EXCITATION TIME MODULATION STUDIES OF MOLECULARLY DOPED POLYMERS

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Steady state vs. pulsed excitation decay kinetics were obtained for naphthalene doped PMMA (plexiglass). The triplet fusion kinetics for dilute samples depend drastically on the initial excitation kinetics. While the initial exciton densities are equal in both cases, the density distributions differ.

1. Short-time fractal reactions (exciton fusion)

If the excitons are created by a short light (laser) pulse, their initial ($t = 0$) distribution is essentially random, i.e., Hertzian, even in media with low dimensionality [1]. The initial reaction probability is high (no depletion zones) and the initial rate law will be classical, but will soon cross-over into a fractal rate law (as the depletion zones develop). On the other hand, if the excitons are created under steady-state (continuous illumination) conditions, the exciton distribution will be a KOPE (kinetically ordered particle ensemble) distribution, with a non-Hertzian nndd (nearest neighbor density distribution). As soon as the excitation source (laser) is cut off (defining $t = 0$), the exciton fusion reaction will obey a fractal rate law. It is also obvious that the initial ($t = 0$) decay rate will be slower than for the pulsed excitation, as the depletion zones are in place already at $t = 0$. For simplicity we assume that the $t = 0$ *global* exciton densities (i.e., ρ) are the same. This condition is actually maintained experimentally:

$$\rho_s(t = 0) = \rho_p(t = 0),$$

where s designates steady-state and p pulsed excitation. In practice this equidensity condition is achieved via neutral density filters (placed between the light source and the sample) introduced so as to have equal phosphorescence signals ($P_s = P_p$) at $t = 0$. We note that classically we would expect under these conditions to have $P_s = P_p$ and $F_s = F_p$ (equal delayed fluorescence) *at all times*. However, this is not true in low-dimensional geometries where steady-state excitation leads to self-ordering (i.e., a KOPE).

2. Molecularly doped polymer samples

We present here a study of naphthalene doped PMMA (polymethylmethacrylate). Experimental details and similar studies on polymer blends, molecularly em-

bedded porous membranes and Vycor, crystalline films, as well as isotopic mixed crystals, are given elsewhere [1,2]. This particular sample is of interest because dilute molecularly doped polymers (MDP) have been described by two diametrically opposed models [3]: 1) Total segregation. Here the doped molecules form microscopic crystallites (submicron ones, which do not scatter light). 2) Random aggregation. Here the guest molecules form random clusters, which grow with concentration like percolation clusters.

The naphthalene doped PMMA films begin to scatter light at about 20% concentration (by weight). It is generally agreed [2] that at this concentration there are
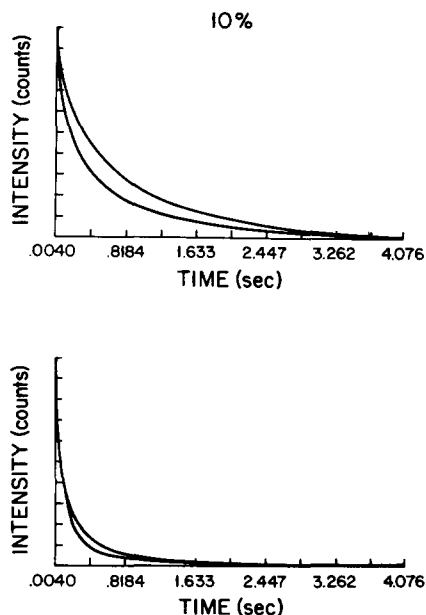

Fig. 1. Phosphorescence (top) and delayed fluorescence (bottom) of 10% naphthalene/PMMA (77 K) with pulsed vs. steady-state excitation. *Note*: The faster decays are produced by the pulsed excitations.
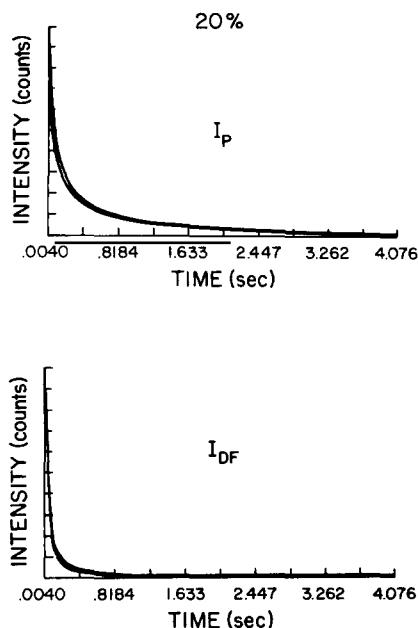
Fig. 2. Phosphorescence (top) and delayed fluorescence (bottom) decay of 20% naphthalene/PMMA (77 K) with pulsed (10 n) vs. "steady-state" (several second of 100 Hz pulse excitation. Note: There is little difference between the decay produced by pulsed and steady excitation.

segregated, micron-size, naphthalene crystallites. Under these conditions we expect to see classical behavior, i.e., $P_s = P_p$ as well as $F_s = F_p$ for all times for the short-time experiments. However, at lower concentrations, one might expect a non-classical behavior.

Figure 1 shows phosphorescence and delayed fluorescence of naphthalene/PMMA at 77 k with pulsed versus steady illumination conditions for a 10% sample. This result of faster decay for pulsed excitation conditions is also typical, for both phosphorescence and fluorescence decays at lower concentrations. However, in the 20% sample behavior (fig. 2) there is practically no difference between the decays of excitations produced by short pulses (20 ns) and those produced under quasi-steady-state excitation (over several seconds). These results support our conclusion that the dilute samples do not contain naphthalene crystallites but only aggregates (less than 1000 Å). The low-dimensional naphthalene aggregates show non-classical reaction kinetics, which is typical of diffusion-limited reactions in restricted geometries. This kinetic method is thus useful for the characterization of mesoscopic samples, i.e., aggregates much larger than the molecular size (10 Å) but smaller than micron size crystallites. We have observed similar behavior in a large variety of other microsystems [1,4].

3. Summary

Steady state vs. pulsed excitation decay kinetics were obtained for naphthalene doped PMMA (plexiglass). The triplet fusion kinetics for dilute samples depend drastically on the initial excitation kinetics. While the initial exciton densities are equal in both cases, the density distributions differ.

Acknowledgement

References

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