Table 3 Photopolymerization of MMA micelle as a function of the pH of the aqueous phase. Initiator, DMPA. Irradiation wavelength, λ = 365 nm

	pH = 3	pH ≈ 4	pH = 11
OD	0.4	0.4	0.4
I_0 (photon cm^{-2} s^{-1})	2.9 x 10^{16}	2.9 x 10^{16}	2.9 x 10^{16}
R_p (M s^{-1})	247 x 10^{-5}	194 x 10^{-5}	190 x 10^{-5}
ρ_m (s^{-1})	1.23	0.95	0.95
ϕ_m	55.5	43.6	42.7
$A\sqrt{\phi_i}$ (M$^{-1/2}$ s$^{-1/2}$)	0.65	0.52	0.5

polymerization. Through steady-state and laser spectroscopy experiments, extensive work is now in progress in order to obtain a better insight into the photophysical and photochemical processes involved in the first steps of initiation.

References

1 Pappas, S. P. *Progr. Org. Coatings* 1973, **2**, 333

2 Heine, H. G., Rudolph, H. and Rosenkranz, H. J. *Appl. Polym. Symp.* 1975, **26**, 157

3 Oster, G., Oster, G. K. and Moroson, H. *J. Polym. Sci.* 1959, **34**, 671

4 Hérold, R. and Fouassier, J. P. *Angew. Makromol. Chem.* in press

5 Hutchinson, J. and Ledwith, A. *Polymer*, 1973, **14**, 405

6 Carlblom, L. H. and Pappas, S. P. *J. Polym. Sci.* (*Polym. Chem. Edn*) 1977, **15**, 1381

7 Merlin, A. and Fouassier, J. P. *J. Polym. Sci.* (*Polym. Lett. Edn*) 1979, **17**, 709

8 Fouassier, J. P., Lougnot, D. J. and Faure, J. *CR Acad. Sci.* (*Paris*) 1977, **284C**, 643

9 Kuhlmann, R. and Schnabel, W. *Polymer* 1977, **18**, 1163

10 Fouassier, J. P. and Merlin, A. J. *Photochem.* 1980, **12**, 17

11 Schauber, C. and Riess, G. Personal communication

Laser flash photolysis characterization of the triplet state of poly(*p*-methoxyacrylophenone)[*]

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Carbonyl chromophores play an important role in polymer photochemistry, in aspects such as photodegradation, photostabilization, photocuring and photooxidation[1,2]; quite frequently that role is directly related to the physical and chemical properties of the triplet state. Few polymers are known where the carbonyl triplet state reactivity can be directly examined in time resolved experiments, at room temperature. Even in the case of poly(phenyl vinyl ketone)[3–8], which has been widely studied using flash techniques, the species directly observable is the biradical generated in the Norrish Type II reaction[4,7,8], rather than the triplet state. Examples where the triplet state can be observed are the cases of poly(vinyl benzophenone)[9] and copolymers of phenyl vinyl ketone and methyl methacrylate[10], where the absence of labile γ – hydrogen atoms prevents the fast triplet decay. In this communication we report preliminary results on the characterization and reactions of the triplet state of poly (*p*-methoxyacrylophenone), PPMA.

The monomer, *p*-methoxyacrylophenone (PMA), was prepared according to a procedure reported by Hrdlovič *et al.*[11], distilled under vacuum (with considerable loss) and the polymerizations carried out in benzene with azobisisobutyronitrile as initiator. Conversions were below 20% and the polymer purified by multiple precipitations with methanol. In contrast to Hrdlovič's samples[11], our freeze-dried polymers prepared by this technique were sufficiently soluble in benzene to carry out the kinetic measurements; all other properties agreed well with those reported[11].

The transient spectrum obtained in the laser flash photolysis of PPMA in benzene using pulses from a nitrogen laser for excitation (337. 1 nm, ~8 ns, up to 10 mJ) is shown in *Figure* 1. The spectrum is similar to that reported for the triplet state of *p*-methoxyacetopheone[12] and *p*-hydroxypropiophenone[13] except for the presence of an additional long wavelength band in the 630 nm region. At low excitation doses the signals decay with first order kinetics and a lifetime of ~800 ns. The decay can be accelerated by addition of dienes or 1-methyl naphthalene; with the latter quenching is accompanied by the formation of the easily detectable triplet state of the quencher[14]. The rate constant for triplet quenching by 1-methyl naphthalene is 2.0 × 10^9 M^{-1} s^{-1} in benzene at 27°C.

At high light intensities we observe that the decay of the triplet state is more complex, and presents an initial fast component which can account for a considerable fraction of the decay. We believe that this fast process reflects intramolecular triplet–triplet annihilation. We note that the laser dose, when not attenuated may be enough to put more than one quanta per macromolecule. Such a

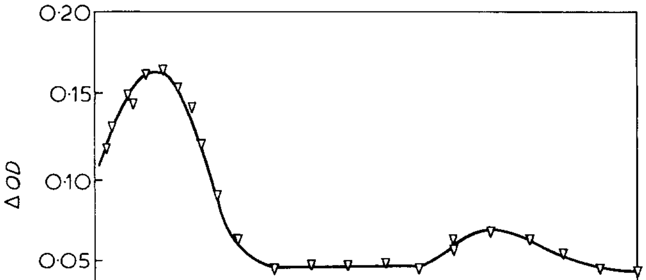

Figure 1 Transient spectrum observed immediately after laser excitation of a solution of PPMA in benzene at 27°C

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process, if it occurs by migration along the chain requires fast energy hopping, which in the case of poly(phenyl vinyl ketone) has been estimated to occur with a frequency of 10^{12} s^{-1} [15].

In order to examine further the importance of energy migration between carbonyl chromophores, we prepared a copolymer containing 20% phenyl vinyl ketone (PVK) moieties and 80% PMA units. Under the same conditions used for PPMA we observe only one triplet state, with a lifetime of 230 ns and a transient spectrum which should be essentially attributed to the PMA moieties. The lifetime is intermediate between those for PPMA and for PPVK and requires efficient energy migration, presumably energy equilibration within segments in the polymer. We note that the longer triplet lifetime for PPMA compared with PPVK should be attributed to a low lying π,π^* triplet state which makes the methoxy-substituted chromophore relatively unreactive in the Norrish Type II reaction which largely controls the lifetimes[11,16–19].

PPMA seems to be an excellent model polymer for the study of carbonyl triplets in polymer systems. The combination of long lifetimes and intense T–T absorption signals largely facilitates the studies. While PPMA will frequently be less reactive than unsubstituted ketones the difference in reactivity is well-documented in the literature[17–19] and it would be easy to estimate rates for systems with low lying n,π^* states.

In order to test the possibilities of PPMA as a model polymer, we have examined the quenching of the triplet state by *o*-hydroxybenzophenone, a commonly-used polymer photostabilizer[1]. The rates are easily measured even when *o*-hydroxybenzophenone screens most of the excitation light and leads to $k_q = 9.0 \times 10^8$ M^{-1} s^{-1}. The quenching process is presumed to occur largely by energy transfer.

Current studies centre on temperature effects on the lifetimes and on the possibility of obtaining an absolute measure for the rate of energy hopping from the study of the intensity dependence of transient processes.

Note The laser facility used for these experiments has been described in detail elsewhere[20].

REFERENCES

1 Ranby, B. and Rabek, J. F. 'Photodegradation, Photooxidation and Photostabilization of Polymers', Wiley, London, 1975
2 For example, see papers presented at the 'International Symposium on Photodegradation, Photooxidation and Photostabilization of Organic Coatings', (179th Am. Chem. Soc. meeting, Houston, Texas, 1980) published in 'Organic Coatings and Plastics Chemistry', Vol. 42, ACS Publications, 1980.
3 Faure, J., Fouassier, J.-P. and Lougnot, D.-J. *J. Photochem.* 1976, **5**, 13
4 Faure, J., Fouassier, J.-P., Lougnot, D.-J. and Salvin, R. *Nouv. J. Chim.* 1977, **1**, 15
5 Beck, G., Dobrowolski, G., Kiwi, J. and Schnabel, W. *Macromolecules*, 1975, **8**, 9
6 Kiwi, J. and Schnabel, W. *Macromolecules*, 1976, **9**, 468
7 Small Jr, R. D. and Scaiano, J. C. *Macromolecules*, 1978, **11**, 840
8 Bays, J. P., Encinas, M. V. and Scaiano, J. C. *Macromolecules* 1980, **13**, 815
9 Schnabel, W. *Makromol. Chem.* 1979, **180**, 1487
10 Kiwi, J. and Schnabel, W. *Macromolecules*, 1975, **8**, 430
11 Lukáč, I., Moravčik, M. and Hrdlovič, P. *J. Polym. Sci.* (*Polym. Chem. Edn*) 1974, **12**, 1913
12 Lutz, H., Bréhéret, E. and Lindqvist, L. *J. Phys. Chem.* 1973, **77**, 1758
13 Das, P. K., Encinas, M. V. and Scaiano, J. C.. *J. Phys. Chem.* submitted for publication
14 Porter, G. and Windsor, M. W. *Proc. Roy. Soc. London* (*A*) 1958, **245**, 238
15 Encinas, M. V., Funabashi, K. and Scaiano, J. C. *Macromolecules*, 1979, **12**, 1167
16 Lukac, I. and Hrdlovič, P. *Eur. Polym. J.* 1979, **15**, 533
17 Wagner, P. J. and Nakahira, T. *J. Am. Chem. Soc.* 1973, **95**, 8474
18 Wagner, P. J., Thomas, M. J. and Harris, E. *J. Am. Chem. Soc.* 1976, **98**, 7675
19 Wagner, P. J., Kemppainen, A. E. and Schott, A. N. *J. Am. Chem. Soc.* 1973, **95**, 5604
20 Scaiano, J. C. *J. Am. Chem. Soc.* 1980, in press