

Identification of the Luminescent Species in Low-Density Polyethylene

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Synopsis

The luminescence properties of two low-density polyethylene samples are examined, one prepared using oxygen and the other using a benzoyl-based initiator as catalysts. The fluorescence emission from both samples is assigned to the presence of an impurity, α,β -unsaturated carbonyl of the enone type. The phosphorescence emissions, on the other hand, are different. The phosphorescence emission from the sample prepared using oxygen as an initiator is assigned to the presence of a dienone impurity chromophore, whereas the emission from the sample prepared using a benzoyl-based initiator is assigned to benzoic acid residues.

INTRODUCTION

Luminescence studies of commercial polyolefins have provided valuable information on the nature of light-absorbing chromophores believed to participate in sunlight-induced oxidation.¹⁻⁸ The earlier studies^{1,2} showed a distinct difference between the phosphorescence emissions from low-density polyethylene and polypropylene samples. In the former case, the emission was attributed to the presence of mixtures of aromatic ketones and/or benzoic acid. Recently, in studies of the photo-oxidation of polypropylene we found no evidence of luminescent impurities other than simple enone and dienone unsaturated carbonyl groups.^{4,5,8}

It is well known that organic peroxides, among which are benzoyl-based initiators, may be used in the manufacture of low-density polyethylene⁹ and not in polypropylene, and the presence of the residual amounts of these initiators may be responsible for the difference in luminescence between the two polymers. To examine this possibility, we report on the emission properties of two low-density polyethylene samples specially made on a semitechnical scale, one using a typical benzoyl-based initiator and the other, without.

EXPERIMENTAL

Materials

Polyethylene samples, specially prepared using oxygen and *tert*-butylperbenzoate as polymerization initiators, were supplied by I.C.I. (Plastics Division) Ltd. They contained no commercial additives. Polypropylene powder, also

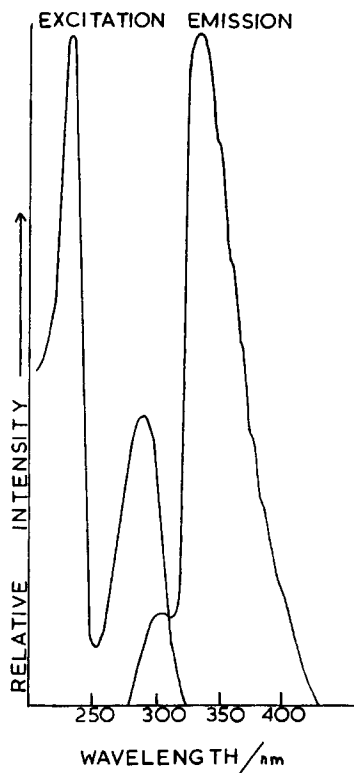


Fig. 1. Fluorescence excitation and emission spectra of polyethylene samples.

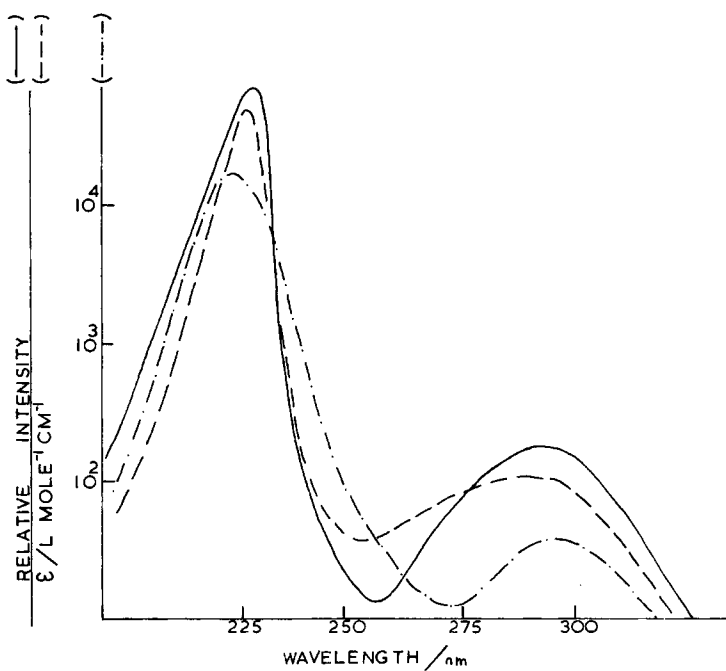


Fig. 2. Comparison of the fluorescence excitation spectra of polyethylene (—) and polypropylene (---) with the absorption spectrum of pent-3-ene-2-one in *n*-hexane (-·-·-).

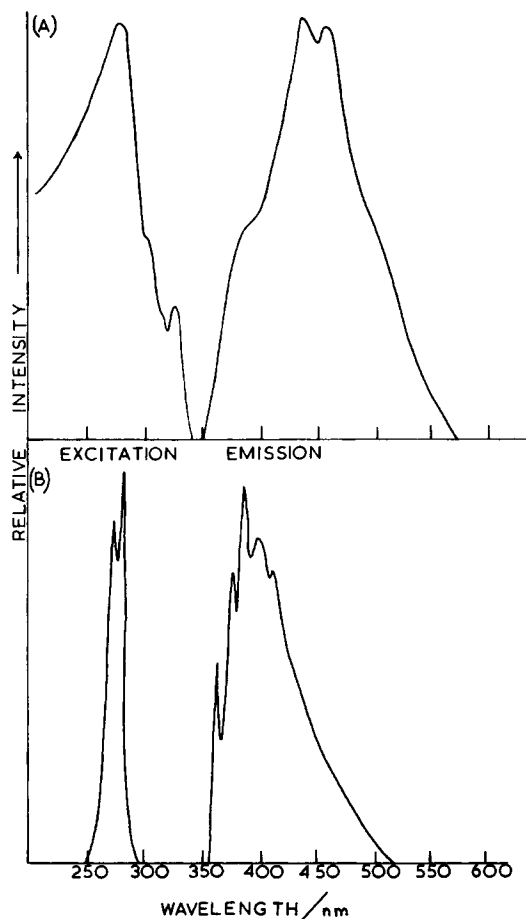


Fig. 3. Phosphorescence excitation and emission spectra of polyethylene chip samples, prepared using oxygen (A) and *tert*-butyl perbenzoate (B) as catalysts. Sample sensitivities were 100 and 3, respectively.

supplied by I.C.I. Ltd. and containing no commercial additives, was vacuum pressed into film (200 μ thick) at 190°C.

The benzoic acid was recrystallized twice from ethanol, and the *n*-hexane was of spectroscopic quality.

Instrumentation

Ultraviolet absorption spectra were recorded using a Unicam SP800 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 also obtained using the newly developed spectrofluorometer of Cundall et al.² (instrumental details to be published). Phosphorescence lifetime measurements were obtained by coupling the sample intensity signal from the fluorometer to a Tetrionix DM-64 storage oscilloscope and chopping the exciting light with an electrically controlled shutter.

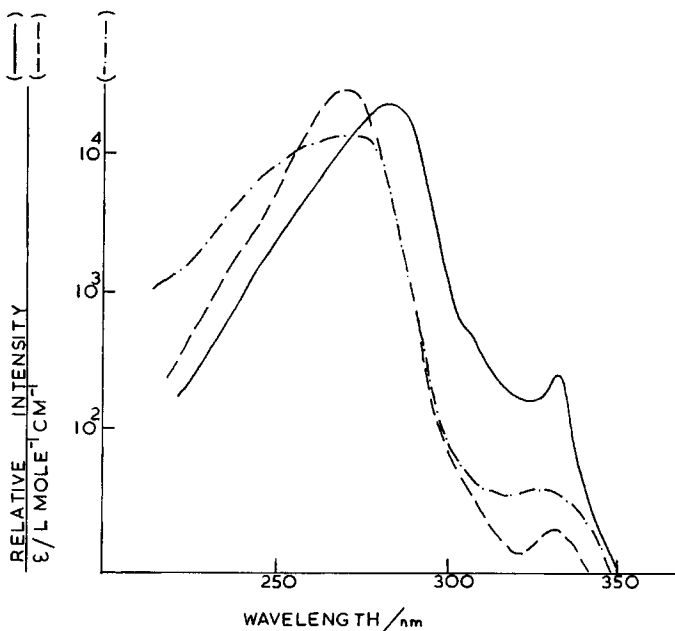


Fig. 4. Comparison of the phosphorescence excitation spectrum of polyethylene, prepared using oxygen as a catalyst (—) and polypropylene (- - -) with the absorption spectrum of *trans,trans*-hexane-2,4-dial in *n*-hexane (- · - · -).

RESULTS AND DISCUSSION

Fluorescence Spectra

The fluorescence excitation and emission spectra of both polyethylene samples were identical, and an example is shown in Figure 1. The spectrum is also similar to that obtained earlier for polypropylene^{4,5,8} and is attributed to the presence of enone chromophoric impurity groups.

Figure 2 compares the fluorescence excitation spectrum of polyethylene with that of polypropylene and the absorption spectrum of a simple enone (pent-3-ene-2-one).¹⁰ The excitation spectrum does not show the highly structured absorption in the region of 220–260 nm that is exhibited by polynuclear aromatic hydrocarbons.^{4,5} Boustead and Charlesby² have suggested that a significant proportion of the fluorescence from polyethylene could be due to these species.

Phosphorescence Spectra

In contrast to the fluorescence spectra, the phosphorescence excitation and emission spectra of the polyethylene samples are significantly different and are shown in Figure 3. The phosphorescence emission lifetimes were 2.15 and 2.3 sec for the polyethylene samples prepared using oxygen (A) and *tert*-butyl perbenzoate (B) as initiators. Thus, it is clear from these results that the major phosphorescent chromophoric species in both polymers cannot be the same. In

TABLE I
Phosphorescence Lifetimes and Wave Numbers of Peaks in the Phosphorescence Emission Spectra of Benzoic Acid and Polyethylene (B)

λ , nm	ν , $\text{cm}^{-1} \times 10^2$	$\Delta\nu$, $\text{cm}^{-1} \times 10^2$	τ , sec
368	271.7	8.22 \pm 0.10	2.30
380	263.2		
390	255.8		
406	246.3		
417	239.8		

fact, the phosphorescence spectrum of the polyethylene sample prepared using oxygen is similar to that obtained earlier for polypropylene.^{4,5,8} Here, the source of the emission was attributed to the presence of dienone chromophoric impurity groups. The phosphorescence spectrum of the sample prepared with *tert*-butyl perbenzoate, on the other hand, is similar to that of benzoic acid.²

Figure 4 compares the phosphorescence excitation spectrum of the former sample (A) with that of polypropylene and the absorption spectrum of a simple dienal (*trans,trans*, -hexa-2,4-dienal).¹⁰ In Table I, we compare the phosphorescence excitation and emission λ_{max} of the latter sample (B) with that of benzoic acid in *n*-hexane. The lifetimes and magnitudes of the vibrational splittings of both emissions are also identical and are also given in Table I. It is evident from these results that the benzoic acid present in the polyethylene samples originates from the polymerization initiator *tert*-butyl perbenzoate.

Finally, the intensity of the phosphorescence emission from the polyethylene sample prepared using *tert*-butylperbenzoate was much greater than that from the sample prepared using only oxygen (Fig. 3). Thus, although the phosphorescence spectrum of the former sample may contain a component due to dienone chromophoric impurity groups, it is evidently overlaid by the much stronger emission from the benzoic acid.

CONCLUSIONS

Our work shows that polyethylene using a benzoyl-based initiator exhibits the presence of strongly phosphorescent benzoic acid residues. When the polymer does not contain the remains of this initiator, it exhibits the phosphorescence emission of dienone impurity units found in polypropylene. Further work in this area of study is in progress.

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