European Polymer Journal, Vol. 15, pp. 533 to 536
© Pergamon Press Ltd 1979. Printed in Great Britain

0014-3057/79/0601-0533$02.00/0

PHOTOLYSIS OF COPOLYMERS 4-METHOXYACRYLOPHENONE WITH 2-HYDROXY-4-(2-METHACROYLOXYETHOXY) BENZOPHENONE

I. LUKÁČ and P. HRDLOVIČ
Polymer Institute of Slovak Academy of Sciences, 809 34 Bratislava,
Dúbravská cesta 9, Czechoslovakia

(*Received* 23 *October* 1978)

Abstract—The photolysis of copolymers of 4-methoxyacrylophenone with 2-hydroxy-4-(2-methacroyloxyethoxy) benzophenone (4MAP/PBMA) containing 0–8 wt/wt 2% of BPMA was compared with that of poly-4-methoxyacrylophenone (P4MAP) in the presence of 2-hydroxy-4-(2-isobutyroyloxyethoxy) benzophenone (BPIB) in ethyl benzoate at 366 nm. In the photolysis of P4MAP proceeding through the long-lived triplet state, it was possible to separate quenching and screening effects of BPIB. The dependence of the ratio of quantum yields of main chain scission without and with quencher was linear for free quencher; for copolymerized quencher, however, the dependence indicated static quenching. Using the Perrin model for copolymers, the quenching sphere of 1.56 nm was calculated. Study of the emission decay of copolymers 4MAP/BPMA in poly(methyl methacrylate) films at 77 K give 1.86 nm for the quenching sphere. Similar values were found for quenching of 4-methoxyacrylophenone chromophore by built-in acceptors naphthalene and diphenyl (1.60 nm). These results indicate that energy transfer in carbonyl copolymers, both in dilute solution and in film, at 77 K proceeds at a distance a little greater than the sum of donor and acceptor diameters (about 1.2 nm) showing that the extent of triplet energy migration is limited.

INTRODUCTION

Study of the efficiency of light stabilizers confirmed the possibility of energy transfer from an excited carbonyl to a low molecular stabilizer [1–3]. This study is rather difficult because separation of screening and quenching effects needs rather an elaborate procedure. Energy transfer was established for thin films [1, 2, 4] and for systems where the u.v. absorber was used in bulk and as a screener, the difference being assigned to quenching [2, 3]. Details of energy transfer between polymeric donor and free and bound u.v.-stabilizer have not been studied so far. The photolysis of P4MAP proceeds through a reactive triplet state with a life 20 times larger than that for polyacrylophenone (PAP) [5] making the separation of screening and quenching effects easier since the necessary concentration of additives is lower than for PAP. The quenching effect can be enhanced by binding donor and acceptor in one molecule [6] or a macromolecule [7]. The difference between intramolecular and intermolecular quenching increases in more viscous solvents. For this reason, the photolysis of 4 MAP/BPMA copolymers was studied in ethyl benzoate and the emission decay in poly(methyl methacrylate) doped with 10 wt/wt% of copolymers. The aim of this study is to elucidate some aspects of energy transfer in systems important for light stabilization of polymers.

EXPERIMENTAL

The preparations of 4-methoxyacrylophenone (4MAP) [5]; 2-hydroxy-4-(2-methacroyloxyethoxy)benzophenone (BPMA) [8]; 2-hydroxy 4-(2-isobutyroyloxyethoxy)benzophenone (BPIB) [8]; and poly-4-methoxyacrylophenone (P4MAP) were described previously. Copolymers of 4MAP/BPMA were prepared as described earlier [7]. Characteristics of copolymers are summarized in Table 1.

Table 1. Characteristics of polymers

Polymer	Composition of Monomer mixture % [wt/wt]	Copolymer* % [wt/wt]	$[\eta]\cdot 10^2$† (ml/g)	C (mol/kg)	ϕ_0/ϕ‡	η_0/η§	$\bar{\tau}$ sec
P4MAP			2.08				0.30
4MAP/BPMA K	1.34	1.05	2.40	0.037	3.0	4.3	0.24
4MAP/BPMA M	2.37	3.54	2.29	0.082	3.3	4.5	0.21
4MAP/BPMA L	3.58	4.57	2.36	0.134	4.8	11.3	0.22
4MAP/BPMA O	4.90	6.60	2.47	0.189	5.5	22.4	0.21
4MAP/BPMA N	5.82	8.25	2.65	0.213	8.7	26.7	0.19

* Determined using i.r. band 1745 cm^{-1}; † ethyl benzoate, 30°C; ‡ quantum yield ratio based on photolysis; § quantum yield ratio based on emission decay curves.

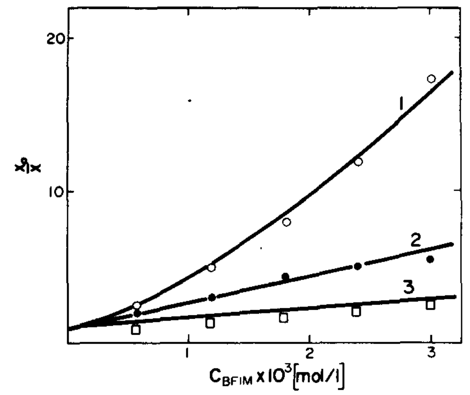

Fig. 1. Dependence of x_0/x during P4MAP photolysis in ethyl benzoate, on BPIB concentration, x_0/x being (1) ratio of main chain scission without and with stabilizer; (2) ratio of radiation absorbed by polymer in the absence and in the presence of stabilizer; (3) ratio of quantum yield of main chain scission without and with stabilizer.

Turbidimetric titration of copolymers with the highest content of BPMA and a mixture of homopolymers in the system chloroform-methanol showed the absence of homopolymers. The content of BPMA in copolymers was determined using the i.r. band of ester valence vibrations at 1745 cm^{-1} in a mixture of CCl_4 and $CHCl_3$ (1:1) [7].

Solutions of copolymers (4 g/l) were irradiated in sealed 1 cm thick spectroscopic cuvets at 366 nm [5]. Oxygen was removed from solutions by bubbling with purified nitrogen for 10 min. The cuvets were irradiated in a rotating apparatus [5] giving equal dose for 8 cuvets.

Viscometric, osmotic and spectral (i.r., u.v. and emission) measurements were similar to those described previously [5, 7, 9]. The decay curves of emission were taken on an apparatus using photographic flash (Mikrotechna n.e., Prague, Czechoslovakia) filtered through UG 5 glass filter for excitation of PMMA film (50 μm) doped with copolymers (10 wt/wt%) dipped in liquid nitrogen and placed in a partially silvered quartz Dewar vessel. The emitted radiation was passed through an SPM-2 monochromator (C. Zeiss, Jena, GDR) and detected with an EMI 6256 B head-on photomultiplier. The signal was recorded on a storage oscilloscope OG 2-31 with VV 300 amplifier at different sensitivities and KG 301 time base. The trace from CRT was transferred on a transparent foil and manually digitized.

RESULTS

It was shown that there are some limitations in the evaluation of screening and quenching effects during polyacrylophenone photolysis both in solution [11] and film [1]. The same procedure was used for P4MAP photolysis with BPIB in ethyl benzoate (Fig. 1). During PAP photolysis in solution, the screening effect appears over the concentration range 0–10^{-3} mol/l but, during P4MAP photolysis, quenching contributes substantially to the overall effect ($K_{SV} = 600$ mol/l).

For copolymers, the quantum yield ratio is given by

$$\frac{\phi_0}{\phi} = \frac{s_0}{s} \times \left(\frac{[\eta]}{[\eta]_0}\right)^{1/\alpha} \times \frac{I_p}{I_p^0}$$

where the quantities with index 0 refer to P4MAP and those without index to copolymers, s being the number of main chain scissions, $[\eta]$ the initial limiting viscosity number, I_p^0 and I_p are radiations absorbed by 4MAP chromophore in homopolymer and copolymers respectively and α is the Mark–Houwink coefficient (0.75). The ratio $([\eta]/[\eta]_0)^{1/\alpha}$ represents correction for unequal initial molecular weights of copolymers [7] and I_p/I_p^0 defines correction for the screening effect [11]. Figure 2 shows the ratio ϕ_0/ϕ plotted against quencher concentration for copolymers.

The copolymers show lower intensity of emission than homopolymer P4MAP (Fig. 3). Precise measurement of the emission intensity for homopolymer and copolymers was not possible in our experimental arrangement since the optical density of liquid nitrogen varies during measurement. The reproducibility of decay curves was much better. The ratio of quantum yields η_0/η was calculated according to the relation [12]

$$\frac{\eta_0}{\eta} = \frac{\int_0^\infty I_t^0\,dt}{\int_0^\infty I_t\,dt}$$

where I_t^0 and I_t are the decay curves of P4MAP and copolymers taken at different sensitivities. Integration was performed numerically. The decay of the emission for P4MAP and for copolymers is non-exponential (Fig. 4) and the life time was calculated using

$$\bar{\tau} = \frac{\int_0^\infty t I_t\,dt}{\int_0^\infty I_t\,dt}$$

Function tI_t was calculated using experimental values I_t up to time 0.6 sec. For $t > 0.6$ sec, I_t was taken from linearly extrapolated dependence log I_0/I on time. The function tI_t was calculated up to the limit when tI_t is 10% of the maximal value. The integral

$$\int_0^\infty t I_t\,dt$$

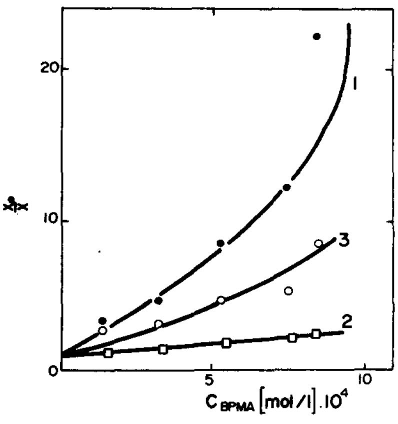

Fig. 2. Dependence of x_0/x on concentration of BPMA during photolysis of copolymers in ethyl benzoate, x_0/x being defined as in Fig. 1.

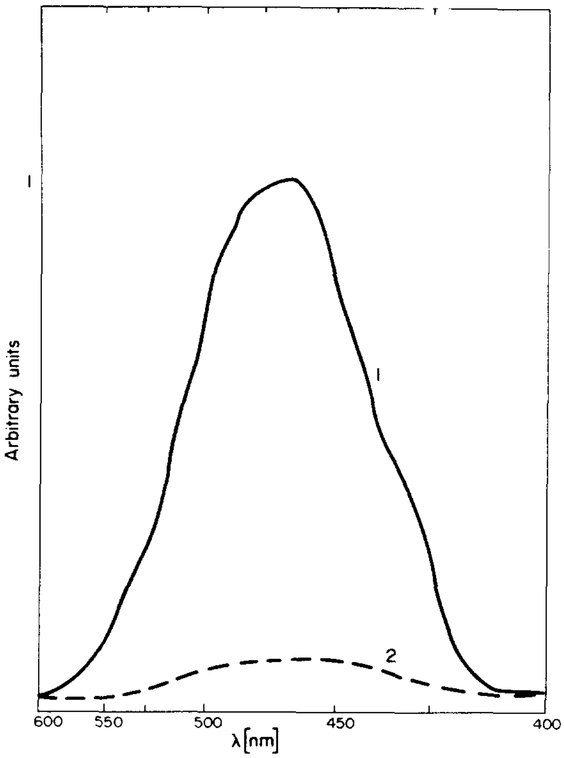

Fig. 3. Emission spectrum of poly(methyl methacrylate) films doped with 1 P4MAP (10 wt/wt%) and 2 copolymer 4MAP/BPMA ○ (10 wt/wt%) at 77 K.

was evaluated numerically with 0.1 step. In this way, approximate values of mean life-time are obtained only.

The life-time for P4MAP was 0.31 (Table 1). The most rapid decay is exhibited by copolymer *N* (Fig. 4). Using the above described evaluation, the calculated mean life-time is 0.19 sec, indicating that our evaluation emphasizes the later stage of the decay rather than the earlier. Moreover, the reason for more rapid emission decay of copolymers is not well understood in the framework of the Perrin model but perhaps the new deactivation path opens in copolymers with increasing quencher concentration.

DISCUSSION

The transfer of triplet energy in polymeric systems has been described by several models [13, 14], Perrin and Stern–Volmer models being extreme cases. The Stern–Volmer model is characterized by the fact that, during the life of the excited state of donor, there is mixing resulting in shortening of the donor life-time with quencher concentration. The limiting value of the energy transfer rate is equal to the rate of the diffusion controlled biomolecular reaction. In the Perrin model, the quenching sphere is introduced. This model is suitable for static quenching mainly in the solid phase. Energy transfer proceeds in this quenching sphere only but sometimes at higher rate than for diffusion controlled process, without altering the life time.

Quenching of P4MAP photolysis with light stabilizer of the 2-hydroxybenzophenone type fits the Stern–Volmer model. As seen from Fig. 1, this compound is as effective as a quencher as naphthalene [5]. Laser flash photolysis of polyacrylophenone–naphthalene in solution revealed that the donor life-time decreases with increasing quencher concentration according to the Stern–Volmer model [14]. The dependence of ϕ_0/ϕ on quencher concentration for copolymers in solution is curved upward, indicating inadequacy of the Stern–Volmer model. In dilute solution, macromolecules of copolymers are isolated and intermacromolecular energy transfer is improbable. In an isolated macromolecule, static quenching seems to become important leading to curvature of the dependence of ϕ_0/ϕ on quencher concentration. In this situation, the Perrin model appears to be better. The same conclusion is valid to an even greater extent for quenching in PMMA film at 77 K. It is difficult to exclude completely intermacromolecular energy transfer in film; on the other hand, quenching is confined to a certain sphere since all segmental,

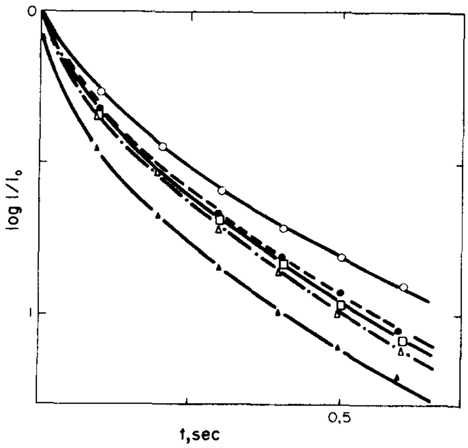

Fig. 4. Emission decay curves of P4MAP (○) copolymers K (●), L (△), M (□) and N (▲), doped in poly(methyl methacrylate) film (10 wt/wt%) at 77 K.

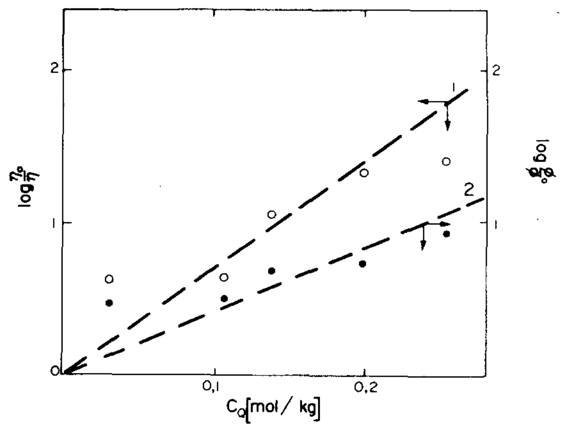

Fig. 5. Dependence of log ϕ_0/ϕ and log η_0/η on quencher concentration according to the Perrin model. Curve 1 (open circles) corresponds to solid solutions at 77 K, curve 2 (solid circles) corresponds to solution.

diffusion and other motions are frozen. The quenching spheres calculated using the slope of the concentration dependence of log ϕ_0/ϕ (Fig. 5) are 1.56 nm for solution and 1.86 nm for film. Although the variance of experimental values is considerable, the diameters of quenching sphere are similar to those for other organic donors and acceptors. For the system benzophenone-naphthalene, the quenching sphere has $r = 1.2$ nm in solid solution at 77 K [15]. The higher quenching sphere for film than for solution may be caused by intermacromolecular transfer or by a more dense structure in the film. Values exceeding 1.2 nm for the sphere for copolymer quenching in both solution and film may result from greater diameter of structural units of donor and acceptor. Isothermal triplet energy transfer cannot be fully excluded either.

Since the mean life-time of copolymers is about 30% lower than that of homopolymer and the copolymer with lowest concentration of quencher shows definitely higher quenching, the application of Perrin model seems to be limited.

Recently Nakahira *et al.* [16] investigated intramolecular quenching of photosensitizer-terpolymer-2-(9,10-anthraquinone) methyl methacrylate with 2-naphthyl methyl methacrylate and benzyl methacrylate for redox reaction of Fast Red A with ascorbic acid. The slope of the plot of the relative quantum yield vs 2-naphthyl content gave a quenching sphere of 0.5 nm according to the Perrin model. To explain this discrepancy, Nakahira *et al.* [16] suggested that solvation lowers the effective concentration of the quencher. The quencher concentration calculated on weight unit of polymer used in our paper is the upper limit and the value calculated on the volume of solution is the lower limit for the effective quencher concentration. Based on a quenching sphere of a 0.5 nm, the Japanese authors calculated that the effective concentration is 20 times lower than that calculated on polymer weight which seems to be rather high. Moreover, their low value of quenching sphere may be due to some other mechanistic reason since their system is rather complicated. Our measurements showed clearly that the quenching spheres in copolymers in film and solution are similar, indicating that the solvent effect is not so important.

REFERENCES

1. P. Hrdlovič, I. Lukáč and Z. Maňásek, *Chemical Papers* **26,** 433 (1972).
2. J. F. Guillory C. F. Cook, *J. Am. chem. Soc.* **95,** 4885 (1973).
3. D. J. Carlsson and D. M. Wiles, *J. Macromolek. Sci, Rev. Macromolek. Chem.* **C14,** 155 (1976).
4. H. J. Heller and H. R. Blattman, *Pure appl. Chem.* **30,** 145 (1972).
5. I. Lukáč, M. Moravčik and P. Hrdlovič, *J. Polym. Sci., Polym. Chem. Ed.* **12,** 1913 (1974).
6. A. A. Lannola, In *Energy Transfer and Organic Photochemistry* (edited by P. A. Leermakers and A. Weisberger), p. 70. Wiley, New York (1969).
7. I. Lukáč and P. Hrdlovič, *Europ. Polym. J.* **11,** 767(1975).
8. I. Lukáč, P. Hrdlovič, Z. Maňásek and D. Belluš, *Europ. Polym.* J. Suppl. 523 (1969).
9. J. Daněček, P. Hrdlovič and I. Lukáč, *Europ. Polym. J.* **12,** 513 (1976).
10. I. Lukáč and P. Hardlovič, *Europ. Polym. J.* **14,** 339 (1978).
11. P. Hrdlovič, I. Lukáč and I. Paška, *J. Polym. Sci.,* Symp. No. 40, 57 (1973).
12. J. P. Vikesland and F. Wilkinson, *J. Chem. Soc., Faraday Trans. II, Chem. Phys.* **73,** 1082 (1977).
13. N. J. Turro, *Pure appl. Chem.* **49,** 405 (1977).
14. G. Beck, G. Dobrowolski, J. Kiwi and W. Schnabel, *Macromolecules* **8,** 9 (1975).
15. I. L. Ermolaev, *Usp. fiz. Nauk* **80,** 333 (1963).
16. T. Nakahira, E. Shinoniya, T. Fukumoto, S. Iwabuchi and K. Kojima, *Europ. Polym. J.* **11,** 317 (1978).