbonyl absorption as function of irradiation time during outdoor aging tests (all data are corrected for background absorption): (1) HDPE SS 538 F<sub>1</sub> as reference; (2) HDPE SS 538 F<sub>1</sub> plus TPB, 0.3%; (3) HDPE ELTEX A 1050 as reference; (4) HDPE ELTEX A 1050 plus TPB, 0.3%.

process which involves the reaction of singlet oxygen with TPB, according to the scheme already reported by Rio and Berthelot.<sup>12</sup>

The possibility that the benzophenone formed through the above-mentioned mechanism may be the real and only sensitizer of the photodegradation of polyethylene was ruled out on the basis of the photochemical behavior and ESR spectra of the polymer activated by benzophenone.

In fact, polyethylene activated by an amount of benzophenone corresponding to the quantity theoretically obtainable by the reaction of singlet oxygen with TPB gave poor results in accelerated weathering tests when compared with polyethylene activated by the corresponding amount of TPB, as shown by Figures 1 and 2. Moreover, considering that the UV spectrum of TPB shows a very high adsorption at 350 nm, where also benzophenone adsorbs, and considering that a certain amount of TPB is present also after a long period of irradiation, it can be suggested that TPB would have a shielding effect on benzophenone, so hampering its efficiency as sensitizer.

Finally, the samples activated by benzophenone are reported to be extremely crosslinked at irradiation time corresponding<sup>14,15</sup> to % El = 0, contrary to those activated by TPB. The ESR spectra of pure polyethylene, and of polyethylene activated by TPB and benzophenone, irradiated in air ( $\lambda > 290$  nm), are shown in Figures 5, 6, and 7 as a function of temperature. The ESR spectra of the pure polymer at  $-196^\circ\text{C}$  and at higher temperatures agree well with the data reported in the literature<sup>16</sup> (Fig. 5). The broad, six-line signal observed at  $-196^\circ\text{C}$  is assigned to alkyl radicals of the type  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ , formed by hydrogen atom abstraction via a Norrish type I reaction of the carbonyl groups present along the polymer chain, while the signals observed at  $-130^\circ$  and  $-20^\circ\text{C}$  are attributed to peroxy radicals and allylic radicals, respectively.

When polyethylene is activated by TPB, a decrease of the intensity of the ESR signal, compared with the intensity of the ESR spectrum given by the pure polymer, is observed. This fact can be explained by a shielding effect of the additive or by energy transfer from the excited carbonyl groups in the polymer to TPB. However, the intensity of the ESR spectrum increases with prolonged irradiation, and after 25 hr a broad symmetrical singlet (width  $\sim 60$  G,  $g = 2.003$ ) (Fig. 6), attributed to allylic free radicals, is observed at  $-196^\circ\text{C}$ . The shoulders detectable besides the  $g = 2.003$  signal are attributed to alkyl radicals probably due to partial conversion of the allylic radicals under UV irradiation.<sup>17</sup> At  $-130^\circ\text{C}$ , an asymmetric signal (width  $\sim 100$  G,  $g_{\perp} = 2.008$ ,  $g_{\parallel} = 2.034$ ), similar to that given by the pure polymer and assigned to peroxy radicals, is observed. Finally, at  $-20^\circ\text{C}$ , a sharp singlet (width  $\sim 30$  G,  $g = 2.004$ ) assumed to be due to polyenyl radicals of the type  $-\dot{\text{C}}\text{H}-(\text{CH}=\text{CH})_n-$  is obtained. In the case of polyethylene activated by benzophenone (Fig. 7), the formation of a different type of radicals during the photodegradation, and therefore the existence of a different sensitization mechanism, is suggested by the ESR spectra when compared with polyethylene activated by TPB. In fact, at



–196°C, the same signal assigned to alkyl radicals in the pure polymer is observed. Again, a peroxy radical is obtained at –130°C. At –20°C, a broad, asymmetric spectrum is observed, probably due to the overlapping of signals originated by various kinds of radicals.

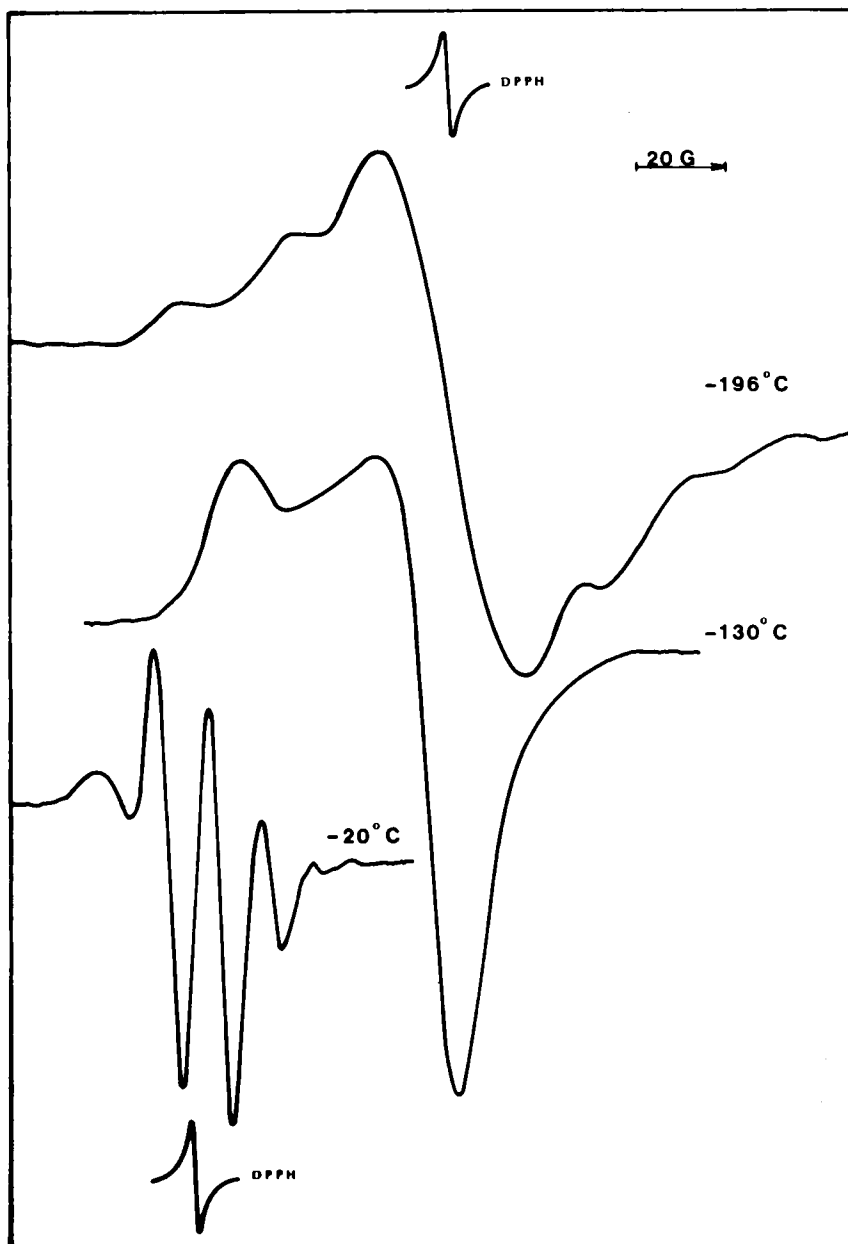


Fig. 5. ESR spectrum as function of temperature of pure polyethylene after 25 hr indoor aging in air.

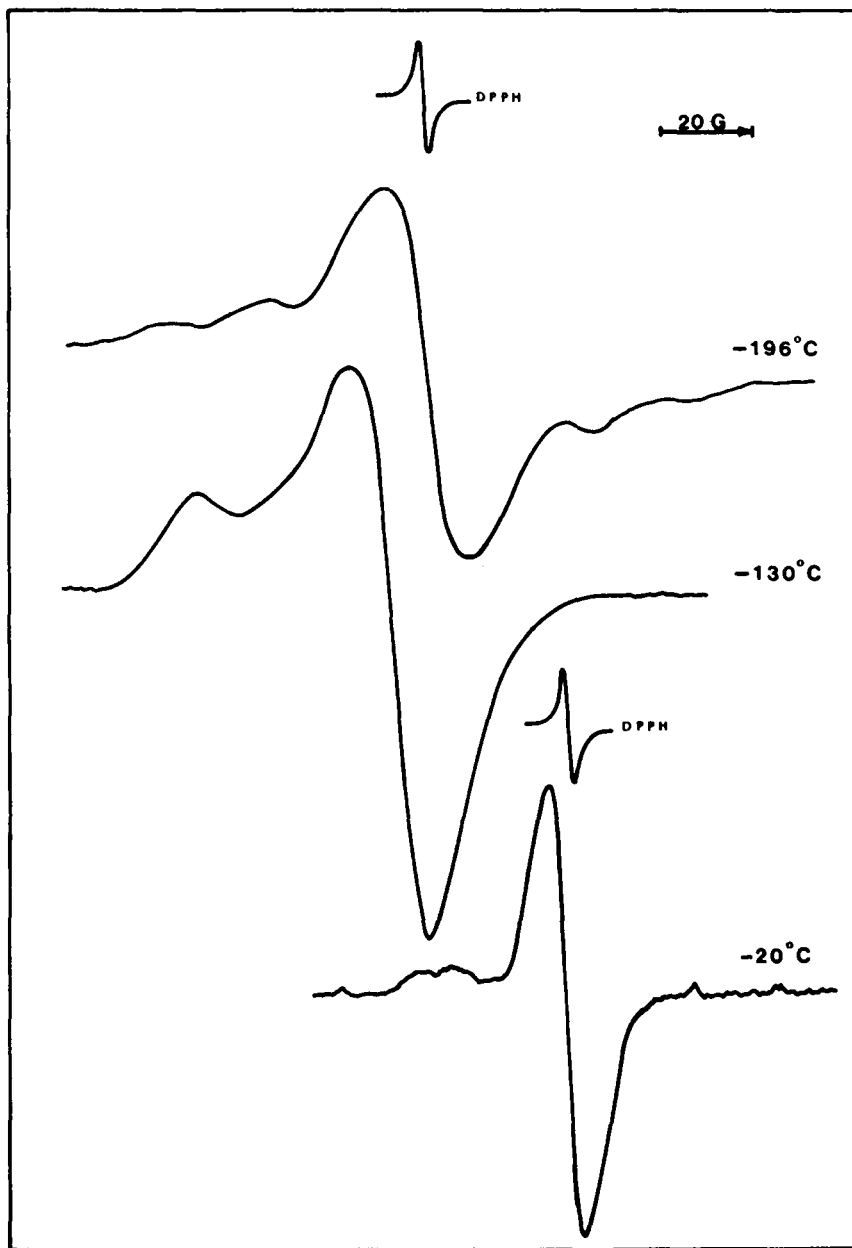


Fig. 6. ESR spectrum as function of temperature of polyethylene activated by TPB after 25 hr indoor aging in air.

ESR measurements of polyethylene activated by TPB and irradiated in the absence of air were also carried out. No growth of radicals is observed with aging and since that corresponds to the absence of any degradation of the polymer, the importance of the role played by oxygen in the photodegradation process is confirmed.

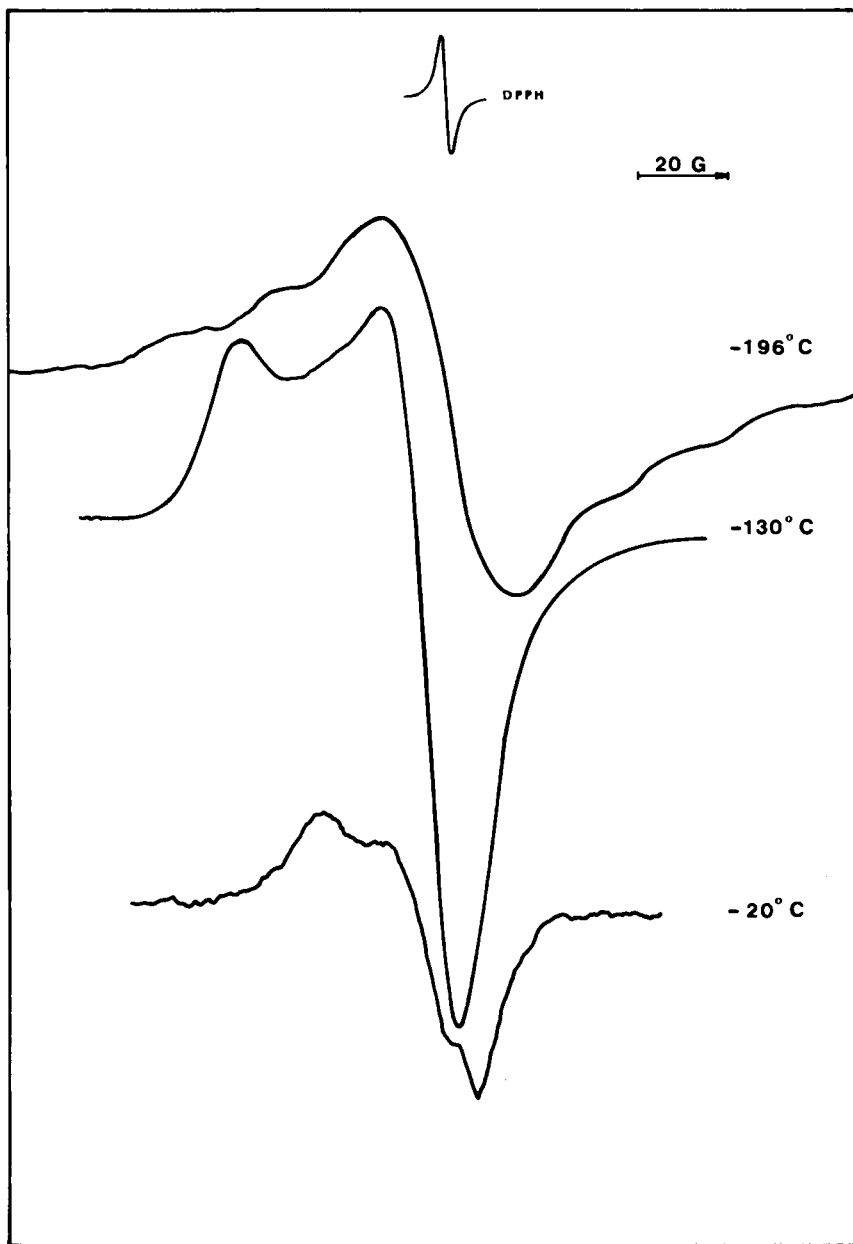


Fig. 7. ESR spectrum as function of temperature of polyethylene activated by benzophenone after 25 hr indoor aging in air.

In conclusion, on the basis of the results so far reported, it could be said that the sensitization of the photodegradation of polyethylene by TPB takes place through a complex mechanism which includes TPB and its photo-oxidation products such as benzophenone and possible active intermediates as peroxides. As said before, the identification of benzophenone

and diphenyl oxetene among the products extracted from the irradiated polyethylene suggests that the primary photochemical process sensitizing the photodegradation of the polymer could be explained according to the scheme proposed by Rio and Berthelot. Considering the spectral features of TPB, the formation of excited singlet oxygen ( $^1O_2$ ) could be due to photosensitization from preexisting carbonyl groups in the polymer chain or from some other impurities also present in the polymer. However, the fact that the degradation process seems not to depend on the type and degree of purification of polyethylene rules out this latter possibility.

On the other hand, the identification of benzophenone and related compounds also when pure TPB was irradiated in a solid matrix or in solution suggests that, although the high fluorescence of TPB indicates a poor i.s.c., it could be assumed that TPB itself might be the sensitizer of singlet oxygen formation. The identification of benzpinacol among the products of extraction indicates that the benzophenone formed from the photo-oxidation of TPB indeed participates in the degradation process, but considering the higher efficiency of TPB as additive when compared with benzophenone in the same molar concentration and the experimental results just now reported, it can be excluded that benzophenone plays the dominant role in the sensitization mechanism.

Therefore, although we were not able to detect unequivocally by TLC and GS-MS any peroxides from the extraction of irradiated polyethylene, the efficiency of TPB as sensitizer could be explained by supposing that besides benzophenone, other active intermediates such as peroxides are formed from the photo-oxidation of TPB and that these compounds may in turn be responsible for the hydrogen abstraction from the polymer which starts the degradation process.

Finally, the absence of photodegradation when the irradiation of polyethylene is carried out in the absence of oxygen leads us to exclude any direct participation of TPB in the photodegradative process via an excited state capable of direct hydrogen abstraction, as suggested for other aromatic additives.<sup>6</sup>

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