

# Luminescence Emission of Isotactic Polypropylene

ZENJIRO OSAWA, HIDEYUKI KURODA, and YUTAKA KOBAYASHI,  
*Research Institute of Composite Materials, Faculty of Engineering, Gunma  
University, Kiryu, Gunma 376, Japan*

## Synopsis

In order to elucidate the origin of luminescent species in unstabilized commercial isotactic polypropylene (IPP), effects of hexane extraction and exposure of the extracted IPP film to the atmosphere on both fluorescence and phosphorescence emissions were examined. Fluorescence emission from the unextracted IPP film disappeared by the extraction, and only a very weak phosphorescence emission was found. During the exposure of the extracted IPP film to the atmosphere, both fluorescence and phosphorescence emissions appeared again. The intensity of the spectra increased with the exposure time and finally almost reached that from the unextracted IPP film. The results indicated that main fluorescent species in IPP are foreign impurities originating from an ambient atmosphere, and that contribution of a very minor amount of phosphorescence species such as carbonyl groups incorporated with the polymer was scarce.

## INTRODUCTION

Considerable attention has been paid to the nature of the luminescent species in commercial polyolefins. The luminescence emission was originally postulated by Charlesby and Partridge<sup>1</sup> to come from macroaldehyde or ketone. From the further works,<sup>2-4</sup> it was, however, believed to result largely from polynuclear aromatics (PNA) impurities which are released into the atmosphere in large quantities from the combustion and pyrolysis of fuels and lubricants. On the other hand, Allen et al.<sup>5</sup> reported lately that fluorescence emission is primarily associated with the presence of enone and phosphorescence with dienone chromophoric units.

In a previous paper,<sup>6</sup> we reported that luminescent species in high density polyethylene were ascribed to foreign impurities originating from the atmosphere. We are naturally interested in phosphorescence emission as well as fluorescence emission from isotactic polypropylene. We found that behavior of both fluorescence and phosphorescence emissions from isotactic polypropylene was quite similar to that of high density polyethylene and that luminescent species mainly originated from the atmosphere; but in the case of phosphorescence emission there was a minor contribution of anomalous structures such as carbonyl groups incorporated with the polymer chain.

## EXPERIMENTAL

### Materials

The powdery isotactic polypropylene (IPP) samples containing no additives were commercial products and finer than 100 mesh.

The powdery IPP (ca. 5 g) packed into a filter thimble was placed in a Soxhlet extractor and was extracted with 180 mL of extra pure grade of hexane (Wako Pure Chemical Co., Ltd., Japan) for 24 h. Immediately after the extraction hexane in the sample was removed under reduced pressure (1 mm Hg) for 12 h. Sample films (ca. 0.07–0.08 mm thick) of unextracted and extracted IPP were prepared by vacuum pressing at ca. 175°C.<sup>7,8</sup> Extract was concentrated to ca. 50 mL by a rotary evaporator.

For the absorption test of luminescent species, a film prepared from the extracted IPP showing no fluorescence emission at all was covered with a thin aluminum foil to avoid contamination by dust, and exposed to the ambient atmosphere (for fluorescence emission measurement) or in a quartz tube ( $\phi = 5$  mm) while an attached stopper was kept open (for phosphorescence emission measurement).

For the comparison, the extracted IPP and HDPE films were exposed to air flow (ca. 1 L/min) passed through concentrated sulfuric acid and a column ( $\phi = 3.2$  cm; *length* = 50 cm), packed with 5–10 mesh silica gel, for 1 and 5 h. In addition, sample films were kept in a sealed cell and tube for more than a week.

### Photoirradiation

Photoirradiation of the IPP film and the extract was carried out with a Toshiba Model H-400 ultraviolet light generator, which was equipped with a high-pressure mercury lamp with main emission at 2537, 2900 and 3650 Å (the highest intensity is 2537 Å and luminous intensity is 200 cd/cm<sup>2</sup>). Each sample was placed at right angles to and at 10 cm from light source.

For the measurement of fluorescence emission film samples were irradiated directly and the extract in a quartz cell. For the phosphorescence emission, photoirradiation was carried out in a quartz tube ( $\phi = 5$  mm) *in vacuo*.

### Emission Spectra

Fluorescence and phosphorescence spectra were recorded on a Hitachi MPF 2 A fluorescence spectrophotometer with a xenon source and a photomultiplier. The fluorescence spectra were measured at room temperature and the phosphorescence at 77 K. All spectra recorded are uncorrected for spectral distribution and photomultiplier response.

## RESULTS AND DISCUSSION

As shown in Figure 1, IPP film prepared from unextracted powdery sample emits fluorescence and phosphorescence light. However, the fluorescence emission from IPP film prepared after hexane extraction is not found, and the intensity of the phosphorescence spectrum becomes extremely weak. On the contrary, the extract (hexane solution) shows fluorescence and phosphorescence spectra whose shapes are similar to that of the unextracted film.

The results apparently indicated that luminescent species were extracted from the powdery sample by hexane and transferred to the hexane. When

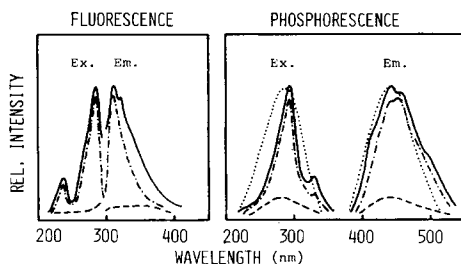


Fig. 1. Fluorescence and phosphorescence spectra of IPP, (—) unextracted film, (---) extracted film, (-.-) extract and (....) extracted film (high sensitivity):

	Normal	High sens.
Sensitivity	6	6
Ex. slit (nm)	9	14
Em. slit (nm)	9	14

measurement of phosphorescence emission of the extracted film was carried out at high sensitivity, the spectrum became appreciably clear (see the dotted line in Fig. 1), suggesting the presence of a very small amount of unextractable phosphorescent species incorporated with the polymer chain. The shape of the spectrum resembled that of alkyl ketone compounds such as hexanone. Therefore, the weak phosphorescent emission is ascribed to carbonyl groups, which remained in the polymer chain after the hexane extraction. In this context, a weak phosphorescence spectrum was also observed in high density polyethylene (see Ref. 6).

Decay of the intensity of luminescence emission from polyolefins during the very early stage of the photoirradiation was already observed.<sup>2-7</sup> As shown in Figures 2 and 3, during the photoirradiation the intensity of the fluorescence and phosphorescence emission from the unextracted IPP film and the extract decays rapidly. However, a weak phosphorescence emission is still observed after 20 min irradiation.

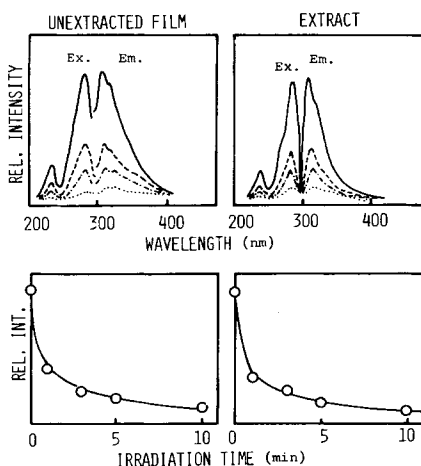


Fig. 2. Changes in fluorescence spectra of unextracted film and extract of IPP during UV irradiation. Irradiation time (min): (—) 0; (---) 1; (-.-) 3; (....) 10.

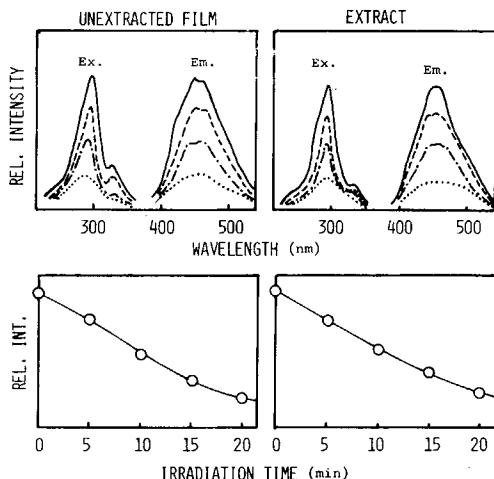


Fig. 3. Changes in phosphorescence spectra of unextracted IPP film and extract of IPP (hexane solution) during UV irradiation. Irradiation time (min): (—) 0; (---) 5; (- - -) 10; (· · ·) 20.

The results definitely indicate that main chromophoric impurities in the polymer are transferred to the solvent and that photochemical reaction of the chromophores takes place either in the film or in hexane solution.

The aforementioned results apparently suggest that main luminescent species are not covalently bound with the polymer chain and can be removed easily from the polymer by the solvent extraction, and only a very minor amount of phosphorescence species, e.g., carbonyl groups are incorporated with the polymer chain.

To confirm this, the extracted IPP film showing no fluorescence emission and a very weak phosphorescence emission was exposed to the atmosphere (for the measurement of phosphorescence emission, a stopper of the quartz

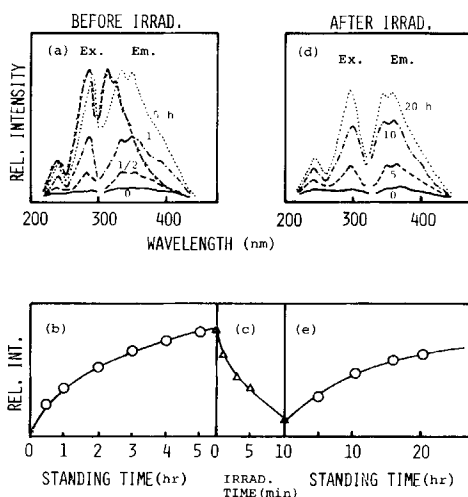


Fig. 4. Changes in fluorescence spectra of extracted IPP film. During exposure to the ambient atmosphere [(—x—) in (a): unextracted IPP film].

tube was kept opening). As shown in Figure 4, a fluorescence emission appears again fairly fast and the intensity of the spectrum increases with exposing time. After ca. 5 h, the relative intensity of the spectrum almost reaches that of the unextracted film [see Fig. 4(a)]. In addition, the intensity of the fluorescence emission recovered during the exposure to the atmosphere rapidly decays by the photoirradiation, and the emission disappears completely after ca. 10 min [see Fig. 4(c)]. This sample film was kept again in an ambient atmosphere. Fluorescence emission of the sample appears again, but the recovery rate of the relative intensity of the emission is slower than that of an unextracted film [see Fig. 4(e)]. The similar phenomena were also observed in high density polyethylene.<sup>7</sup>

The analogous measurement was carried out for phosphorescence emission from the polymer, and the results are shown in Figure 5. It is apparent that the intensity of the phosphorescence emission from the polymer increases during the exposure to the atmosphere in a quartz tube, but its increase is fairly slow in comparison with that of the fluorescence emission. This is probably ascribed to the different exposing conditions. On the photoirradiation of the polymer, the phosphorescence emission observed after the exposure in the atmosphere disappears very rapidly [see Fig. 5(c)]. The decay of the intensity of the phosphorescence emission is much faster than that of unextracted IPP film (see Fig. 3). The reason is not clear, but if phosphorescence species are absorbed exclusively on the surface of the film, the photochemical reaction of the chromophers may be facilitated.

In this context, measurement of luminescence emission from unstabilized commercial high density polyethylene supplied immediately after the polymerization by a manufacturing company (during the transportation it was kept under nitrogen atmosphere) definitely support our results. As shown in Figures 6 and 7, the polymer shows no fluorescence spectrum at all, and only a weak phosphorescence spectrum is observed. In addition, during the exposure of the polymer to the atmosphere both fluorescence

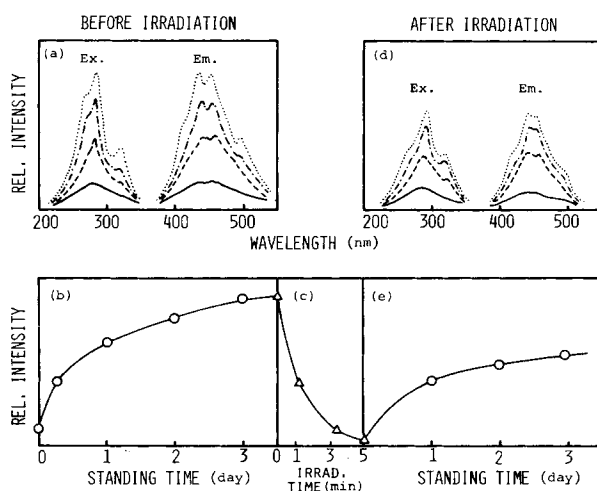


Fig. 5. Changes in phosphorescence spectra of extracted IPP film during exposure to the ambient temperature. Standing time (days): (—) 0; (---) 1; (- · -) 2; (· · ·) 3.

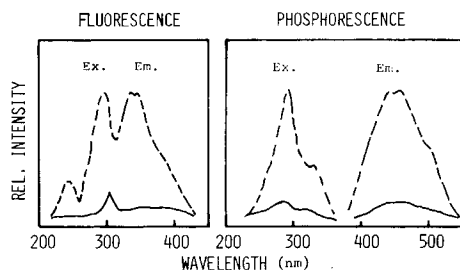


Fig. 6. Fluorescence and phosphorescence spectra of high density polyethylene powder supplied immediately after the polymerization (—) and exposed to the ambient atmosphere for 10 days (---).

and phosphorescence emissions appear, and the intensity of the fluorescence spectrum decays by the photoirradiation. These phenomena apparently coincide with that observed previously in high density polyethylene<sup>6</sup> and isotactic polypropylene of this work.

Furthermore, when the extracted IPP and HDPE films were exposed to cleaned air flow passed through concentrated sulfuric acid and a silica gel column for 5 h, no appreciable increase in the relative intensity of the fluorescence emission was found (see Fig. 8). In addition, when the extracted films were kept in a sealed cell and tube, no increase in luminescent emission was found at all.

### CONCLUSION

Unstabilized commercial isotactic polypropylene shows fluorescence and phosphorescence emissions, and most of these luminescent species could be removed easily from the polymer by solvent extraction. Only a very minor

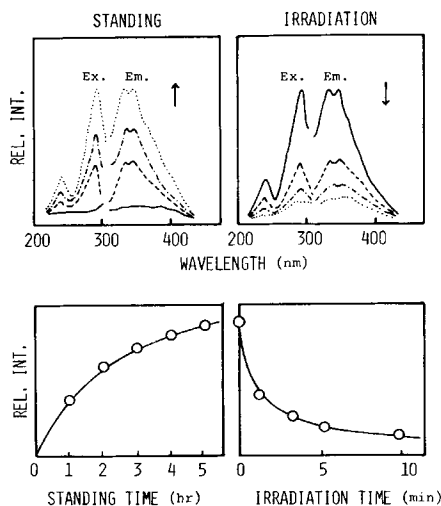


Fig. 7. Changes in fluorescence spectra of high density polyethylene film supplied immediately after the polymerization during exposure to the atmosphere and UV irradiation. Standing time (h): (—) 0; (---) 1; (-·-) 3; (··) 5. Irradiation time (min): (—) 0; (---) 1; (-·-) 3; (··) 10.

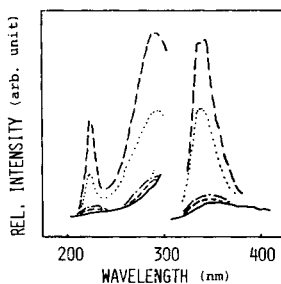


Fig. 8. Comparison of changes in fluorescence spectra of IPP films during exposure to the air: extracted film (—); exposed to cleaned air flow (1 L/min) passed concd  $H_2SO_4$  and a silica gel column for 1 h (---) and 5 h (- · -), and exposed to uncleaned air flow (1 L/min) for 1 h (····) and 5 h (— —).

amount of phosphorescence species incorporated with the polymer chain remained in the sample after the extraction. During the exposure of the polymer to the atmosphere after the solvent extraction both fluorescence and phosphorescence emissions appeared again, and their intensities increased with exposure time reaching almost that of the unextracted film. The intensities of these emission spectra decayed rapidly at the early stage of the photoirradiation of the polymer with UV light, main emission at 2537, 2900, and 3650 Å.

From the results we concluded that main fluorescent species in isotactic polypropylene, like those in polyethylene, are foreign impurities originating from an ambient atmosphere, and that contribution of a very minor amount of phosphorescence species such as carbonyl groups incorporated with the polymer was scarce.

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