

Preliminary Note

Intramolecular energy transfer in polymers containing benzoyl and naphthalene moieties

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Energy transfer processes are of considerable importance in macromolecular systems. The migration of electronic energy can lead to the occurrence of chemical and physical processes at a considerable distance from the initial excitation site. For example, some photostabilizers rely on the transfer of the excitation to a site where the energy can be dissipated in radiationless processes [1].

In recent studies from this laboratory we have reported several examples of triplet excitation transfer in solution between chromophores of the same type in monoketones [2], diketones [3] and polymers [4 - 6]. In this communication we wish to report some preliminary results on the photochemistry of copolymers of methylmethacrylate-phenyl vinyl ketone-2-vinylnaphthalene. Solutions of these copolymers were examined using nanosecond laser flash photolysis techniques. Although a few studies in the literature have been concerned with energy transfer from aromatic carbonyls in polymers to bound and free naphthalene moieties in solution [7 - 9] and at 77 K [10 - 12], the direct measurement of the kinetics of intramolecular processes of this nature has not been carried out.

1. Results and discussion

For all samples the main component in the polymers was methylmethacrylate (82.1 - 93.9%), the light absorbing benzoyl groups accounted for 4.6 - 15.3% of the monomer units and the naphthalene groups accounted for approximately 1.4 - 3.9%. The compositions were determined by comparison of the UV spectra of the polymers with those of isobutyrophenone and 2-ethylnaphthalene.

Oxygen-free samples, usually in benzene, were excited with the pulses (337.1 nm, 8 ns and 3 mJ) from a nitrogen laser. At this wavelength only the benzoyl groups are excited. Although many polymers and copolymers con-

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taining phenyl vinyl ketone undergo the Norrish type II process efficiently, this was not the case in our system; the relatively low abundance of these chromophores leads to a situation where most benzoyl groups do not have easily abstractable hydrogen atoms in the γ position [13]. The aromatic carbonyls undergo fast and efficient intersystem crossing to the triplet manifold; the triplet carbonyl then transfers the energy to the naphthalene quenchers. A typical trace obtained at 425 nm is shown in Fig. 1. At this wavelength the extinction coefficient of the naphthalene triplet is much greater than that of the benzoyl triplet [14], and thus a build-up trace is obtained. At 360 nm, where the situation is reversed, there is a decay of the triplet carbonyl into the naphthalene triplet. However, the measurements under these conditions are subject to large errors and are only feasible with samples containing low concentrations of naphthalene groups. At 425 nm all our samples could be examined without difficulty. Our experiments were carried out at sufficiently low polymer concentrations so that intermolecular transfer could be ignored, *i.e.* the rates observed were independent of the polymer concentration in the range $0.3 - 1.8 \text{ g (100 ml)}^{-1}$. In all cases, we also examined copolymers of methylmethacrylate and phenyl vinyl ketone (no naphthalene groups) of similar composition to confirm that the lifetimes of the carbonyl groups were substantially longer than those observed in the copolymers with naphthalene groups. This ensured that the rates measured (see Fig. 1) were determined by energy transfer and not by alternative modes of decay of the benzoyl chromophores. The excitation doses used ($0.5 - 3 \text{ mJ}$) were sufficiently low so that only one triplet per macromolecule could be generated. This was confirmed in experiments which showed that a sixfold change in light intensity had no effect on the rates measured.

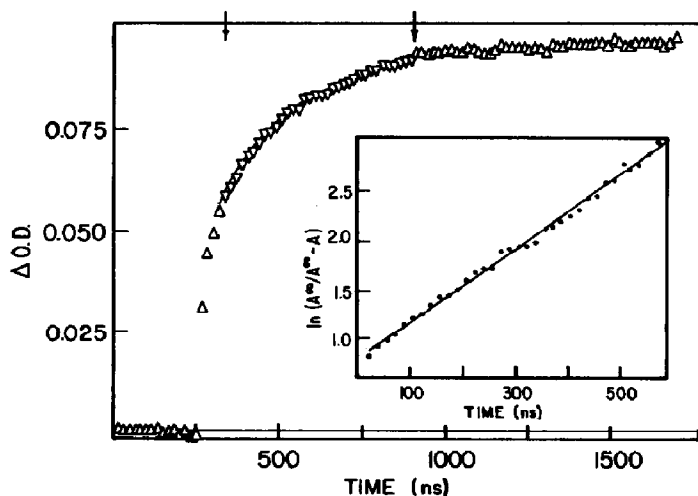


Fig. 1. An experimental trace monitored at 425 nm for a sample of the first polymer in Table 1 in benzene at 22°C . A first order plot obtained using eqn. (1) is shown in the inset; the time scale has been offset with respect to the main part of the figure. The arrows indicate the region of the trace used to calculate the rate constant.

The trace in Fig. 1 consists of an initial "jump" which is followed by a build-up curve. The initial jump can be attributed to (1) T-T absorption due to the benzoyl group at the monitoring wavelength and (2) an "instantaneous" formation of naphthalene triplets, where the term instantaneous refers to a process occurring in less than 10 ns. A comparison with similar copolymers, but which do not contain 2-vinylnaphthalene, shows that T-T absorption by benzoyl groups can only account for a small fraction (typically 10 - 15%) of the initial jump and the rest is caused by the instantaneous formation of naphthalene triplets. We attribute this fast formation of naphthalene triplets to a "close neighbor" effect; *i.e.* triplet energy transfer, which can only occur by the exchange mechanism, can be expected to be extremely sensitive to the distance between donor and acceptor. It is not yet clear whether the close neighbor effect is caused by the nearest neighbor exclusively or whether units two or three links away from the donor can still generate triplet naphthalene in less than 10 ns*.

The build-up of triplet naphthalene which follows the "jump" obeys first order kinetics, as illustrated in the inset in Fig. 1 which was obtained from

$$\ln \frac{A_{\infty}}{A_{\infty} - A} = kt \quad (1)$$

Here A and A_{∞} are the transient absorbances at time t and in the plateau region respectively, and k is the experimental rate constant for the transfer process provided that other modes of decay can be ignored.

In Table 1 the values of k for a series of polymers of different compositions are shown. As expected, the values of k increase with increased abundance of naphthalene groups. Also k is independent of the relative abundance of benzoyl chromophores, showing that carbonyl groups do not have a cooperative effect in the energy transfer process. This means that the migration of the energy towards the acceptor must occur largely as a result of molecular motion in the polymer bringing the excited chromophore and quencher together, with the contribution due to transfer between carbonyl chromophores being unimportant. However, in systems with sequential carbonyl groups, the rates of energy migration are in the picosecond time domain [5]; again, this dramatic difference illustrates the importance of distance in controlling the efficiency of energy transfer by the exchange mechanism.

Experiments to determine the activation parameters, as well as the effect of solvents in systems involving remote energy transfer, are currently in progress.

*Our preliminary data suggest that there is involvement of other groups in addition to the nearest neighbor; *e.g.*, for the first sample in Table 1, the probability of a given phenyl vinyl ketone moiety having a naphthalene group as next neighbor is 3.2%, and is approximately 4% if naphthalene units separated only by phenyl vinyl ketone groups are included.

TABLE 1

Rates of energy transfer for various polymer compositions

Ketone (%)	Naphthalene (%)	k^a (μs^{-1})
12.5 ^b	1.6	3.5
15.3	2.6	7.7
13.2	3.5	9.1
7.1	1.4	3.8
7.6	2.6	6.4
8.4	3.9	10.8
4.6	1.5	4.1
4.9	2.9	7.2
4.9	3.9	9.9

^a At 22 °C in benzene; typical polymer concentration, 0.5 g (100 ml)⁻¹.

^b The trace in Fig. 1 corresponds to this sample.

2. Experimental

The copolymers were prepared by free radical (azo-bis-isobutyronitrile was used as initiator) polymerization of monomer mixtures in benzene. The conversion was always below 15%. The copolymers were precipitated with methanol, were redissolved in benzene and the process was repeated five or six times. The samples were finally freeze dried from benzene.

The samples (1 ml) were contained in Suprasil cells with an optical path length of 3 mm; they were deaerated by bubbling through oxygen-free argon. The laser photolysis system used a Molelectron UV-400 nitrogen laser for excitation. Further details have been given elsewhere [15].

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