

FRACTAL-LIKE ENERGY TRANSPORT AND FUSION IN A NAPHTHA-
LENE-DOPED POLYMERIC GLASS*

E. Irene NEWHOUSE and Raoul KOPELMAN

Department of Chemistry, University of Michigan, Ann Arbor,
Michigan 48109 USA

Singlet energy transport in naphthalene-doped poly(methylmethacrylate) (PMMA) samples has been found, by doping with anthracene, to follow Stern-Volmer kinetics with a transfer rate constant ca. 2×10^9 . Delayed fluorescence is easily observed; triplet energy transport seems to have fractal-like properties.

Previous studies of energy transport in doped polymers have determined triplet transport in anthracene/polystyrene to be better than in crystalline anthracene¹, while no evidence for energy transport could be found in pyrene/PMMA². The reasons for this variation in exciton mobility are unknown. We study energy transport in naphthalene-doped polymers as energy transport in naphthalene³ is well-understood, making possible comparisons between the two systems.

Singlet energy transport gives a transfer rate constant of ca 2×10^9 from a Stern-Volmer plot of lifetime against anthracene trap concentration. This is about 500 times poorer than in doped naphthalene crystals⁴; the experiments were done at 77K.

In the presence of anthracene traps, the triplet lifetime does not decrease, though the phosphorescence intensity does. Triplet migration does occur, as the phosphorescence spectrum, unlike the fluorescence spectrum, does change with concentration (Fig 1) at 77K, while at 4K all samples have the same emission spectrum. This spectrum is similar to that of dilute glasses containing naphthalene. The emitting species at high concentrations, at 77K, may be a triplet excimer, but its spectrum is unlike the -----

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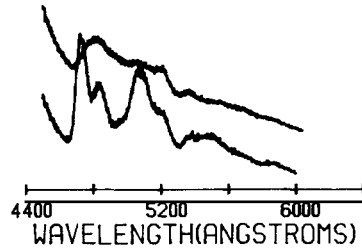


FIGURE 1

Phosphorescence of naphthalene/PMMA at 77K. Top:18% . Bottom: 8.4% .

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triplet excimer observed in dinaphthylalkanes.

The phosphorescence is bi-exponential, with only the short decay time (.2 s) corresponding to the decay time of the delayed fluorescence (.1 s), as seen in Fig 2. The long decay time is about .8 s, still less than the "natural" decay time (ca 2.5 s).

Typical plots of the ratio of fluorescence intensity to phosphorescence intensity vs. time are shown for two temperatures in Figs 3. This method of presentation was chosen to search for fractal behavior . It is evident that the data are inconsistent with heterofusion, whether classical or fractal (no

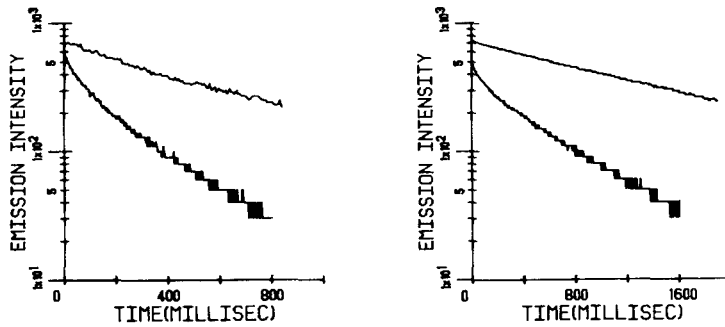


FIGURE 2

Typical delayed emission decays. Left: 18% naphthalene/PMMA at 77K. Right: 8.4% naphthalene/PMMA. Top curve: phosphorescence. Bottom curve: delayed fluorescence.

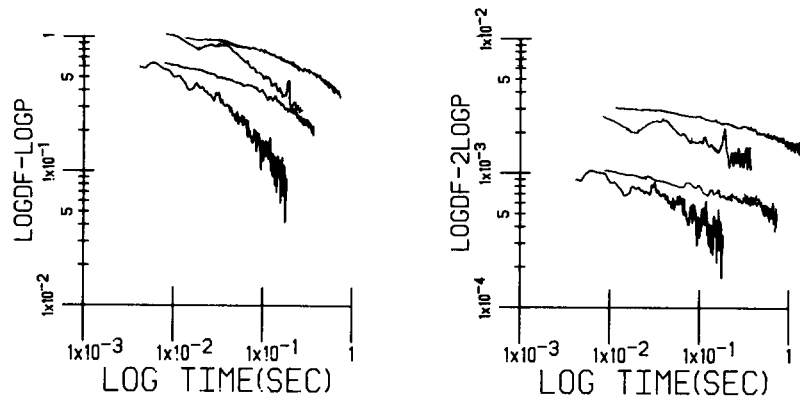


FIGURE 3

Plots testing decays for homofusion vs. heterofusion, and for fractal kinetics: Left: test for heterofusion. Right: test for homofusion. On both sides, (top to bottom): 8.4% at 77K, 8.4% at 165K, 18% at 77K, 18% at 165K. Logdf = log(delayed fluorescence intensity), Logp = log(phosphorescence intensity).

straight lines). They are also inconsistent with classical homofusion (no horizontal lines) but appear to be consistent with fractal-like homofusion (slopes between .3 and .5). This is similar to results on naphthalene mixed crystals (fractal homofusion), and disordered naphthalene at low temperatures (fractal heterofusion).

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