

Photosensitized Degradation of Polyolefins. II.

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Synopsis

The oxydative photodegradation of polyethylene sensitized by aromatically substituted dienes such as 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,4-diphenyl-1,3-butadiene (DPB) has been investigated. The rate of degradation has been monitored by following the change of the mechanical properties of the polymer during accelerated indoor aging tests. It was found that both additives are efficient sensitizers of the photodegradation of polyethylene. The mechanism of photo-oxidation has been investigated by ESR and IR spectroscopy and it has been interpreted on the basis of a complex mechanism which includes excited singlet oxygen (1O_2) and the products of photodegradation of the additives.

Singlet oxygen, produced by DPB and DPH and/or by impurities present in the polymer, reacts with the additives themselves and, directly, with polyethylene. In turn, the products of photodegradation of the additives react with the polymer via hydrogen atom abstraction, further promoting the photodegradation.

Irradiation carried out in absence of air seems to rule out the possibility of direct hydrogen atom abstraction by DPB and DPH.

In a previous paper,¹ we reported a study on the photo-oxidation of polyolefins sensitized by 1,1,4,4-tetraphenylbutadiene (TPB). This compound was found to be an efficient sensitizer of the photo-oxidation of the polymer, and the sensitization process was interpreted on the basis of a complex mechanism including singlet oxygen (1O_2) and the products of photodegradation of the additive.

On the basis of these results, we decided to extend our study to other substituted dienes, and here we report our investigations on the photodegradation of polyethylene sensitized by 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,4-diphenyl-1,3-butadiene (DPB). The polymer used in this study was high-density polyethylene, HDPE (A 1050 Solway; SS 538 ANIC). DPB and DPH of very high purity were supplied by Kock-Light Lab. and used without any further purification. The methods of sample preparation, irradiation, and ESR measurements have been already described.¹ The gas-chromatographic-mass-spectrophotometric determinations were carried out on a Varian MAT 111 GS-MS spectrometer. Figures 1 and 2 show the accelerating effect of DPB and DPH on the rate of carbonyl formation and loss of elongation of polyethylene used to evaluate the photodegradation rate of the polymer during accelerated indoor weathering tests.

In Figure 3 is shown the ESR spectrum as a function of temperature of pure polyethylene irradiated in air ($\lambda > 290$ nm). In agreement with the literature,² the spectrum observed at -196°C is identified as due to alkyl radicals formed in the polymer via a Norrish-type I reaction of the carbonyl groups present in

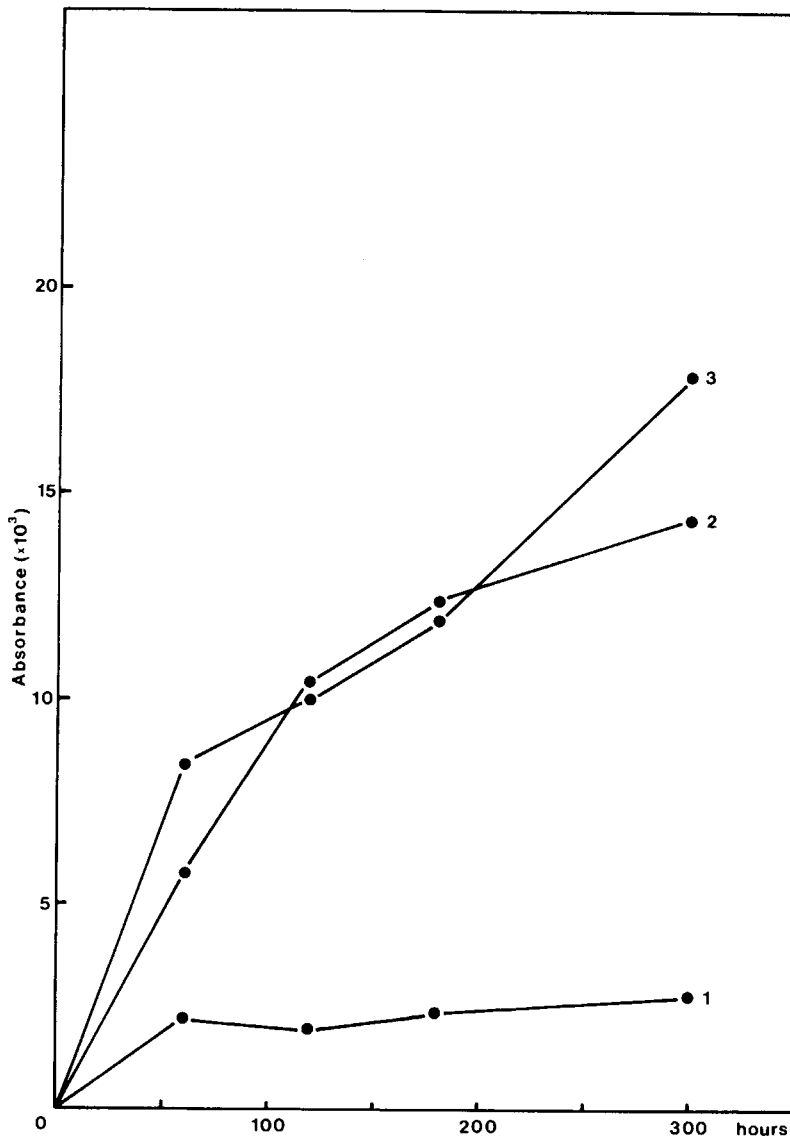


Fig. 1. Carbonyl absorption as function of irradiation time during indoor aging tests (xenon lamp, $\lambda > 290$ nm) (all data are corrected for background absorption): (1) HDPE ELTEX A 1050 as reference; (2) HDPE ELTEX A 1050 + DPB 0.3%; (3) HDPE ELTEX A 1050 + DPH 0.3%.

the polymer, while the signals observed at -130°C and -20°C are attributed to peroxy and allylic free radicals, respectively.

The addition to polyethylene of DPH and DPB results in a decrease of the intensity of the ESR spectrum, compared to the spectrum of the pure polymer. This can be caused by an optical filtering effect due to absorption by the additives and/or by energy transfer to the additives from excited carbonyl groups in the polymer. However, the intensity of the ESR signal increases with irradiation time; in Figures 4 and 5 are shown the ESR spectra of polyethylene activated with DPH and DPB, after 25 hr of irradiation. As can be seen, the two additives

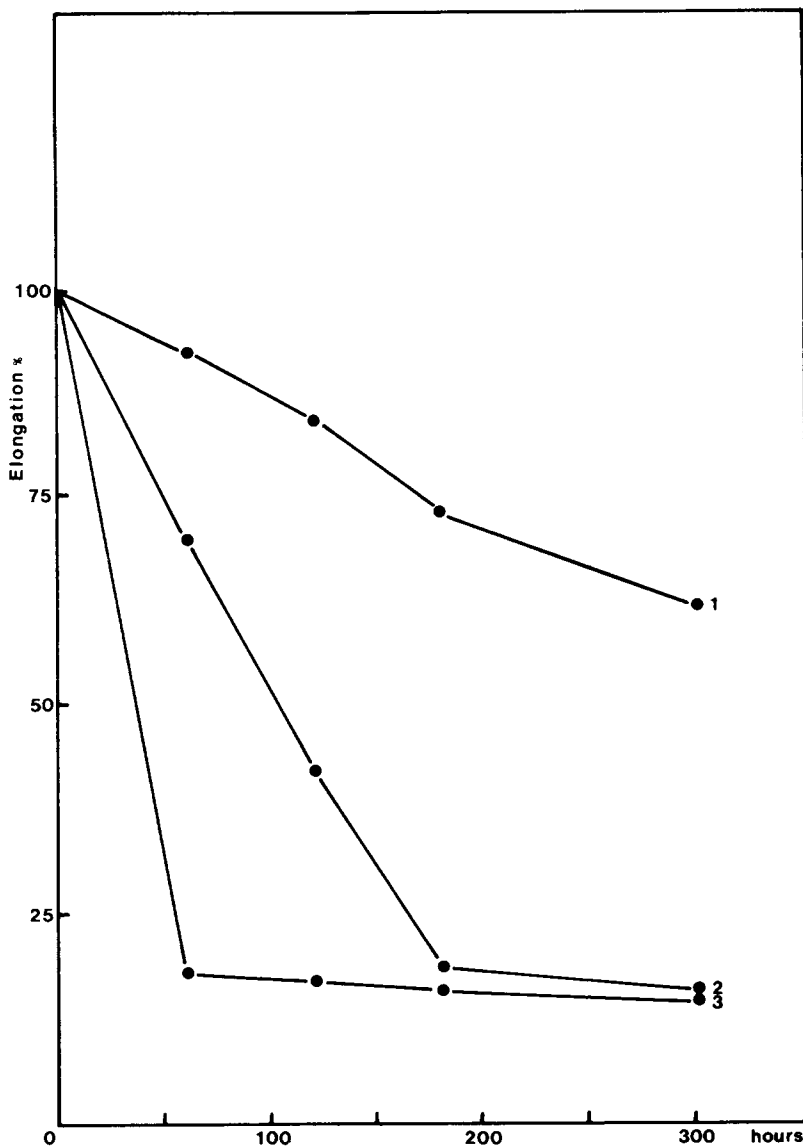


Fig. 2. Per cent elongation loss as function of irradiation time during indoor aging tests (xenon lamp, $\lambda > 290$ nm): (1) HDPE ELTEX A 1050 as reference; (2) HDPE ELTEX A 1050 + DPB 0.3%; (3) HDPE ELTEX A 1050 + DPH 0.3%.

sensitize the formation of the same type of radicals and the broad symmetric singlet (width ~ 60 G, $g = 2.003$), observed at -196°C , is attributed to allylic free radicals of the type $-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}-$. With increasing temperature, again the same type of radicals are observed with both additives and the asymmetric signal (width ~ 100 G, $g_{\perp} = 2.008$, $g_{\parallel} = 2.034$) observed at -130°C is assigned to peroxy radicals, while the sharp singlet (width ~ 30 G, $g = 2.004$) obtained at -20°C is assumed to be due to polyenyl radicals of the type $-\dot{\text{C}}\text{H}-(\text{CH}=\text{CH})_n-$.

In order to identify the products of photodegradation, samples of activated

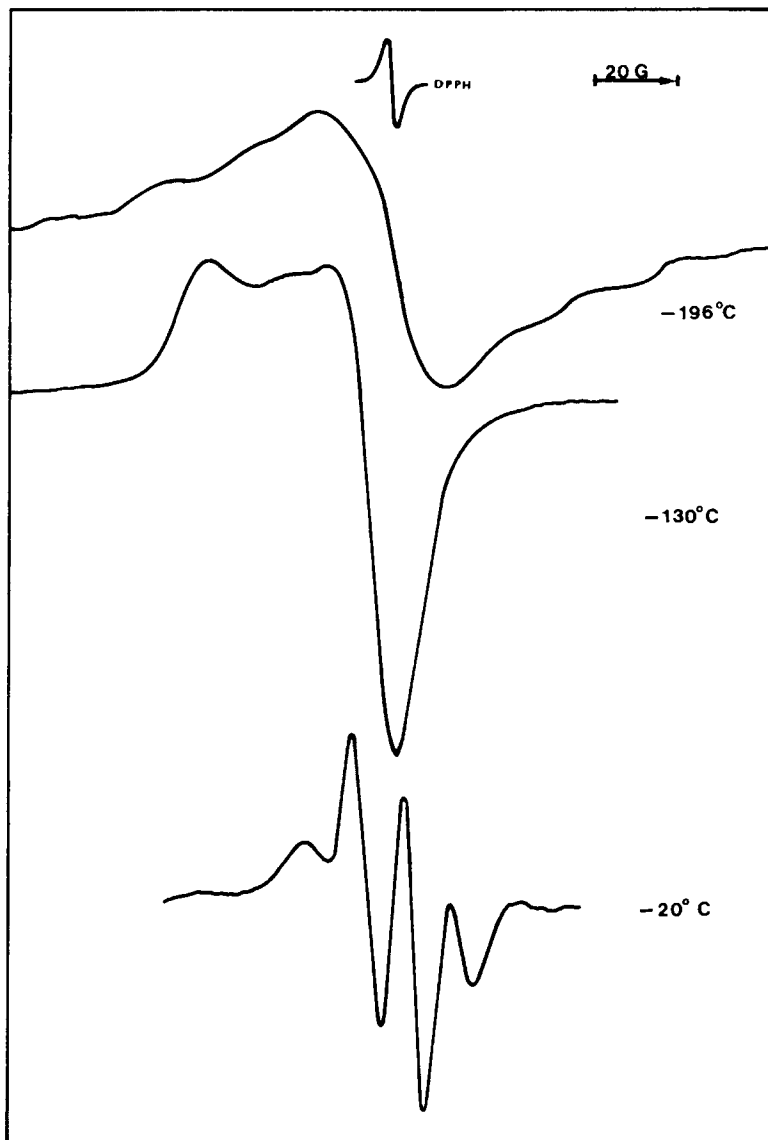


Fig. 3. ESR spectrum as function of temperature of pure polyethylene (HDPE ELTEX A 1050), after 25 hr of indoor aging in air (xenon lamp, $\lambda > 290$ nm).

polyethylene were extracted with toluene at different stages of irradiation. Besides fragments of the polymer and small quantities of the additives, several compounds due to the photodegradation of the additives have been isolated and identified by gas-chromatographic—mass-spectrometric analysis (Table I). The same compounds were identified when DPH and DPB were irradiated in solution of *n*-hexane or as a dispersion on silica gel.

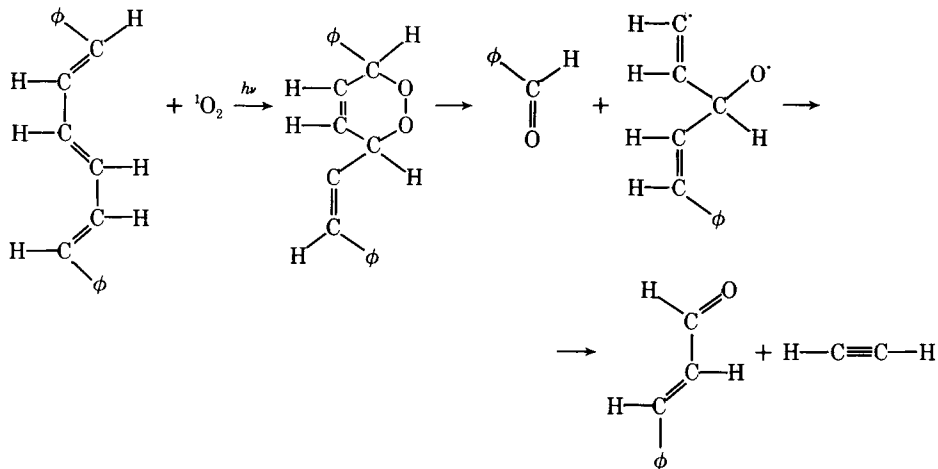
The nonoxygenated compounds supposedly are due to photochemical rearrangement and cyclization reactions of the additives, while the formation of the oxygenated compounds has been interpreted on the basis of a photochemical

TABLE I
 Photodegradation Products of 1,6-Diphenyl-1,3,5-hexatriene (DPH)
 and 1,4-Diphenyl-1,3-butadiene (DPB) Identified from Extracts
 of Irradiated Polyethylene Activated with DPH and DPB

	Photodegradation products
DPH	benzaldehyde cinnamic aldehyde stilbene chrysene
DPB	benzaldehyde cinnamic aldehyde stilbene <i>cis</i> -1,2-diphenyl-3-cyclobutadiene phenylnaphthalene

reaction which involves singlet oxygen (1O_2) according to the scheme already proposed by Rio and Berthelot³ for DPB and by ourselves for TPB:¹

For DPH:



The formation of excited singlet oxygen could be ascribed to photosensitization from the carbonyl groups in the polymer or from some other impurity also present in it. However, considering that the same products of photodegradation were obtained when DPH and DPB were irradiated in solution or absorbed on silica gel and considering also that DPB and DPH possess relatively long-lived triplet states, it could be assumed that the additives themselves are effective in sensitizing the formation of 1O_2 .

In conclusion, on the basis of the experimental results just reported, it can be assumed that DPB and DPH sensitize the photodegradation of polyethylene through a mechanism similar to that observed for TPB.¹ In fact, the absence of photodegradation when the irradiation of the polymer is carried out in absence of oxygen indicates that analogously to TPB, DPB and DPH do not react directly with the polymer as seen for other aromatic additives.^{4,5}

On the other hand, all compounds formed from the photodegradation of the additives can be efficient photosensitizers, and thus the effectiveness of DPB and DPH of promoting the photodegradation of polyethylene can be attributed



Fig. 4. ESR spectrum as function of temperature of polyethylene (HDPE ELTEX A 1050) activated by DPPH, after 25 hr of indoor aging in air (xenon lamp, $\lambda > 290$ nm).

to their products of photodegradation and to their ability to sensitize the formation of singlet oxygen.

Compounds such as benzaldehyde or cinnamic aldehyde can react directly with the polymer via hydrogen atom abstraction, promoting the attack of molecular oxygen, while singlet oxygen ($^1\text{O}_2$) can react with polyethylene to give peroxides and hydroperoxides which, decomposing, also accelerate the photooxidative degradation of the polymer.

The higher rate of photodegradation shown by polyethylene activated by TPB, as compared to that activated by DPB and DPPH, is probably due to the higher efficiency as photosensitizers of the photodegradation products of TPB.

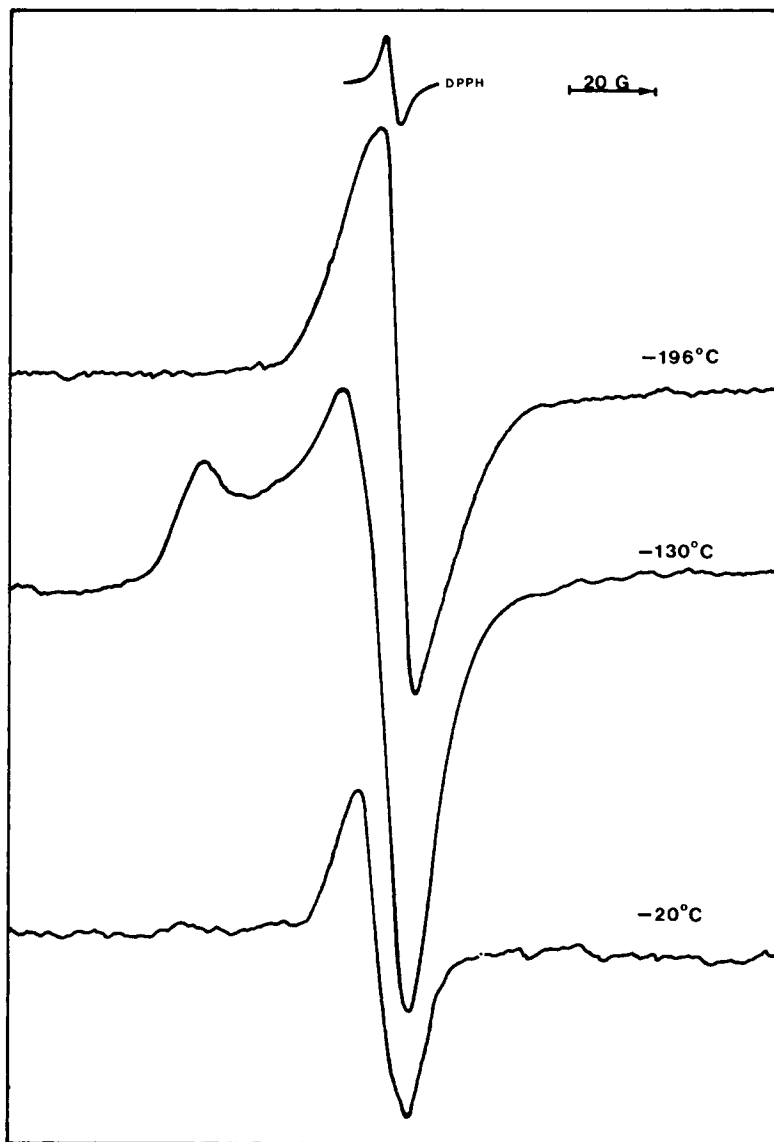


Fig. 5. ESR spectrum as function of temperature of polyethylene (HDPE ELTEX A 1050) activated by DPB, after 25 hr of indoor aging in air (xenon lamp, $\lambda > 290$ nm).

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