

Preliminary Note

Photophysical evidence for intramolecular energy transfer in insoluble polymeric benzophenone (benzoylated polystyrene beads)

F. WILKINSON and C. J. WILLISHER[†]

Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU (U.K.)

J. L. BOURDELANDE, J. FONT and J. GREUGES

Departamento de Química (Orgànica), Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, Barcelona (Spain)

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The transients generated by pulsed laser excitation of benzoylated polystyrene beads are the benzophenone triplet and a radical. When a diene is anchored to benzoylated polystyrene, quenching of the triplet is observed for which intramolecular energy transfer is assumed to be responsible.

Since the pioneering work of Leemakers and James [1], the use of photosensitizers anchored to insoluble polymeric supports has become widespread, and such systems are now commercially available [2]. Bourdelande *et al.* have already published details of an easy preparation of polymeric benzophenone (benzoylated polystyrene) and its action as a photosensitizer in a variety of reactions, *e.g.* sensitized 2 + 2-photocycloadditions, photooxidations, formation of hydroperoxides etc. [3]. Also, *E-Z* photoisomerizations of conjugated dienes have been effected not only when the diene is in solution in the presence of the photosensitizer but also when both the carbonyl chromophore and the diene are attached to the polymer, for which intrapolymeric energy transfer has been invoked to explain the isomerization [4]. Polymeric benzophenone is obtained by Friedel-Crafts benzoylation of 2% divinylbenzene cross-linked polystyrene beads, a preparation method that allows different loadings of the chromophore to be obtained. We have employed samples containing 0.1 and 2.2 milliequivalents g^{-1} of carbonyl group, corresponding to 1% and 29% functionalization of the phenyl groups in the polystyrene, which we shall refer to as P-1 and P-29 respectively.

Very little is known about the photophysical processes that take place in chromophores linked to insoluble polymeric supports because these materials are generally unsuitable for study by transmission flash photolysis. The technique of diffuse reflectance laser flash photolysis (DRLFP) has been

[†] Author to whom correspondence should be addressed.

developed to investigate transient absorption in opaque, light-scattering substances. DRLFP makes use of diffusely reflected analysing light to interrogate transient absorption following pulsed excitation, and it has been successfully applied to monitor triplet-triplet absorption in microcrystalline ketones [5, 6] and dyes bound to a polymer [7] or incorporated in a cotton fabric [8], and to probe the behaviour of ketone molecules intercalated in the channels of "silicalite", a synthetic hydrophobic zeolite [9]. Hitherto we had only chemical evidence concerning the action of polymeric benzophenone, and we now wish to communicate how DRLFP studies of polymeric benzophenone can provide further information on the structural and mechanistic aspects of the chromophore's behaviour. A description of the experimental procedure for DRLFP is given in ref. 5.

The spectra of the transient absorption and emission in P-1 are given in Fig. 1. The emission obviously arises from a triplet carbonyl group and the

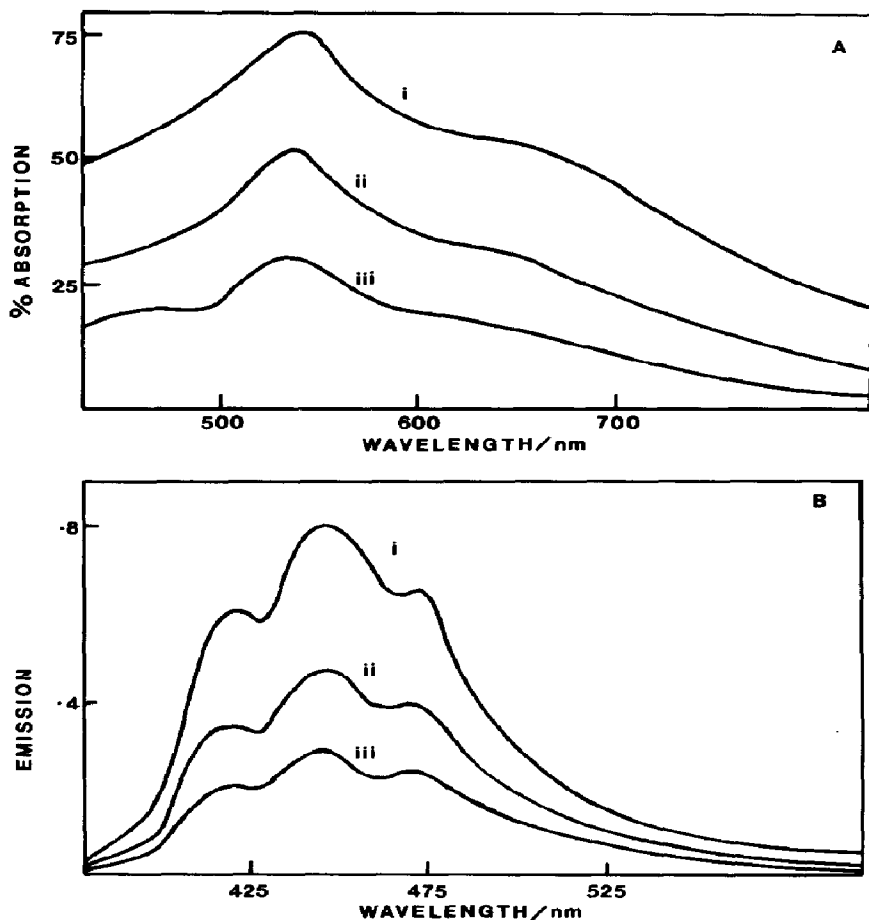


Fig. 1. (A) Transient absorption spectrum of dry, nitrogen-purged P-1 beads ($\lambda_{\text{exc}} = 354$ nm; intensity, 40 mJ pulse^{-1} ; pulse width, 20 ns). (i) 0 ms, (ii) 0.25 ms and (iii) 0.45 ms after laser flash. (B) Emission spectrum of P-1, conditions as above. (i) 0 ms, (ii) 0.2 ms and (iii) 0.5 ms after laser flash.

transient absorption contains a large contribution from the triplet state of benzophenone. Both transient phenomena decay in the same time domain, with an initial half-life of 0.3 - 0.5 ms. As the percentage functionalization of phenyl groups in the polystyrene is increased, several observations can be made: (i) the transient absorption and emission spectra become broader and the structure is less well defined; (ii) the intensity of the phosphorescence decreases; (iii) the decay of the transient absorption becomes slower and more complex while that of the phosphorescence is hardly affected. These observations may be explained by assuming that preferential functionalization of the polymer chain takes place; the phenyl groups exposed at the surface are benzoylated first, followed by those in the less accessible interior of the polymer. For the low percentage functionalization of P-1, benzophenone is believed to be attached predominantly at the surface where the chromophore cannot interact significantly with either adjacent phenyl groups or benzylic hydrogens, and the major transient species is therefore the triplet. When the loading is increased the interior of the polymer chain is also benzoylated and here the geometry is more favourable for benzylic hydrogen abstraction to form a radical, possibly the benzophenone ketyl radical which has a similar absorption spectrum (at least in solution) to that of the triplet [10]. Thus the transient species present in a moderately loaded polymer consist of a mixture of the triplet and a radical. With higher loadings, more

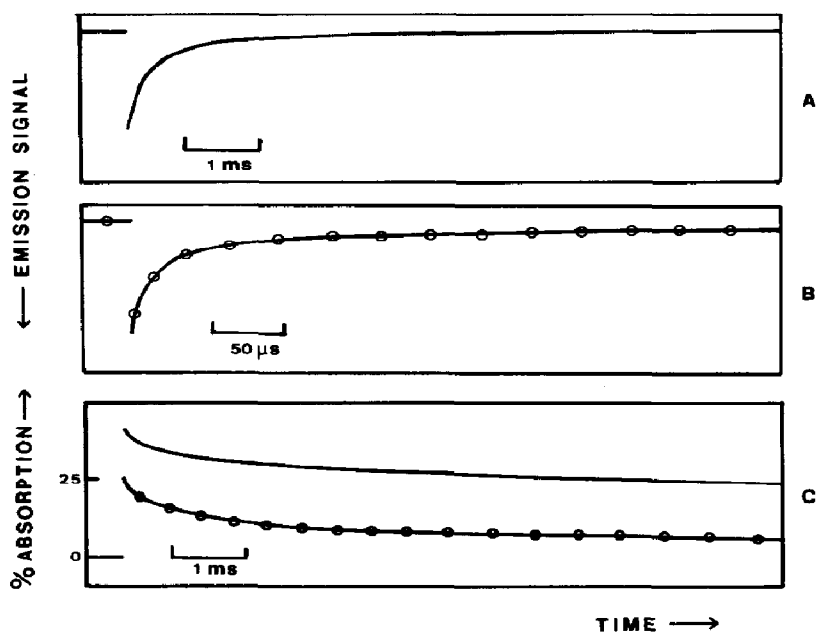


Fig. 2. (A) Trace of phosphorescence decay in dry, nitrogen-purged P-29 beads (conditions as above and $\lambda_{\text{mon}} = 450$ nm). (B) Trace of phosphorescence decay in dry, nitrogen-purged P-29 beads where 20 units of diene quencher per 100 polymer phenyl groups are attached (conditions as in Fig. 2(A)). (C) Transient absorption decay in P-29 (—) and in P-29 containing the diene (—○—). Conditions are as in Fig. 1(A) with $\lambda_{\text{mon}} = 510$ nm.

phenyl groups in the interior of the polymer are benzoylated, resulting in a larger population of radicals.

Cofunctionalization of P-29 with a diene known to quench the benzophenone triplet in fluid solution [11] gives a sample on which intramolecular energy transfer can be demonstrated. Parts (A) and (B) of Fig. 2 illustrate that phosphorescence quenching occurs when 20 units of diene per 100 polymer phenyl groups are included in P-29. Triplet energy transfer from benzophenone to the diene is assumed to be responsible for the quenching. The transient absorption is quenched to a lesser degree (see Fig. 2(C)) which confirms that a substantial proportion of the absorption in P-29 is not due to the triplet but to a species that does not appear to transfer energy to the diene. These observations give the first direct evidence of intramolecular triplet energy transfer in bifunctionalized insoluble opaque polymer beads, and show that low percentage functionalization results in a larger triplet concentration than that found in more highly loaded polymers. The last point is corroborated by the fact that a polymer with a low percentage functionalization is a more efficient triplet sensitizer than one which is more highly benzoylated [3]. A full discussion of the photophysical properties of polymeric benzophenone will be presented in due course.

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