

Origin and Role of the Luminescent Species in the Photo-oxidation of Commercial Polypropylene

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Synopsis

The fluorescence and phosphorescence excitation and emission spectra of commercial polypropylene have been examined using a fully compensated spectrofluorometer. This has made possible the comparison of the excitation spectra of the polymer with model chromophores of those believed to be present in the polymer. The fluorescence emission is primarily associated with the presence of enone, and the phosphorescence with dienone chromophoric units. The behavior of the luminescent enones and dienones during irradiation under sunlight-simulated conditions has also been examined. Possible mechanisms for the participation of these chromophoric units in the photo-oxidation of polypropylene are discussed.

INTRODUCTION

In early papers,¹⁻⁸ we have reported on the nature of the luminescent (fluorescent and phosphorescent) impurity species in commercial polypropylene and have shown that they participate in the sunlight-induced photo-oxidation of the polymer. Our studies indicated that these luminescent species are carbonyl in nature, but we were unable to define precisely the nature of these photoactive carbonyl species. The main problem in identifying these species was that we were unable to obtain fully corrected excitation and emission spectra. However, by using a newly developed, fully corrected far ultraviolet spectrofluorometer,⁵ we now have this capability. For example, we have shown that the fluorescence emission from polypropylene in the region 300-400 nm ($\lambda_{\text{max}} = 340$ nm) cannot be due to the presence of polynuclear aromatics as postulated earlier by Carlsson and Wiles.⁹

In this paper, we report on the evidence for the identification of the carbonyl species responsible for the polymer luminescence and examine their behavior during irradiation under natural sunlight-simulated conditions. The photochemical reactions that these species are known to undergo and how these reactions can initiate photo-oxidation of the polymer are discussed.

EXPERIMENTAL

Materials

Polypropylene powder (I.C.I. Plastics Division Ltd.) containing no commercial additives was vacuum pressed into film (200 μ thick) at 190°C.

The model compounds 3-methylpentanal, 2,2,4,4-tetramethylpentan-3-one, *trans,trans*-hexa-2,4-dienal (sorbaldehyde), and pent-3-ene-2-one were all purified by distillation under vacuum. The *n*-hexane was of spectroscopic quality.

Instrumentation

Ultraviolet absorption spectra were recorded using a Unicam SP 800 spectrophotometer. Fluorescence and phosphorescence spectra were recorded using a corrected double-grating Hitachi Perkin-Elmer MPF-4 spectrofluorometer equipped with two R-446F photomultiplier tubes.

Fully corrected excitation spectra were obtained using the newly developed spectrofluorometer of Cundall et al.⁵ (instrumental details to be published).

Photo-oxidation

Samples of polypropylene film were irradiated in a Xenotest-150 (supplied by Original Hanau, Quartzlampen, G.M.b.H) set up for natural sunlight-simulated conditions (45°C; 50% relative humidity).

RESULTS

Polypropylene Luminescence Spectra

Figure 1 shows typical fluorescence and phosphorescence excitation and emission spectra obtained from commercial polypropylene. It is seen that the excitation spectrum for the fluorescence has two distinct maxima at 230 and 285 nm, while that of the phosphorescence has only one distinct maximum at 265 nm, with rather weak and diffuse structure above 300 nm. Excitation of 230 and 285 nm produces the same fluorescence spectrum at 340 nm, the former band being an upper excited state of the chromophore. It is clear from these results that the fluorescent and phosphorescent species cannot be the same. This, of course, does not rule out the fact that both may arise from carbonyl emitting species, as will be shown later, since these chromophoric groups when linked to ethylenic unsaturation can have quite distinct absorption¹⁰ and emission spectra.¹¹⁻¹³

Origin of the Fluorescence Emission

Figure 2 compares the fluorescence excitation spectrum of the polymer with that of a simple α,β -unsaturated carbonyl compound (pent-3-ene-2-one). It is seen that the two spectra are distinctly similar; and as we have shown earlier,^{5,7} the excitation spectrum does not show the highly structured spectrum in the region 220 to 260 nm that is exhibited by polynuclear aromatic hydrocarbons. Further, as shown below, the excitation spectrum also differs significantly from that of a fully saturated aldehyde or ketone.

Origin of the Phosphorescence Emission

A comparison of the fluorescence and phosphorescence excitation spectra clearly shows that they cannot be due to the same chromophoric species in the

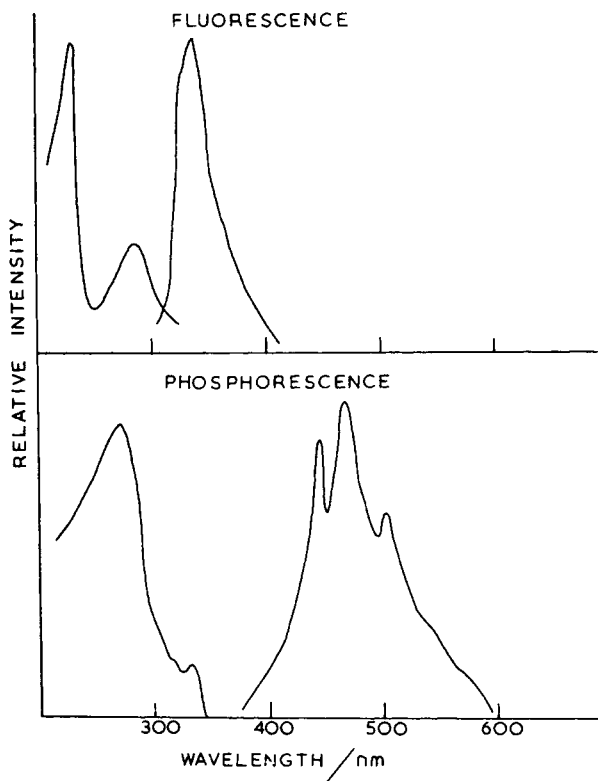


Fig. 1. Fluorescence and phosphorescence spectra of polypropylene film (200 μ thick).

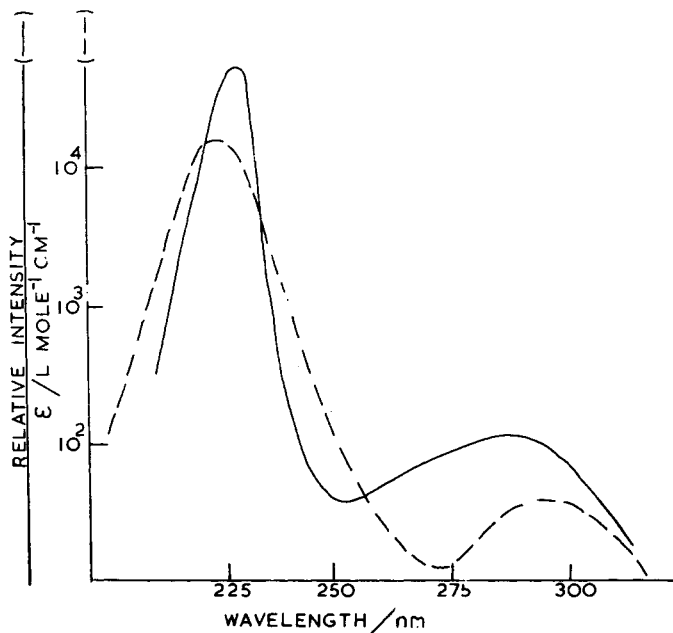


Fig. 2. Comparison of the fluorescence excitation spectrum of polypropylene film (—) with the absorption spectrum of pent-3-ene-2-one in *n*-hexane (- - -).

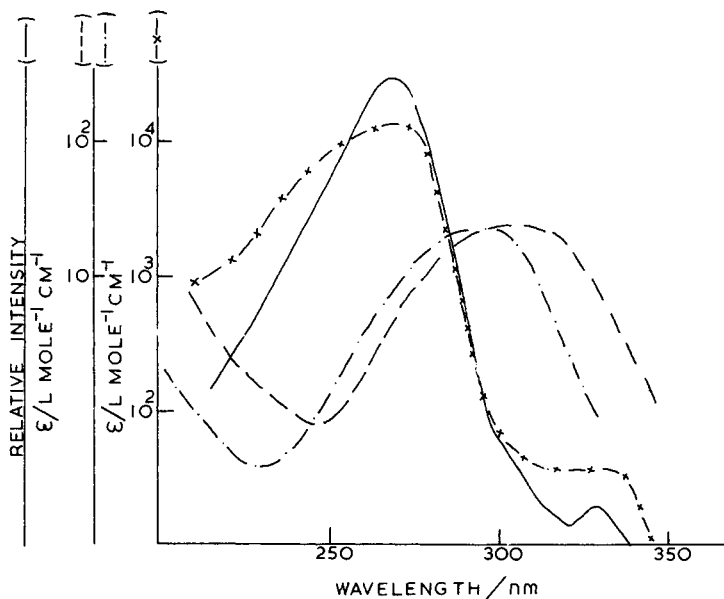


Fig. 3. Comparison of the phosphorescence excitation spectrum of polypropylene film (—) with the absorption spectra of 2,2,4,4-tetramethylpentan-3-one (---), 3-methylpentanal (- · - ·), and *trans,trans*-hexa-2,4-dienal (sorb aldehyde) (- x - x) in *n*-hexane.

polymer. This, therefore, diminishes the possibility of a simple α,β -unsaturated carbonyl chromophore being responsible for the majority of the phosphorescence emission. However, these groups may indeed phosphoresce,^{12,13} but they are evidently overlaid by a much stronger emitting impurity species.

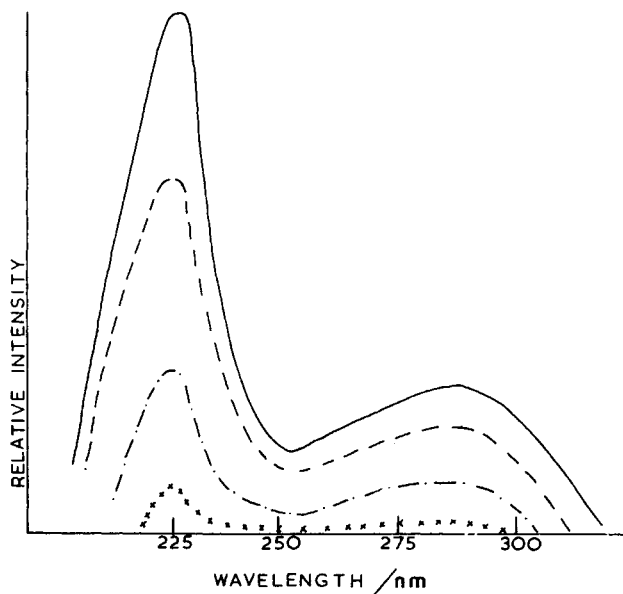


Fig. 4. Intensity of the fluorescence excitation spectrum of polypropylene film before (—) and after 75 hr (---), 150 hr (- · - ·), and 250 hr (xxxx) irradiation in a Xenotest-150 Weatherometer.

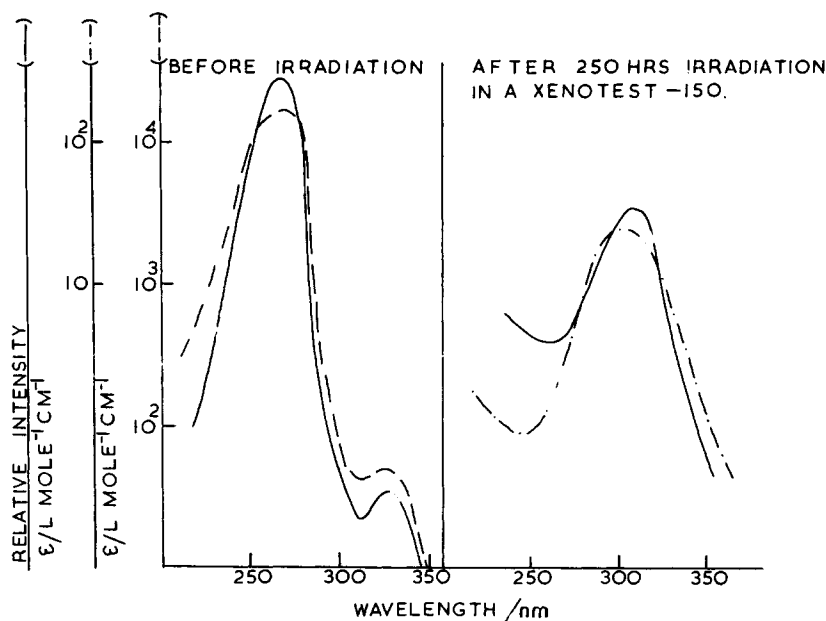


Fig. 5. Comparison of the phosphorescence excitation spectrum of polypropylene film (—) before and after irradiation for 250 hr in a Xenotest-150 Weatherometer with the absorption spectra of *trans,trans*-hexa-2,4-dienal (---) and 2,2,4,4-tetramethylpentan-3-one (- · - ·) in *n*-hexane, respectively.

In Figure 3, we compare the polymer phosphorescence excitation spectrum with other possible phosphorescent carbonyl chromophores known to be present in the polymer.^{14,15} It is seen that the absorption of a typical dienone, *trans,trans*-hexa-2,4-dienal, matches much more closely that of the polymer excitation than does a typical long-chain aliphatic aldehyde or ketone. Indeed, Charlesby and Partridge¹⁴ pointed out that an isolated ketonic carbonyl group on an "infinite polymethylene chain" may be virtually nonluminescent. A further feature of the phosphorescence emission from the polymer is that it is highly structured. This type of structured spectrum is exhibited by rigid cyclic dienones,^{11,12} and it is thus evident that such groups could exist as units held within the molecular backbone of the polymer. Further, when present in the polymer matrix, deactivation of these groups by rotation round the C=C bond will be inhibited, and a relatively long lifetime in the excited triplet state should be expected.¹² This is precisely what is observed with the highly crystalline polyolefins.^{3,4} Interestingly, long-lived phosphorescence emission of a similar type has been reported from other commercial polymers such as the polyamides^{3,16} and polybutadiene.¹⁷

Effect of Photo-oxidation on the Luminescent Species

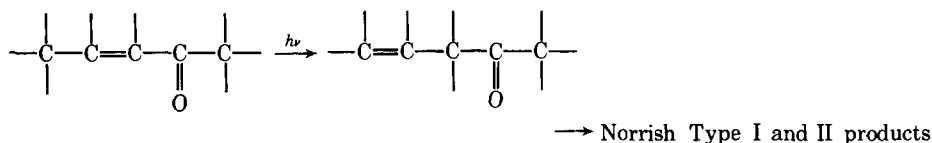
During irradiation in a Xenotest-150, the fluorescent enones are gradually consumed as shown by a gradual reduction in the intensity of the fluorescence excitation spectrum (Fig. 4). The phosphorescent dienones were also consumed during irradiation as observed by a decrease in the phosphorescence excitation

spectrum. During the same period of irradiation, however, there was also a gradual bathochromic shift in the phosphorescence excitation wavelength maximum. Figure 5 shows that this bathochromic shift is due to the conversion of dienones to saturated carbonyl groups which absorb at longer wavelengths and have a smaller extinction coefficient. The fluorescence excitation spectrum shows no such corresponding shift (Fig. 4), since ketonic/aldehydic carbonyl groups do not fluoresce.¹⁸

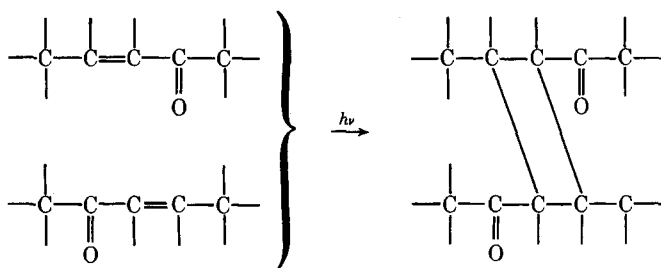
DISCUSSION

The identification of the nature of the fluorescent and phosphorescent species and knowledge of their behavior during irradiation under natural sunlight-simulated conditions enables us to consider possible mechanisms by which they can act as initiators of the photo-oxidation process. Our results show that during the initial stages of photo-oxidation of the polymer, the α,β -unsaturated carbonyl groups are converted into saturated ketonic/aldehydic carbonyl groups which are themselves subsequently converted during the photo-oxidation process to nonluminescent products, e.g., carboxylic acids.^{2,3}

The photochemistry of α,β -unsaturated carbonyl compounds is well documented.^{17,19} If we consider the enone case, for simplicity, these chromophoric units are well known to undergo two possible photoreactions.¹⁷ These are: (1) The formation of β,γ -carbonyls followed by the well-known Norrish Type I and II reactions,²⁰ e.g.,



(2) Crosslinking between adjacent α,β -unsaturated carbonyls to produce saturated carbonyls, e.g.,



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