

Photostabilization of Commercial Polypropylene by a Hindered Amine Stabilizer

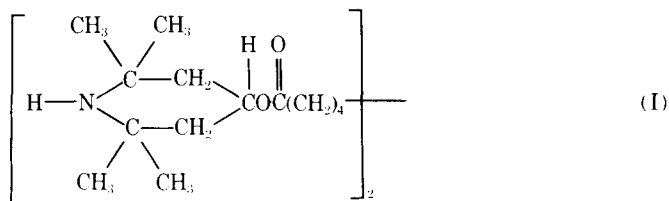
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Synopsis

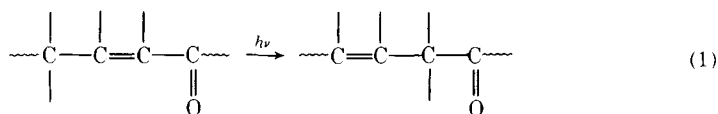
The photostabilization of commercial polypropylene by a hindered amine stabilizer is examined by luminescence and ESR spectroscopy. The presence of the amine stabilizer inhibits the photolysis of the α,β unsaturated carbonyl impurity groups present in the polymer. Examination by ESR, of the stabilized polymer before and after irradiation shows the development of a highly stabilized free radical indicating that the stabilizer can act as an ultraviolet stable antioxidant. Possible mechanisms whereby the hindered amine inhibits the photolysis of the α,β unsaturated carbonyl groups are discussed.

INTRODUCTION

It would appear from recent work that several important commercial light stabilizers may play a multifunctional role in protecting the light sensitive polyolefins from photodegradation.¹⁻³ However, the relatively new hindered amine stabilizers such as that shown by stabilizer (I) have proved to be very effective while our understanding of their mechanisms of protecting polyolefins from photodegradation remains uncertain.⁴ Certainly they do not appear to operate by mechanisms of optical screening or quenching of photoactive impurities.⁵



In recent studies^{6,7} we have shown that the photoactive α,β unsaturated carbonyl impurity groups in commercial polypropylene are converted into β,γ unsaturated carbonyl groups by the following mechanism:



It is seen that this mechanism involves a hydrogen atom shift from the γ - to the α -carbon atom. Following this step, photodegradation may then proceed via Norrish type-I and -II processes.¹⁻³

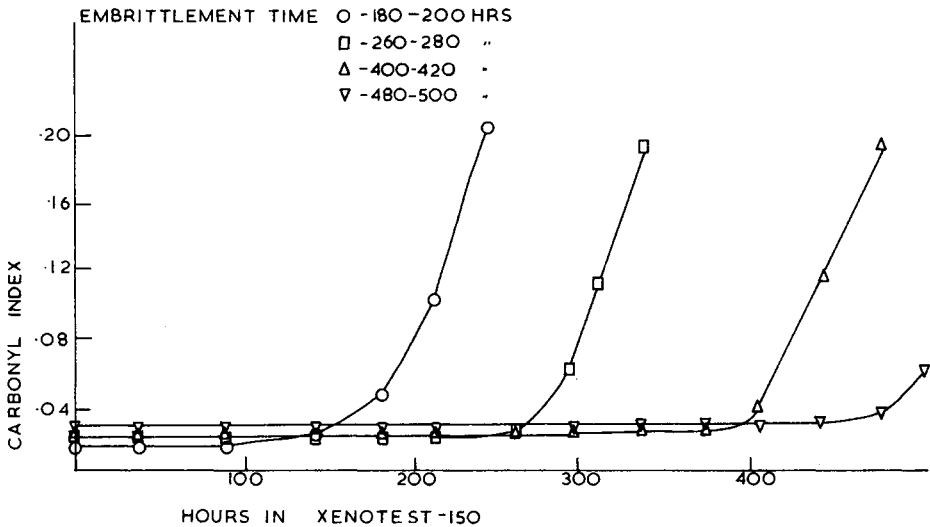


Fig. 1. Rate of photooxidation of commercial polypropylene film in a xenotest-150 weatherometer containing: ○, no stabilizer; —, 0.01%; △, 0.1%; and ▽, 0.5% of the hindered amine stabilizer.

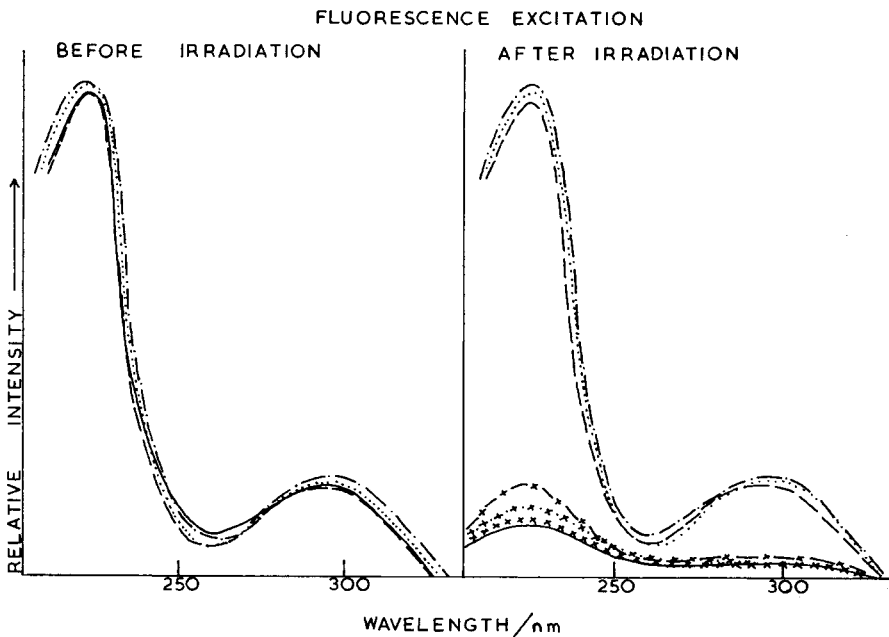


Fig. 2. Fluorescence excitation spectrum of the enone, α,β unsaturated carbonyl impurities in commercial polypropylene containing: no stabilizer (—), 0.01% (- - -), 0.1% (- · - ·), and 0.5% (· · ·) of the hindered amine stabilizer before and after 180 hr of irradiation and 0.01% (× × × ×), 0.1% (· × · × · × ·) and 0.5% (× · × ·) of the hindered amine stabilizer after 260, 400, and 480 hr of irradiation in a xenotest-150 weatherometer, respectively.

Here we have examined the effect of the stabilizer (I) on the photolysis of α,β unsaturated carbonyl impurities in commercial polypropylene. The same stabilized polymer was examined by ESR spectroscopy since it is believed that hindered amine stabilizers give rise to highly stabilized free radicals during polymer degradation.^{4,5}

EXPERIMENTAL

Materials

Commercial polypropylene powder containing no commercial additives was supplied by I.C.I. (Plastics Division) Ltd.

The hindered amine stabilizer, structure (I), was solvent blended into the polymer powder at 0.5%, 0.1%, and 0.01% concentrations using dichloromethane as solvent. The solvent was removed under reduced pressure using a rotary evaporator. The polypropylene powders were then pressed into film of 200 μ thickness at 190°C for 1 min. A control sample without stabilizer was similarly prepared.

Spectroscopic Measurements

Corrected fluorescence and phosphorescence spectra were obtained using a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter as described earlier.^{6,7}

ESR spectra were obtained under ambient conditions using a Varian 4502 ESR spectrometer. ESR measurements could only be carried out on polymer films prior to embrittlement. Embrittled films could not be satisfactorily inserted into the ESR cavity due to their fragility.

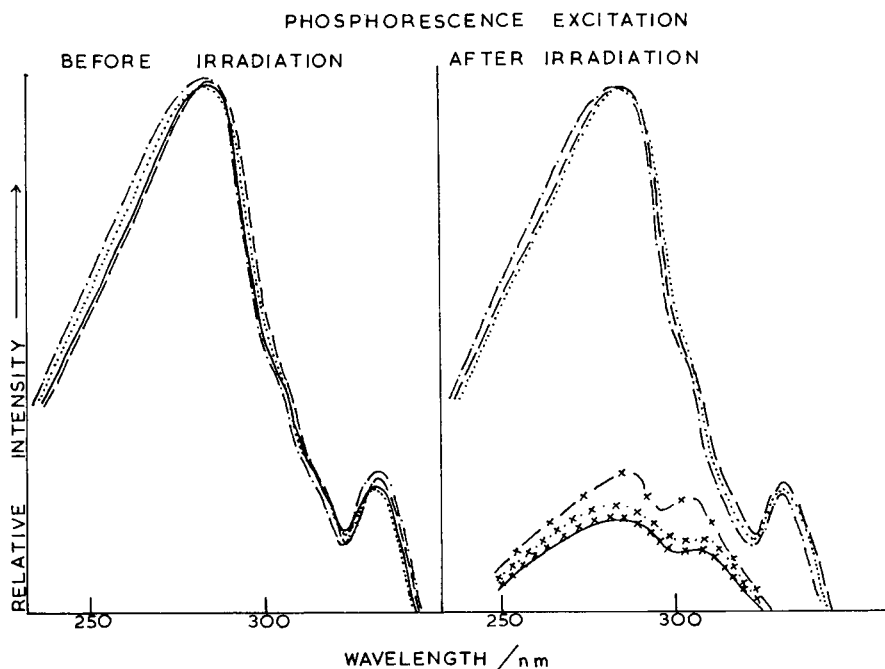


Fig. 3. Phosphorescence excitation spectrum of the dienone, α,β unsaturated carbonyl impurities in commercial polypropylene containing: no stabilizer (—), 0.01% (- - -), 0.1% (- · - ·), and 0.5% (· · ·) of the hindered amine stabilizer before and after 180 hr of irradiation and 0.01% (x x x x), 0.1% (· x · x · x ·) of the hindered amine stabilizer after 260, 400, and 480 hr of irradiation in a xenotest-150 weatherometer, respectively.

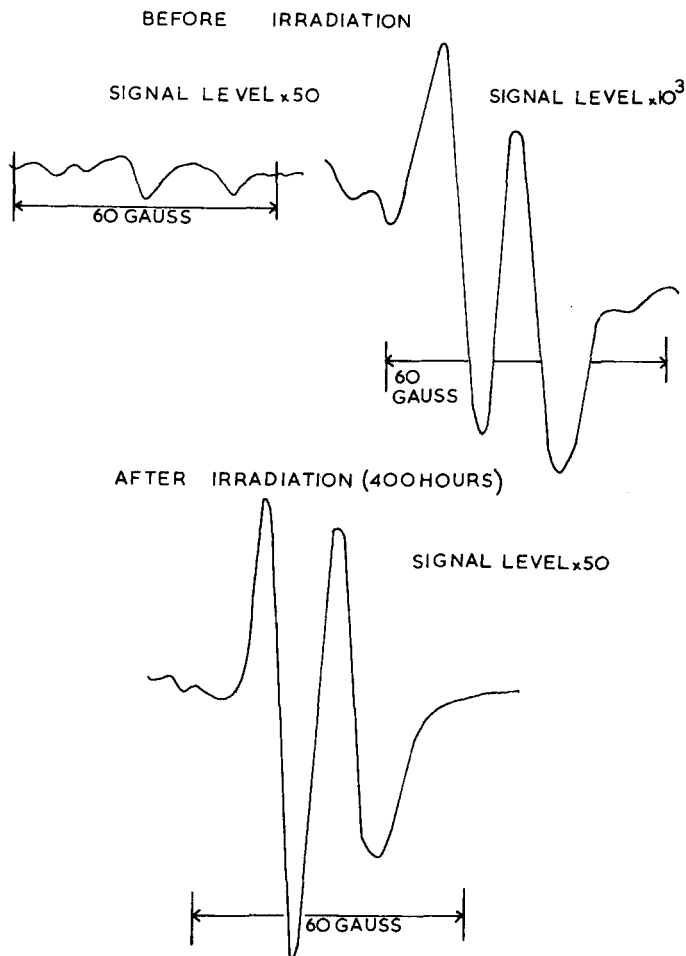


Fig. 4. ESR spectrum of a stabilized hindered amine radical in commercial propylene film (0.5%) at room temperature and in air, before and after irradiation in a Xenotest-150 weatherometer.

Photooxidation

Polymer films were irradiated in Xenotest-150 weatherometer set up for natural sunlight—simulated exposure conditions (45°C; 50% relative humidity). The rate of photooxidation of the polymer films was measured by monitoring the buildup in the nonvolatile carbonylic oxidation products absorbing at 1710 cm^{-1} using a Perkin-Elmer 157G infrared spectrophotometer:

$$\text{Carbonyl index} = [(\log_{10} I_0/I_t)/d] \times 100$$

where I_0 is the initial light intensity, I_t is the transmitted light intensity, and d is the film thickness.

RESULTS

The stabilizing efficiency of the hindered amine (I) in polypropylene is demonstrated in Figure 1. It is seen that its stabilizing effect decreases with a decrease in concentration but that this effect does not really become evident until the concentration of stabilizer is less than about 0.1% (by weight).

Figures 2 and 3 show 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.^{6,7} Prior to irradiation it is seen that the presence of the hindered amine (I) has 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 this type of stabilizer.

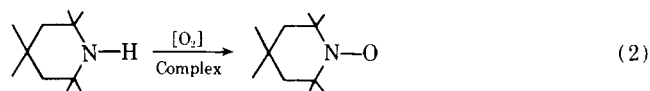
After about 180 hr of irradiation it was found that the unstabilized film began to embrittle. As seen from Figure 1 this onset of embrittlement occurred at about the same time as the polymer developed a marked increase in its carbonyl index. During the irradiation period prior to embrittlement there 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 180 hr of irradiation, was the conversion of unsaturated carbonyl to saturated carbonyl groups completed^{6,7} (Figs. 2 and 3).

In contrast, the stabilized polymers did not reach their period of embrittlement until after much longer irradiation times. Further, during the periods prior to embrittlement no significant change was observed in the intensity of the α,β unsaturated carbonyl group emissions. Again, only with the onset of embrittlement was there a comparable decrease in the intensity of the α,β unsaturated carbonyl spectra with that of the embrittled unstabilized polymer film (Figs. 2 and 3).

Figure 4 shows that an ESR spectrum was observed from the stabilized film and that its intensity level was markedly enhanced by irradiation. Since the unstabilized polymer did not give this spectrum either before or after irradiation we can conclude that the source of the signal must be from the "stabilized" free radical (I) suggested earlier by Heller and Blattman⁴ as an essential intermediate in its protective mechanism.

DISCUSSION

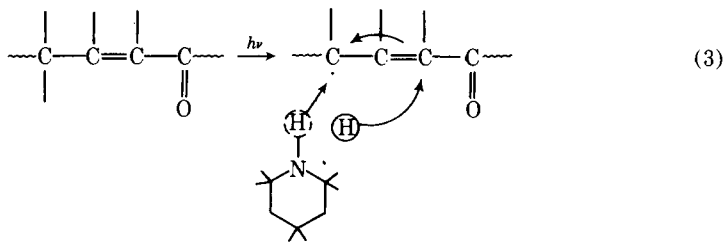
It has been postulated⁸ from model system work that hindered amines of the type examined here may owe their antioxidant action to the formation of a nitroxyl radical by a series of complex processes as summarized as follows:



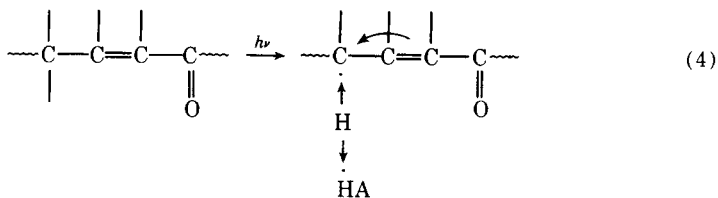
Such radicals are relatively stable and it would be expected that they would inhibit the well-known Bolland-Gee⁹ autooxidation mechanism for polypropylene. However, the nitroxyl radicals, in addition to being relatively stable are also highly colored. Throughout the period of irradiation we carefully inspected the polymer but we did not observe the development of any coloration that could be attributed to the presence of these radicals in the polymer matrix.

Although we cannot as yet give a positive identification of the free radical that is detected by ESR it is unlikely to be a nitroxyl radical for the following reasons: (i) the spectrum does not match that of any known nitroxyl radical spectra,⁸ and (ii) the nitroxyl radical is reported to be relatively unstable to light⁸ and thus it would be unlikely to continue to increase in concentration throughout the period of irradiation used in our experiments.

Clearly, therefore, since these hindered amines do not operate by screening and excited state quenching,^{4,5} then our results show that a new mechanism is required to explain their inhibiting action. Such a mechanism is obtained on the basis that a major primary photochemical process in commercial polypropylene is, as indicated above, a process of isomerization of α,β unsaturated carbonyl impurity groups.^{6,7} Thus, the main inhibition process during the early stages of photooxidation of the polymer must be due to the ability of the hindered amine to rapidly donate a hydrogen atom to the photolytically severed γ C—H bond before the hydrogen atom from that bond attaches itself to the α -carbon atom, i.e.,



A further possible mechanism is that the α -hydrogen atoms produced on irradiation develop a facile equilibrium condition with the hindered amine stabilizer radicals present in the polymer i.e.



where HA is a stable hindered amine radical.

Further work should resolve this point, particularly when the source of the ESR spectrum has been established.

References

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