

Photochemical Reactions in Commercial Poly(Ethylene 2,6-Naphthalate)

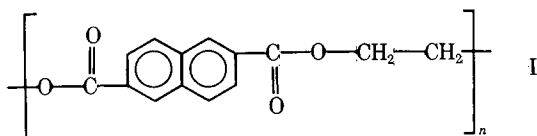
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Synopsis

The photodegradation of poly(ethylene 2,6-naphthalate) is examined by absorption and emission spectroscopy and by flash photolysis techniques. A comparison of the emission spectra with that of a model compound 2,6-dimethylnaphthalate (DMN) shows that the chromophoric species responsible for light absorption in the near ultraviolet is the unit structure of the polymer itself. A flash photolysis study of DMN indicates that the major primary process in photodeterioration of the polymer involves scission by decarboxylation at the naphthyl-carbon bond.

INTRODUCTION

Poly(ethylene 2,6-naphthalate) of unit structure I can be extruded into colorless and transparent films with good physical and chemical properties.¹



Ouchi et al.² have recently reported that on prolonged exposure to near ultraviolet light, the polymer shows significant deterioration in its physical properties. However, these workers presented no evidence of the nature of the light-induced processes that could be responsible for photodeterioration.

Here we report on a study of the luminescence and photochemical behavior of the polymer so that mechanistic information on photodeterioration can be established. As will be shown later, this objective also necessitated a study of the photochemical properties of a suitable model for the unit structure of the polymer. The model selected was 2,6-dimethylnaphthalate (DMN).

EXPERIMENTAL

Materials

Samples of poly(ethylene 2,6-naphthalate) film (25 μm thickness) containing no commercial additives were supplied by the Plastics Research Institute, Teijin Ltd. (Japan).

The model compound 2,6-dimethylnaphthalate (melting point 189°C) was supplied by the Fine Chemicals Service of I.C.I. Ltd., and was purified by recrystallisation from ethanol.

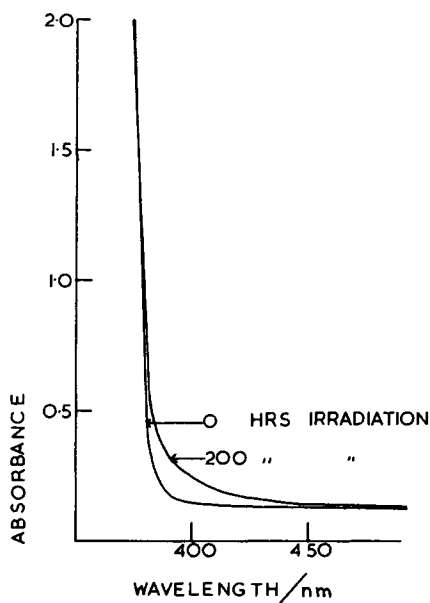


Fig. 1. Effects of irradiation in a Xenotest-150 weatherometer on the ultraviolet-visible absorption spectrum of poly(ethylene 2,6-naphthalate) film (25 μm thickness).

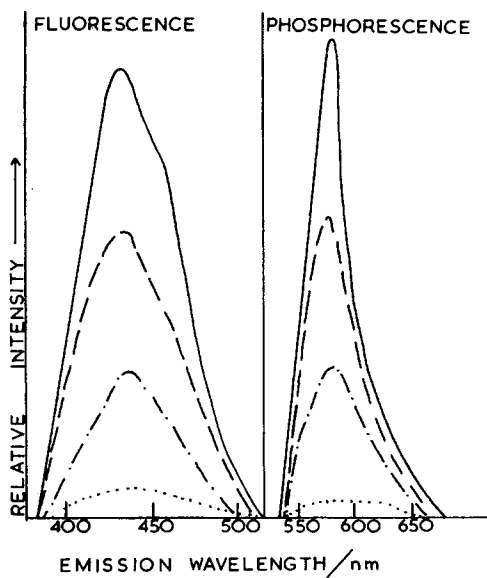


Fig. 2. Fluorescence (300 K) and phosphorescence (77 K) emission spectra of poly(ethylene 2,6-naphthalate) film (—) before and after (---) 50 hr, (----) 100 hr, and (···) 200 hr irradiation in a Xenotest-150 weatherometer (excitation $\lambda_{\text{max}} = 375 \text{ nm}$).

The propan-2-ol was of Analar quality and was further purified by fractional distillation over 2,4-dinitrophenylhydrazine to remove traces of acetone.

Luminescence Measurements

Corrected fluorescence and phosphorescence excitation and emission spectra were obtained using a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter.^{3,4}

Flash Photolysis

The flash photolysis experiments were carried out using (a) a microsecond apparatus with a photoflash of 300 J and a half-life of 10 μ sec and (b) a nano-second apparatus with a photolysis flash (at 347 nm) of 50 mJ and a half-life of 20 nsec.^{3,4}

Continuous Photolysis

The continuous photolysis experiments were carried out using two sets of emission sources that are close in their spectral output to that of natural sunlight. These were a Xenotest-150 weatherometer and a Microscal Light Fastness Tester with a 500 W Hg/W lamp. Both have been described earlier.⁵

RESULTS AND DISCUSSION

Polymer Experiments

Figure 1 shows the effect of prolonged sunlight simulated exposure on the absorption spectrum of the polymer. It is interesting that although under these conditions there are marked changes in the mechanical properties,² there was no significant increase in absorption to longer wavelengths. Indeed, by about 200 hr the effect of the light exposure had resulted in embrittlement although no obvious discoloration had occurred.

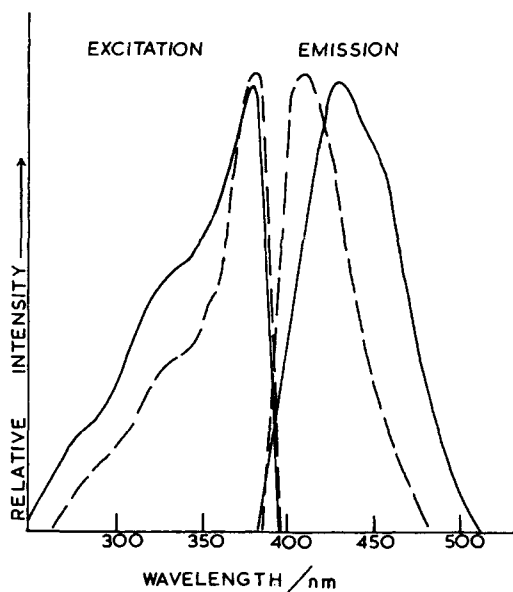


Fig. 3. Comparison of the fluorescence excitation and emission spectra (300 K) of poly(ethylene 2,6-naphthalate) film (—) with that of the DMN (- - -). Sample sensitivity (S_x) = 0.1.

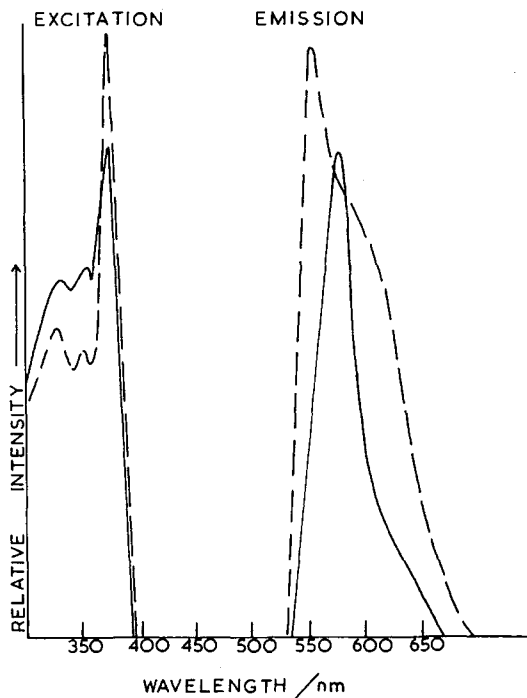


Fig. 4. Comparison of the phosphorescence excitation and emission spectra (77 K) of poly(ethylene 2,6-naphthalate) film (—) with that of the DMN (- - -). Sample sensitivity (S_x) = 100.

Figure 2 shows the fluorescence and phosphorescence spectra of the unirradiated polymer. Their intensity gradually decreases during irradiation. In order to identify the source of these emissions the emission properties of the model for the unit structure of the polymer, i.e., DMN were compared with those of the polymer. The close similarity of the emission and, particularly, the excitation spectra shown in Figures 3 and 4 leave no doubt that the polymer fluorescence and phosphorescence emissions originate from the unit structure I. Further, the fact that the rates of decrease in the intensity of both emissions shown in Figure 2 are similar is consistent with this conclusion. The small differences in the wavelength maxima of the emission spectra of the polymer and model DMN are probably due to distortion effects caused by strong reabsorption. A similar effect was observed in our recent study of the photochemistry of a poly(ethersulphone).⁴

In earlier studies of photounstable polymers based on aromatic isocyanates³ and an ethersulphone⁴ it was possible to observe the primary photochemical processes directly. When similar experiments were carried out with this polymer, however, the strong absorption and emission properties made it impossible for any definite transient species to be detected. Thus, in order to establish the identity of the primary photochemical processes it was necessary to study the model DMN by microsecond flash photolysis. Further, it was hoped that a study with this technique would also lead to information on the photodecomposition products.

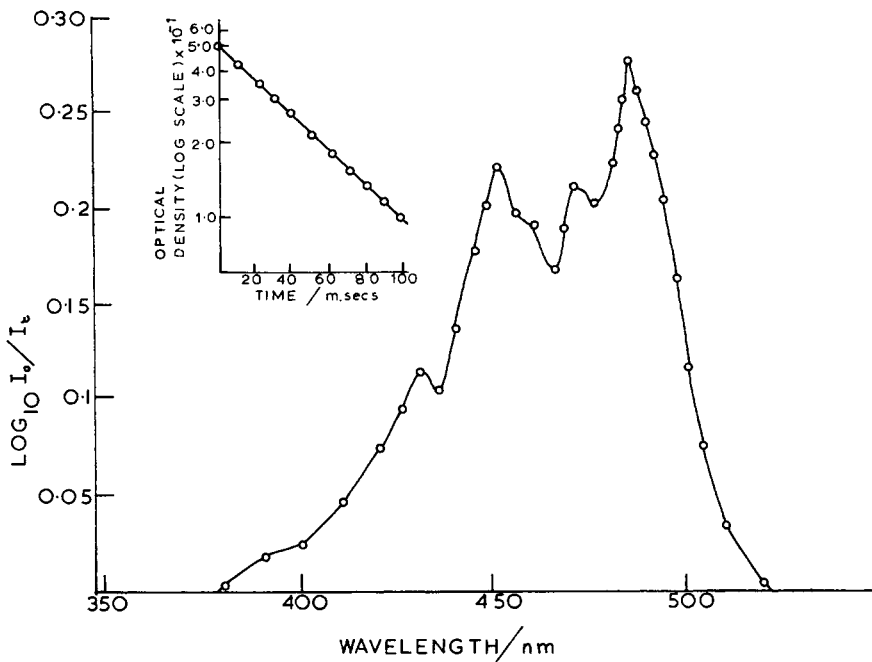
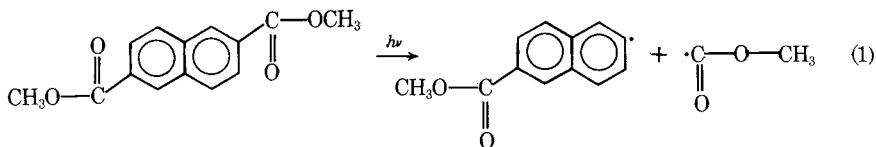


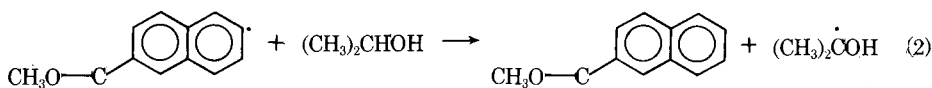
Fig. 5. Transient absorption spectrum produced in the flash photolysis of nitrogen saturated (<5 ppm oxygen) 10^{-5} molar solution of DMN in propan-2-ol. The inset shows that a plot of the decay of the transient exhibits first-order kinetics.

DMN Experiments

Figure 5 shows the transient species that is observed on flash photolysis of DMN in propan-2-ol. This transient has a mean lifetime ($\tau_{1/e}$) of about 40 msec. Earlier flash photolysis studies⁶⁻⁸ of aromatic carboxylic acids and esters have shown that the primary photochemical process involved with these compounds is bond scission at the carbon atom adjacent to the aromatic ring. Thus the transient observed with DMN is likely to be the corresponding naphthyl radical formed by this process:



Earlier evidence⁶⁻⁸ has also shown that the scission process occurs via an excited singlet state and again this is consistent with the observation of very strong fluorescence from the polymer (Fig. 3). Further, the fact that a first-order decay process is observed in propan-2-ol would indicate that the dominant decay process of the radical is by a hydrogen atom abstraction process from the solvent.



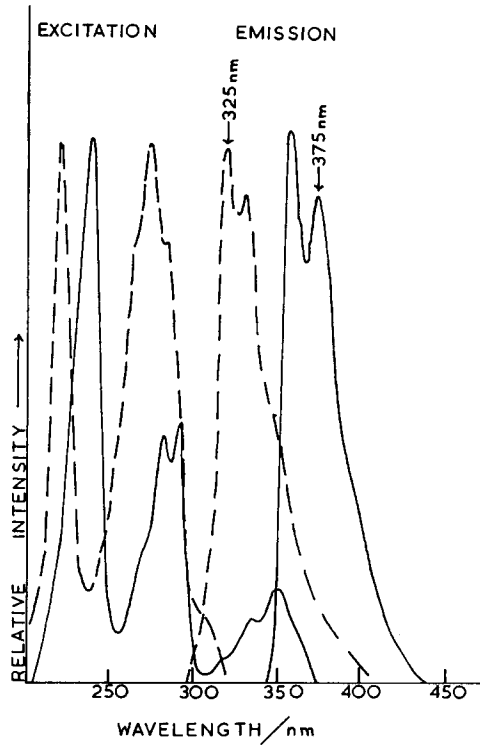


Fig. 6. Fluorescence excitation and emission spectra of DMN (—) (*Sx* 0.1) and naphthalene (---) (*Sx* 10) in propan-2-ol. Both solutes were at a concentration of 1×10^{-4} M.

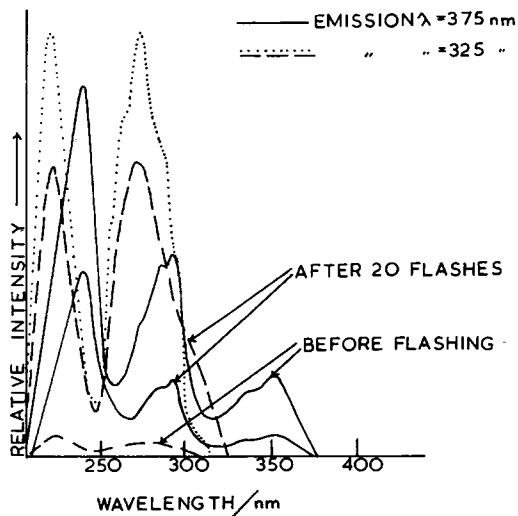


Fig. 7. Comparison of the fluorescence excitation spectrum of (—) DMN (10^{-5} M) (*Sx* 0.3) and (---) its photoproduct before and after twenty photoflashes in the absence of oxygen with that of (···) naphthalene (10^{-5} M) (*Sx* 30) in propan-2-ol.

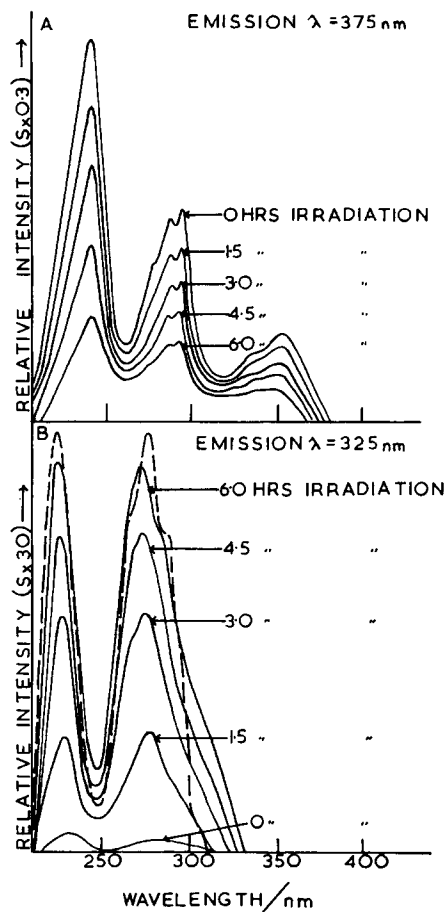
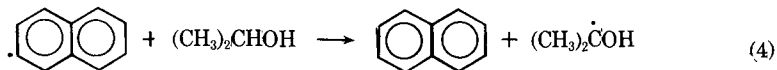
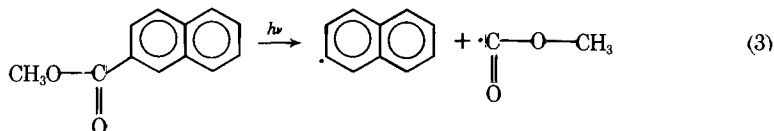


Fig. 8. Comparison of the fluorescence excitation spectrum of (a) DMN (10^{-5} M) and (b) its photoproduct before and after continuous irradiation in a deoxygenated Pyrex cell in the Microscal (—) with that of naphthalene (10^{-5} M) (- - -) in propan-2-ol.

Indeed, the product of reaction (1), 2-methylnaphthalate, could be photolyzed further to naphthalene by the analogous processes:



The hydrogen atom abstraction reactions (2) and (4) occur with propan-2-ol in many reactions involving photoactive excited states or free radicals.⁹ As a result of processes (1)–(4) it is seen that naphthalene should be a major product of the flash photolysis of DMN in propan-2-ol.

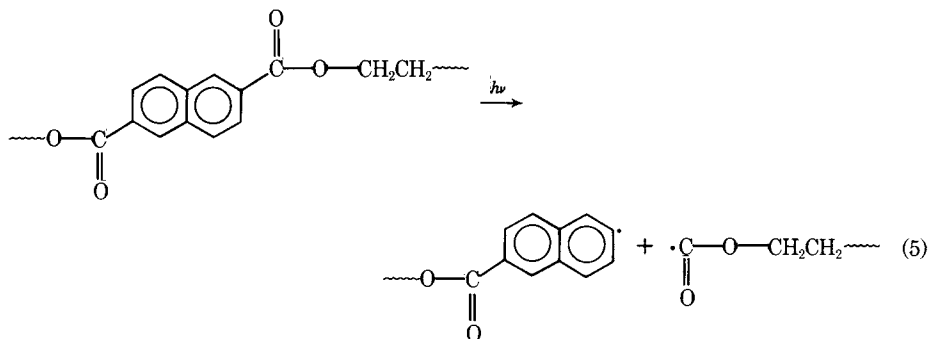
Since naphthalene and DMN have distinctive fluorescence emission and excitation spectra, using spectrofluorimetry¹⁰ it is possible to selectively examine

for the formation of naphthalene in the presence of DMN. Figure 6 shows the emission and excitation spectra of these two species and it is seen that if the emission at 375 nm of DMN is monitored this will give the corresponding excitation spectrum and it will be unaffected by the presence of the naphthalene. Also if the same procedure is carried out monitoring at 325 nm then there will be a minimum of interference from the excitation overlap of the DMN.

Figure 7 shows the result of the repetitive flash photolysis of DMN and it is seen that as the DMN is photolyzed a product spectrum closely matching that of naphthalene is observed. The same analytical procedure was carried out with DMN in propan-2-ol using the sunlight simulated irradiation sources and the same result was observed (Fig. 8).

CONCLUSIONS

From the model system work it would appear that one of the major primary photochemical processes involved in the degradation of the polymer is scission at the naphthyl-carbon bond in the unit structure I:



This would probably result in the formation of naphthalenic chain ends with little extended conjugation. This would explain the results of both Ouchi^{1,2} and Figure 1 above which shows that little discoloration occurs on photodegradation. Interestingly, from our earlier studies on polyurethanes³ and a polyethersulphone⁴ where the mechanism of photodegradation does indicate extended conjugation then discoloration of the polymer is observed.

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References

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