

PHOTOCHEMICAL REACTIONS OF AROMATIC MOLECULES IN SOLID SOLUTION

D. J. Morantz and R. Young

London College of Printing, London S.E.1 (Gt. Britain)

Czarnecki and Kryszewski¹, and Bilen and Morantz², have studied a phenomenon which the latter termed "induced phosphorescence". This is the process which occurs when poly(methyl methacrylate), PMMA, containing a small amount of an aromatic additive is subjected to intense ultra-violet or x-ray radiation. The phosphorescence, which is characteristic of the dopant, may then be produced using a low intensity UV light source. Dopants giving this effect include homo-aromatic and hetero-aromatic hydrocarbons, and their substituted derivatives. Czarnecki and Kryszewski proposed this effect was due to reaction of polymer radicals with oxygen, which is an efficient triplet-quencher. Bilen and Morantz observed an oxygen effect in the post-irradiation period but on evidence such as an observed anomalous temperature dependence of intensity³ felt that energy transfer involving chain-propagating radicals also occurred and was the major factor in the process. Our studies have shown that the phosphorescence is identical in respect of spectra (but not intensity), lifetimes, and temperature dependence to that obtained⁴ with oxygen-free samples. Thus we have to consider that the increase in phosphorescence intensity may be caused, as Czarnecki and Kryszewski originally postulated, by a decrease in oxygen concentration.

It is found that light which the dopant absorbs but the matrix does not, e.g. in the 300-400nm region (OX1 band-pass filter, Scientific Supplies Co.) gives induced phosphorescence. Figure 1 shows radical production, using this light, to be dopant dependent, being almost negligible for undoped systems (spectrum A). Figure 2 indicates that significant (> 2:1; signal:noise) radical production occurs only at, or near, the maximum of phosphorescence intensity.

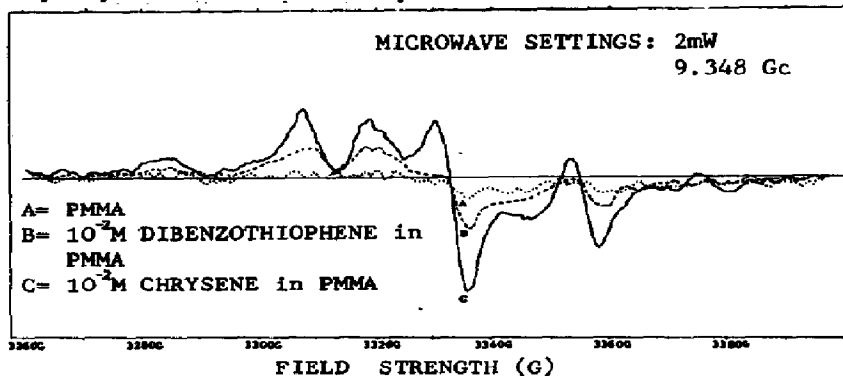


Fig.1 E.P.R. spectra of samples exposed to 300-400nm light for 25 minutes

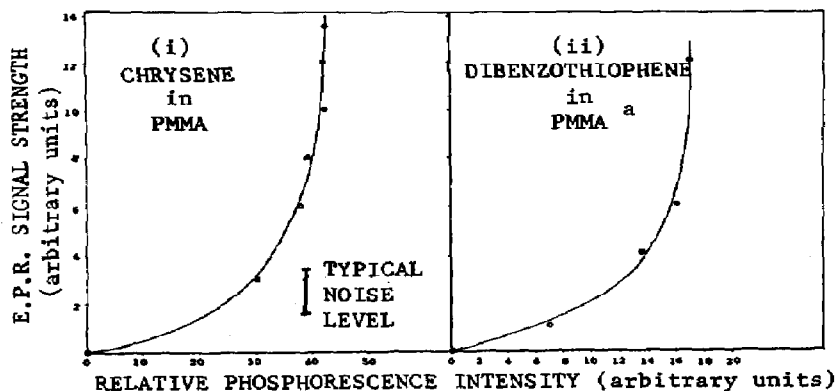


Fig. 2.

E.P.R. signal vs phosphorescence intensity during UV irradiation :
 (i) 300-400nm; (ii) full output of HBO 200W lamp.
 a, data from reference 2.

Figure 3 demonstrates an initial period of decrease in the amount of dopant, indicated by the reduction in fluorescence intensity, before any significant phosphorescence appears. The phosphorescence then increases linearly with the further decrease in fluorescence (figure 3b). These results are consistent with consumption of oxygen via photo-oxidation of the dopant.

Figure 4a shows the spectral changes that occur on irradiation. Dibenzothiophene is shown here, but equivalent changes can be seen with all dopants used. The appearance of phosphorescence (spectrum B) corresponds to the removal of oxygen quenching effects, as verified by lifetime measurements. The product emission (spectrum C) thus increases long after the oxygen consumption is complete, and therefore represents a different photochemical process. This product emission increases linearly with a decrease in phosphorescence (figure 4b); the latter may

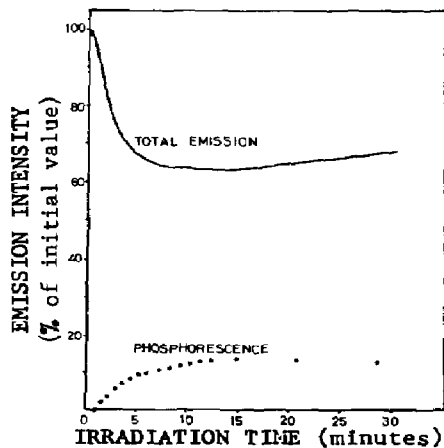


Fig. 3a

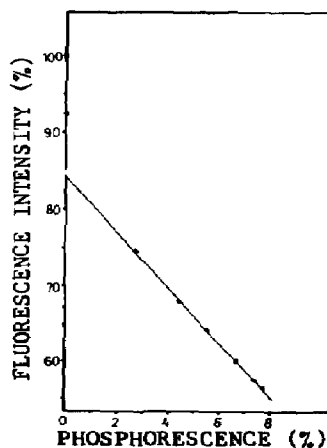


Fig. 3b

Changes in intensities at 434nm during irradiation of $10^{-2}M$ triphenylene in PMMA with 300-400nm light

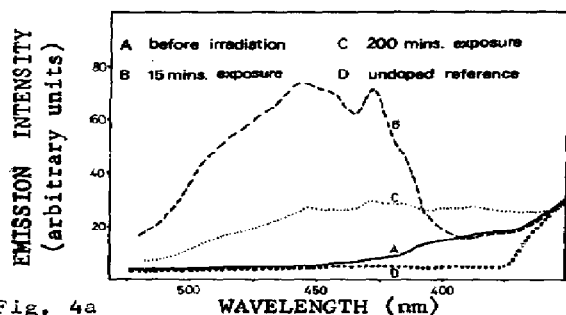


Fig. 4a

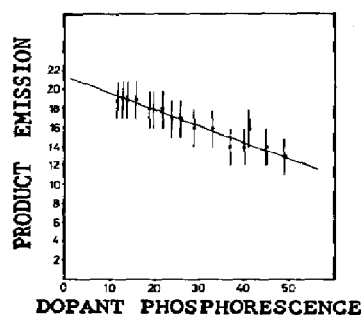
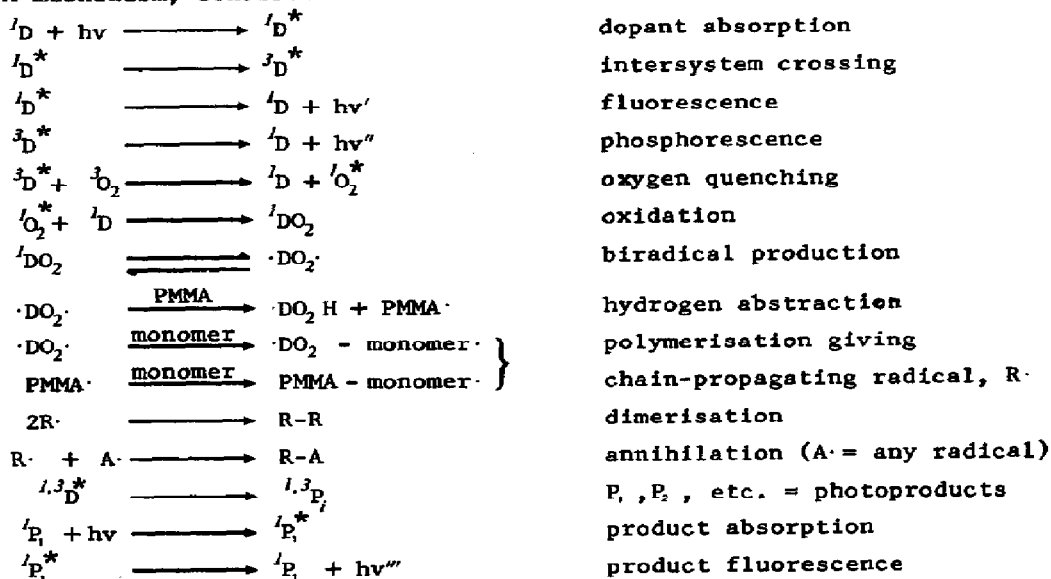


Fig. 4b

Uncorrected emission spectra of irradiated (300-400nm) 10^{-2} M dibenzothiophene in PMMA.

be taken to indicate, in the absence of quenchers, the amount of dopant. Bilen and Morantz have also noted a decrease in the chain-propagating radical concentration, during the latter stages of irradiation, presumably associated with the dopant decrease. Other radical, or similarly reacting species may, therefore, be produced in a photoreaction, which annihilates with PMMA radicals.

A mechanism, consistent with information to date is :



Induced phosphorescence is also seen to occur in poly(vinyl acetate), poly(vinyl chloride), and poly(styrene), where similar mechanisms may be operative.

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