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PHOTOSTABILIZATION OF COMMERCIAL POLYPROPYLENE BY HINDERED PIPERIDINE COMPOUNDS

AN ESR AND LUMINESCENCE STUDY

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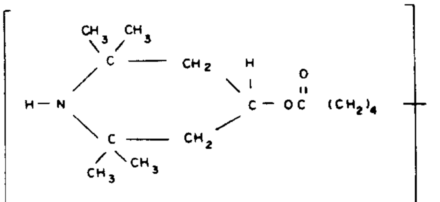
Abstract—The photostabilization of commercial polypropylene by a hindered piperidine stabilizer, bis [2,2,6,6-tetramethyl-4-piperidinyl] sebacate (**I**) and by a model *N*-oxy radical compound, 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy (**II**) is examined using ESR and luminescence spectroscopy. ESR spectroscopy shows that **I** operates through the formation of a stable nitroxyl radical in the polymer. On the other hand, **II** disappears rapidly during the early stages of photo-oxidation but continues to act as an effective stabilizer. A low steady-state equilibrium concentration of nitroxyl radicals is believed to be responsible for the high photostabilizing efficiency of **I**. Both compounds also inhibit the photolysis of the luminescent α,β-unsaturated impurity groups present in the polymer; possible mechanisms are discussed.

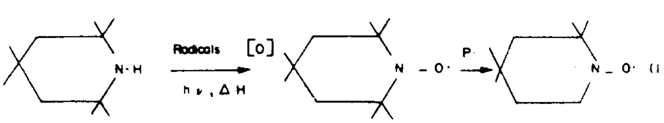
INTRODUCTION

Of the many classes of compounds developed as photostabilizers for commercial synthetic polymers, the relatively new hindered amines based on piperidine have proved to be the most effective [1–5]. The hindered piperidine derivative (**I**), known as Tinuvin 770, has attracted much interest.



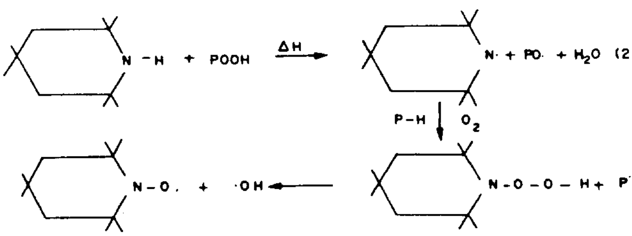
(I)

The stabilizing effectiveness of these hindered piperidines is believed to depend upon their ability to form a stable nitroxyl radical, which then scavenges macroradicals (P˙) produced during photo-oxidation [1–8].



(1)

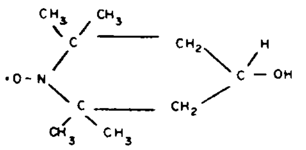
Recently, Chakraborty and Scott [9] attributed the photostabilizing effectiveness of **I** in low density polyethylene to its ability to react with hydroperoxides in the polymer to form a stable nitroxyl radical.



(2)

From kinetic work on model systems, Wiles *et al.* [10] concluded however that the radical scavenging behaviour of nitroxyl radicals could not fully account for their high photoprotective role in polyolefins. For example, the same workers [11] found that nitroxyl radicals can complex with hydroperoxides whereas other workers [12] have shown that nitroxyl radicals are quite effective singlet oxygen quenchers.

To examine the validity of mechanism (1) in the polymer matrix, we have compared, using ESR spectroscopy, the effect on photo-oxidation of **I** with that of a stable piperidino-*N*-oxy radical compound (**II**), in commercial polypropylene.



(II)

We have also examined the effects of these compounds on the photolysis of the luminescent photoactive α,β-unsaturated carbonyl impurities present in the polymer [3, 4, 13].

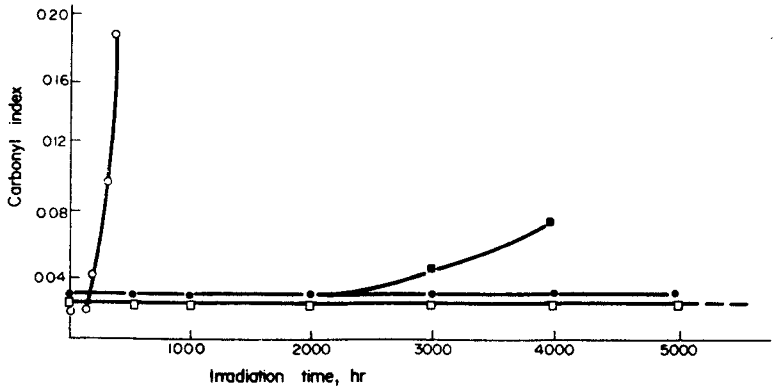


Fig. 1. Rate of photo-oxidation of commercial polypropylene film (200 μm thick) in a Xenotest-150 weatherometer. ○—no stabilizer; □—0.25% **II**; ■—0.1% **I** and; ●—0.25% **I** added before pressing into film.

EXPERIMENTAL

Materials

Polypropylene powder (HF-20) containing no commercial additives was supplied by ICI (Plastics Division) Ltd. The hindered amine stabilizer **I** was supplied by Ciba-Geigy A-G, Basle, Switzerland. The stable *N*-oxy radical compound **II** was purchased from Eastman Kodak Co. The compounds were solvent blended into the polypropylene powder using dichloromethane as solvent. The solvent was removed under reduced pressure using a rotary evaporator. The polymer powders were then pressed at 200° for 1 min followed by water cooling for 4 min, into film 200 μm thick. A control sample was similarily prepared. The cyclohexane was of spectroscopic quality.

Spectroscopic measurements

Corrected fluorescence and phosphorescence spectra were obtained using a double grating (1200 lines/mm) Hitachi Perkin-Elmer MPF-4 Spectrofluorimeter equipped with two R-446F photomultiplier tubes (wavelength response 220–950 nm). ESR spectra were recorded under ambient conditions using a Jeol FE-3X spectrometer.

Photo-oxidation

The polymer films were irradiated in a Xenotest-150 (Original Hanau, Quartzlampen, GmbH) set-up for natural sunlight-simulated exposure conditions (45°; 50% relative humidity). The rates of photo-oxidation of the polymer films were measured by monitoring the increase in the concentration of non-volatile carbonylic oxidation products absorbing at 1715 cm^{-1}, using a Perkin-Elmer 157G infrared spectrometer.

Carbonyl index at 1715 cm = $[(\log_{10} I_0/I_t)d] \times 100$; where I_0 and I_t are the initial and transmitted light intensities respectively and d is the film thickness (μm).

RESULTS

The light stabilizing efficiencies of **I** and **II** in polypropylene are shown in Fig. 1. It is seen that **I** inhibits carbonyl development in the polymer up to about 3000 hr when at 0.1% concentration, and beyond 5000 hr at 0.25% concentration. Compound **II** was examined only at a 0.25% concentration; it inhibits carbonyl development in the polymer beyond 5000 hr

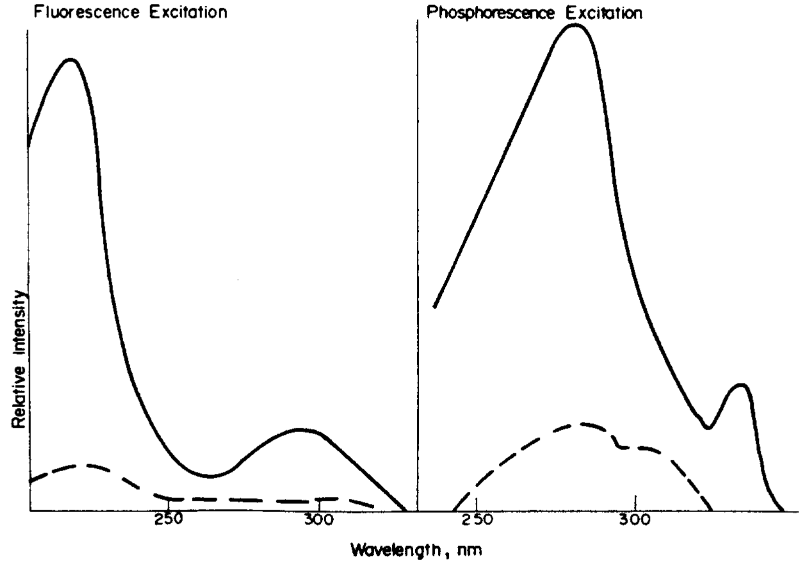


Fig. 2. Typical fluorescence and phosphorescence excitation spectra of commercial polypropylene film containing no additives before irradiation (——) and 0.25% of the hindered piperidine compounds (**I** and **II**) before and after 5000 hr of irradiation (——) and no additives after 150 hr of irradiation and 0.1% of the hindered piperidine stabilizer (**I**) after 3000 hr of irradiation (– – –).

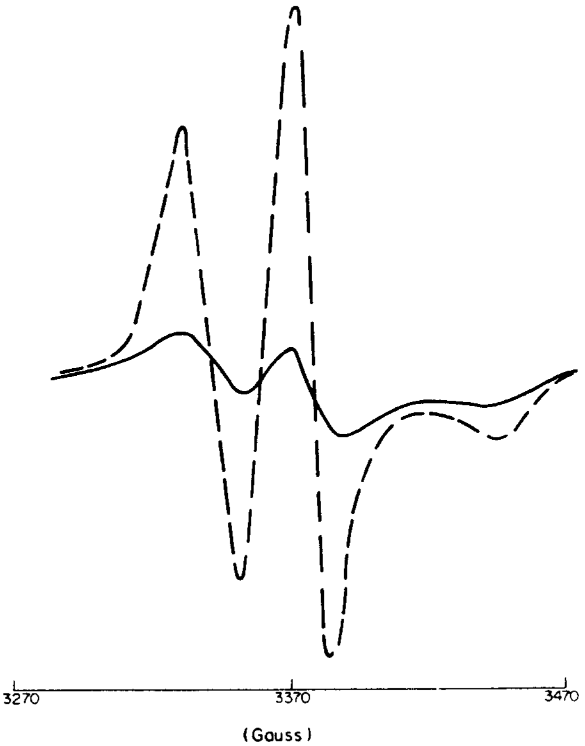


Fig. 3. ESR spectrum of I(0.25%) in commercial polypropylene film before (——) (A = 5 × 100) and after (---) (A = 5 × 100) 5000 hr of irradiation in a Xenotest-150. A = amplitude of signal.

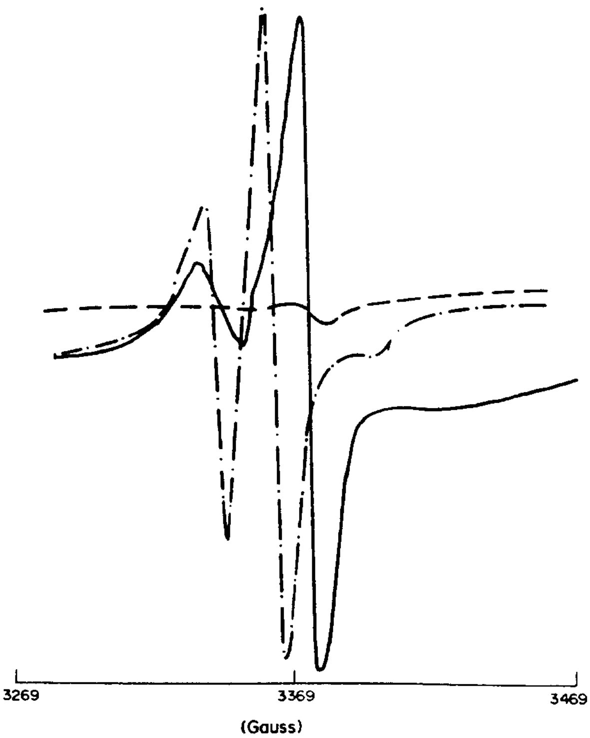


Fig. 4. ESR spectrum of 0.25% II in commercial polypropylene film at room temperature and in air before (——) (A = 10) and after (---) (A = 10), (---) (A = 10^3) 5000 hr of irradiation in a Xenotest—150. A = amplitude of signal.

of irradiation despite the absence of a long alkyl ester chain.

Figure 2 shows the effect of irradiation on the intensity of the fluorescence and phosphorescence excitation spectra of the α,β-unsaturated carbonyl impurity groups in the polymer (the fluorescence and phosphorescence emissions originate from enone and dienone impurities respectively) [13]. Prior to irradiation, **I** and **II** had no significant effect on the intensity of the excitation spectra. Thus protective mechanisms involving optical screening and/or excited state quenching cannot be operative with either **I** or **II**.

After about 150 hr of irradiation, the unstabilized polymer film began to embrittle. The onset of embrittlement approximately coincided with a marked increase in carbonyl index (Fig. 1). During the irradiation prior to embrittlement, there was a gradual reduction in the intensity of the emissions from the α,β-unsaturated carbonyl impurities. Only during the period of embrittlement, i.e. after 150 hr of irradiation, was the conversion of unsaturated carbonyl to saturated carbonyl groups completed [12] (Fig. 2). In contrast, no significant change was observed in the intensity of the emissions from the α,β-unsaturated carbonyl impurities in the polymer films containing 0.25% of (**I**) or (**II**), over the irradiation period studied (Fig. 2). For polymer film containing 0.1% of **I**, only at the onset of embrittlement was there a marked decrease in the intensity of the fluorescence and phosphorescence emissions comparable with that of the embrittled unstabilized polymer film.

Figures 3 and 4 show the ESR spectra of the polymer films containing 0.25% of **I** or **II** before and after irradiation. Figure 3 shows that **I** exhibits a stable ESR spectrum before irradiation. During irradiation, there is an increase in the intensity of the ESR spectrum, but from 2000–5000 hr it attains an almost steady intensity. The polymer film does not give this spectrum either before or after irradiation. The intensity of the ESR spectrum of **II** markedly decreases during irradiation (Fig. 4) but, as for **I**, the spectrum attains a weak but steady intensity from 2000 to 5000 hr of irradiation. At this low concentration, the spectrum of the nitroxyl radical is resolvable into three lines similar to that of **I**. The mT values for the centre of the spectra are also the same i.e. 2.009. A closer match of the spectra is seen in Fig. 5 where the ESR spectrum of **I** is compared with that of **II** in solution. At the relatively high concentration of *N*-oxy radical employed in this work, the presence of the rigid polymer matrix will impair "free-spin" of the radical [11].

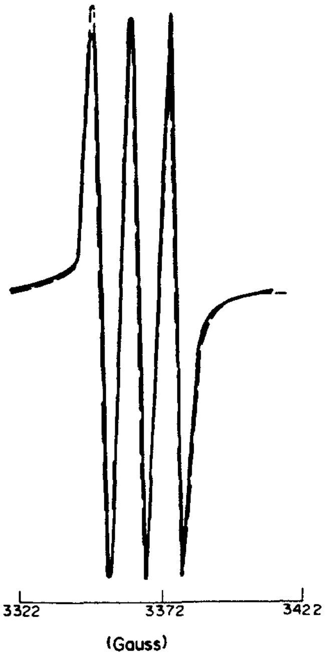
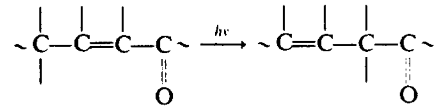


Fig. 5. Comparison of the ESR spectrum of II (10^{-2} mol/l) (——) A = 10^3 with that of (10^{-3} mol/l) (– – – –) (A = 5 × 100) in air saturated cyclohexane at room temperature.

DISCUSSION

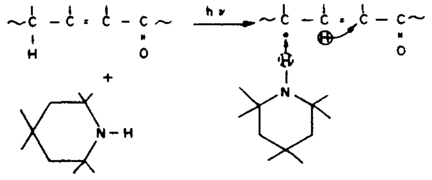
The ESR results show that the radical generated during the photostabilization of the polymer by **I** is a nitroxyl radical, in agreement with the earlier postulate [5–7, 11] that the nitroxyl radical is an essential intermediate formed during the reaction. Consistent with this is the result that the concentration of the nitroxyl radical derived from **I** increases during the initial stages of irradiation but attains a low steady concentration on prolonged irradiation. Although the concentration of **II** decreases during the initial stages of irradiation, it also attains a low stationary concentration [11].

It is also evident that inhibition of the photolysis of the α,β-unsaturated carbonyl impurities in the polymer is another important mechanism by which **I** operates. Since **I** does not operate by screening or excited state quenching then a new mechanism is derived on the basis that one of the major primary photochemical processes in the polymer is isomerization of the α,β-unsaturated carbonyl impurities [12]



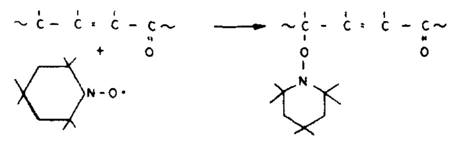
$$\sim\underset{|}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-\underset{\underset{O}{\|}}{C}\sim\ \xrightarrow{h\nu}\ \sim\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}\sim \qquad (3)$$

In this scheme there is a shift of unsaturation from the α,β- to the β,γ- position, so that **I** would effectively inhibit the photolysis of α,β-unsaturated carbonyl impurities by donating the labile hydrogen atom from the nitrogen to the γ-carbon radical site thus preventing the isomerization i.e.



(4)

Inhibition of the photolysis of the α,β-unsaturated carbonyl impurities by **II** is interesting; evidently the mechanism is different from that for **I**. Since nitroxyl radicals are known to react with macroradicals [1–11], then it is possible for the nitroxyl radical to react with the γ-carbon radical intermediate formed during the isomerization:



(5)

The nitroxyl radical may also scavenge any singlet oxygen produced in the polymer [12] thereby preventing attack on the double bond. Such a mechanism can be only speculative until the importance of singlet oxygen in the photo-oxidation of polyolefins has been more clearly established.

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