

Luminescence and Photo-oxidation of Commercial Poly(4-methylpent-1-ene)

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Synopsis

The fluorescence and phosphorescence excitation and emission spectra of commercial poly(4-methylpent-1-ene) are examined using a fully compensated spectrofluorometer. The excitation spectra of the polymer are compared with the absorption spectra of 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 impurity chromophoric units. Bromination of cold hexane extracts of the polymer significantly reduces the intensity of the fluorescence, confirming the presence of ethylenic unsaturation. The behavior of the luminescent enone and dienone groups during irradiation under sunlight-simulated conditions is also examined. Possible mechanisms for the participation of these chromophoric units in the photo-oxidation of poly(4-methylpent-1-ene) are discussed.

INTRODUCTION

In earlier papers,¹⁻⁵ we reported on the nature of the luminescent (fluorescent and phosphorescent) impurity species in commercial polyolefins and have shown that they participate in the sunlight-induced oxidation of the polymers. Recently, using a corrected spectrofluorometer, we found that impurity α,β -unsaturated carbonyl groups of the enone and dienone type were common in both commercial polypropylene and polyethylene.^{6,7}

To conclude our studies of the luminescence of polyolefins and its possible relevance to light-induced oxidation, it was necessary to establish whether impurity α,β -unsaturated carbonyl groups are common in all the commercially important polyolefins, namely, polypropylene, polyethylene, and poly(4-methylpent-1-ene). Of the three, poly(4-methylpent-1-ene) has received little attention regarding its photo-oxidation mechanism. To this end, we report on the evidence for the identification of α,β -unsaturated carbonyl groups responsible for the luminescence from poly(4-methylpent-1-ene). Further, in this paper we have studied the effect of bromination on the extractable fluorescent species in the polymer to confirm the presence of ethylenic unsaturation. The behavior of the luminescent species during irradiation under sunlight-simulated conditions is also examined and possible photo-oxidation mechanisms are discussed.

EXPERIMENTAL

Materials

Commercial polypropylene and poly(4-methylpent-1-ene) powders containing no commercial additives were supplied by I.C.I. (Plastics Division) Ltd. The powders were vacuum pressed into film 200 microns thick at 190° and 280°C, respectively, for 1 min.

Hexane Extraction and Bromination

Poly(4-methylpent-1-ene) powder (20 g) was shaken with spectroscopic-grade *n*-hexane (100 ml) for 48 hr. The hexane extract was then filtered through glass wool. To a portion of the extract (20 ml) was added ~10 μ l liquid bromine which was then allowed to stand for 1/2 hr. The excess unreacted bromine was then removed by bubbling nitrogen through the extract for 15 min until shaking with an aqueous silver nitrate solution gave no precipitate. The solution was then allowed to equilibrate with air and the evaporation of solvent was compensated for.

Luminescence Measurements

Corrected fluorescence and phosphorescence spectra and phosphorescence lifetimes were obtained as described in earlier papers.³⁻⁷

Photo-oxidation

Poly(4-methylpent-1-ene) film was 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 AND DISCUSSION

Poly(4-methylpent-1-ene) Luminescence Spectra

Figure 1 shows typical fluorescence and phosphorescence excitation and emission spectra obtained from commercial poly(4-methylpent-1-ene) film. 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 with some fine structure at 275 and 284 nm and rather weak and diffuse structure above 300 nm. It is clear from these results that the fluorescent and phosphorescent chromophoric species cannot be the same. This, of course, does not rule out that both may be different α,β -unsaturated carbonyl species, as will be shown in the following sections.

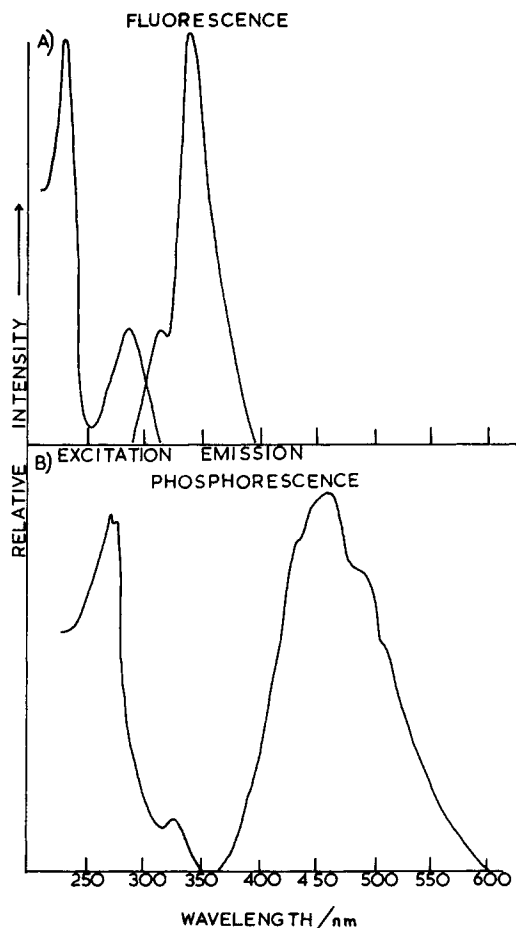


Fig. 1. Fluorescence and phosphorescence spectra of poly(4-methylpent-1-ene) film (200 μ thick).

Identification of the Fluorescent Species

The fluorescence spectrum of commercial poly(4-methylpent-1-ene) is similar to that obtained earlier for polypropylene and was attributed to the presence of enone chromophoric impurity groups.⁶ Figure 2 compares the fluorescence excitation spectrum of poly(4-methylpent-1-ene) with that of polypropylene and the absorption spectrum of a simple enone⁸ (pent-3-ene-2-one).

Identification of the Phosphorescent Species

The phosphorescence spectrum of commercial poly(4-methylpent-1-ene) is also similar to that obtained earlier for polypropylene and was attributed to the presence of dienone chromophoric impurity groups.⁶ Figure 3 compares the phosphorescence excitation spectrum of poly(4-methylpent-1-ene) with that of polypropylene and the absorption spectrum of a simple dienone⁸ (in this case a dienal, *trans,trans*-hexa-2,4-dienal). The phosphorescence emission lifetime of the commercial poly(4-methylpent-1-ene) sample was 0.70 sec.

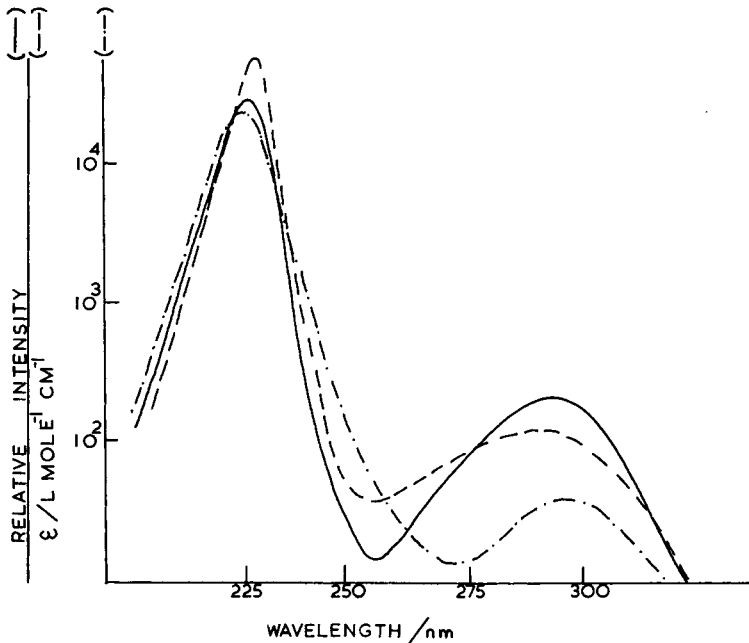


Fig. 2. Comparison of fluorescence excitation spectra of poly(4-methylpent-1-ene) (—) and polypropylene (---) films with absorption spectrum of pent-3-ene-2-one in *n*-hexane (-----).

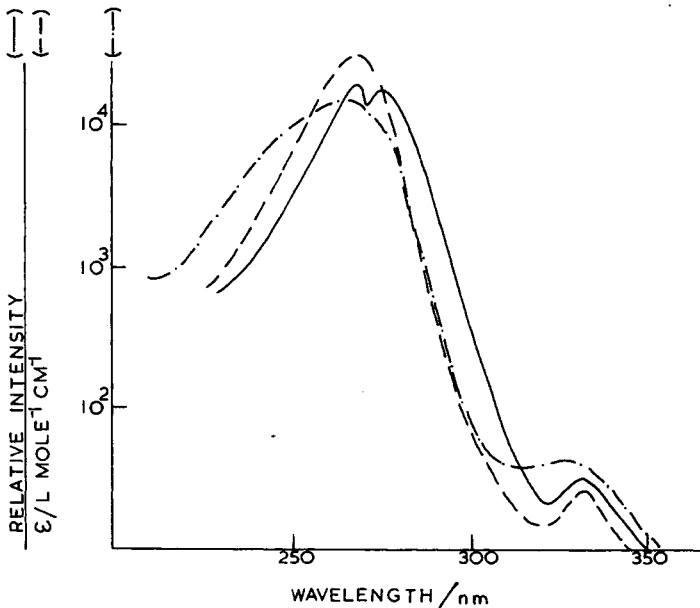


Fig. 3. Comparison of phosphorescence excitation spectra of poly(4-methylpent-1-ene) (—) and polypropylene (---) films with absorption spectrum of *trans,trans*-hexa-2,4-dienal in *n*-hexane (-----).

Hexane Extraction and Bromination

Some of the fluorescent enones are extractable from the amorphous regions of the polymer matrix by cold hexane.⁴ This process enables us to perform

a simple chemical test for the presence of unsaturation, i.e., bromination.⁹ Figure 4 shows the fluorescence excitation and emission spectra of the cold hexane extract of commercial poly(4-methylpent-1-ene) before and after treatment with bromine. It is seen that after bromination there is a significant reduction in the fluorescence intensity, confirming the presence of unsaturation. Excess, unreacted bromine was carefully removed to eliminate quenching of the fluorescence by heavy atom spin orbit coupling¹⁰ (see experimental section). Conventional chemical tests for the presence of the carbonyl group proved unsuccessful, although the excitation spectrum of the luminescent species indicated them to be associated with carbonyl groups in some form. The phosphorescent dienones were not extractable from the polymer matrix.

Effect of Photo-oxidation on the Luminescent Species

The longest wavelength absorption bands of both the enone and dienone chromophoric impurities overlap the high-energy end of the spectrum of natural sunlight known to be harmful to the commercial polyolefins^{11,12} (i.e., 300–350 nm).

During irradiation in a Xenotest-150, the fluorescent enones were gradually consumed, as observed by a gradual reduction in the fluorescence intensity. The phosphorescent dienones were also consumed during irradiation. However, at the onset of embrittlement, there was a gradual bathochromic shift in the phosphorescence excitation wavelength maximum. Figure 5 shows that this bathochromic shift is due to the conversion of the dienones to saturated carbonyl groups which absorb at longer wavelengths and have a much smaller extinction coefficient. During the early stages of irradiation, the bathochromic shift was not observed owing to the much stronger absorption by the dienones than that by the saturated carbonyls (Fig. 5). The fluorescence excitation spectrum showed no such corresponding shift since simple saturated aliphatic carbonyl groups do not fluoresce.¹⁰

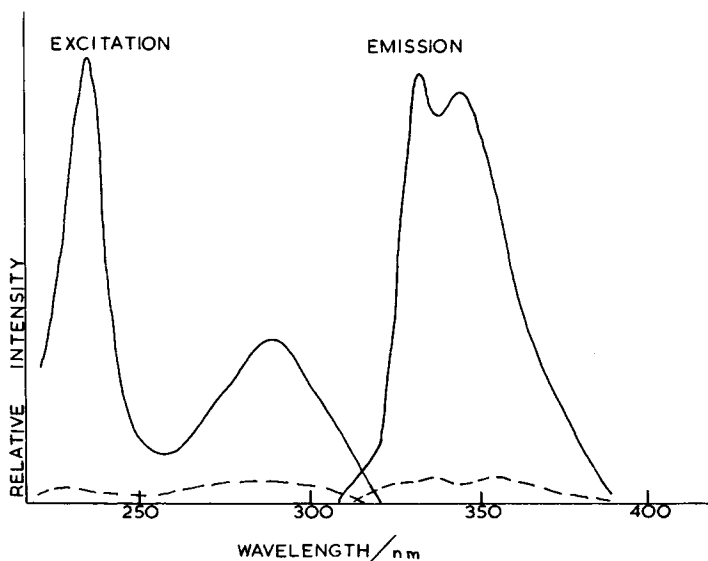


Fig. 4. Fluorescence excitation and emission spectra of a cold hexane extract of poly(4-methylpent-1-ene) before (—) and after (---) bromination.

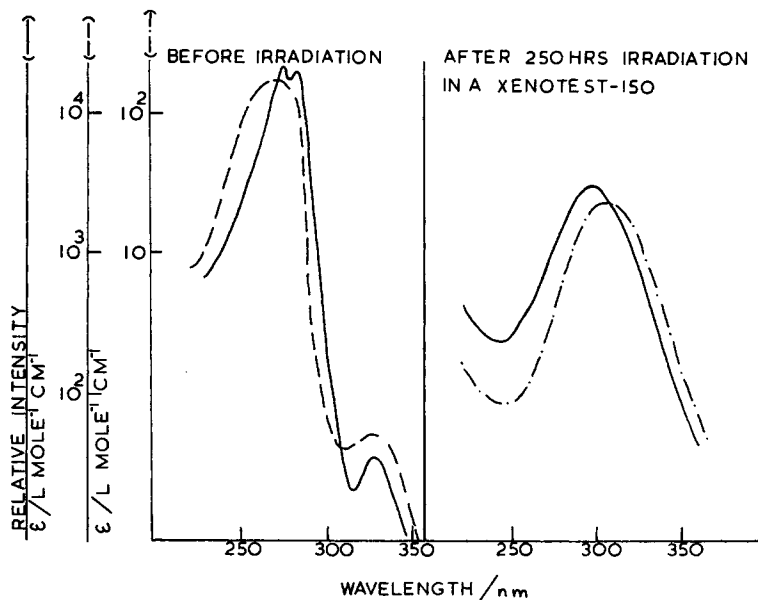
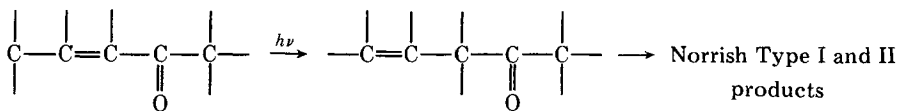


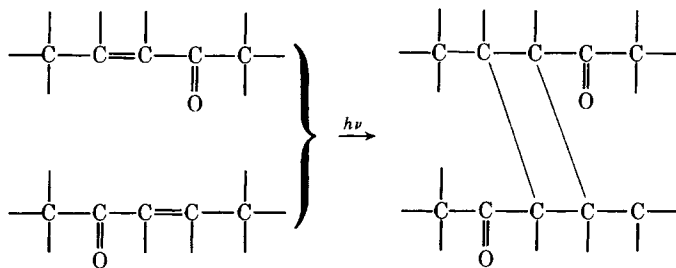
Fig. 5. Comparison of phosphorescence excitation spectrum of poly(4-methylpent-1-ene) film (—) before and after irradiation for 250 hr in a Xenotest-150 Weatherometer with absorption spectra of *trans,trans*-hexa-2,4-dienal (---) and 2,2,4,4-tetramethylpentan-3-one (— · — ·) in *n*-hexane, respectively.

Photo-oxidation Mechanisms

The photochemistry of α,β -unsaturated carbonyl compounds is well documented in the literature.^{13,14} If we consider the enone case, for simplicity, these chromophoric units are well known to undergo two possible photoreactions. These are (1) the formation of β,γ -carbonyls followed by the well-known Norrish Type I and II reactions, e.g.,^{11,12}



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



Our results show that during photo-oxidation of the polymer, the α,β -unsaturated carbonyl groups are converted into saturated ketonic/aldehyde car-

bonyl groups which are themselves subsequently converted during the photo-oxidation process to nonluminescent products, e.g., carboxylic acids.¹² This could occur by either reaction (1) or (2), although the participation of (2) for a "fully saturated" aliphatic polyolefin is likely to be very small.

In an earlier paper,² we suggested that the sources of the fluorescence and phosphorescence emissions from commercial polyolefins may have a common chemical origin. This would now appear to be due to the presence of α,β -unsaturated carbonyl groups. Indeed, many workers have considered that polyolefins are photodegraded by common photoinitiation mechanisms. Photo-reactions involving α,β -unsaturated carbonyls would thus fulfill this role. However, there is also evidence that hydroperoxide and/or allylic hydroperoxide groups are extremely important and have been suggested to be the major photoinitiators.^{15,16} Be this as it may, our work^{4,6} with polyolefins has shown that α,β -unsaturated carbonyl groups may act as primary photoinitiators.

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