Benzoin derivatives as photo-initiators for vinyl polymerization in micellar systems

André Merlin and Jean-Pierre Fouassier
Laboratoire de Photochimie Générale, Equipe de Recherche Associée au CNRS n° 386, Ecole Nationale Supérieure de Chimie, 68093 Mulhouse Cédex, France

(*Received* 20 *May* 1980; *revised July* 17 1980)

Benzoin derivatives are widely used as photo-initiators for vinyl polymerization[1], photocrosslinking[2] or photografting[3,4]. The mechansim of the polymerization reaction both in bulk and in solution[5-7] and the behaviour of the excited states of the initiators[8-10] have received considerable attention.

We wish to report experiments on vinyl polymerization in a micellar system, initiated by a series of benzoin derivatives and to compare the results with those obtained in bulk polymerization. There are few data available in the literature concerning emulsion polymerization where the initiator is soluble in the monomer phase.

Five compounds have been used: 2,2'-dimethoxy-2-phenylacetophenone (DMPA); 2-methoxy-2-phenylacetophenone (MPA); 2-ethoxy-2-phenylacetophenone (EPA); α-isopropyl-2-phenylacetophenone (IPPA); and benzoin (BZ). Methyl methacrylate (MMA) was washed with $NaCO_3$, dried over $CaCl_2$ and distilled under reduced pressure. The aqueous micellar solution was obtained with sodium lauryl sulphate (NaLS). Knowledge of the ternary diagram[11] formed by water, NaLS and MMA shows that the monomer is completely solubilized in the micelle for $[MMA] \sim [NaLS]$. Thus, the photo-initiator is dissolved in MMA which is solubilized in a freshly-prepared aqueous NALS solution (so that $[MMA] = 0.57$ M and $[NaLS] = 0.52$ M) by stirring the mixture at room temperature. The concentration of the initiator is determined from the measurement of the optical density of the micellar solution and of the extinction coefficient at 365 nm. The solution is transparent for $\lambda > 330$ nm (we have also verified that the diffusion of the solution was negligible). The optical density was typically 0.15 at 365 nm.

The micellar solution was placed in a thermostatically-controlled cell ($T = 20°C$), degassed by nitrogen bubbling and irradiated with a high pressure mercury lamp (Philips SP500). The 365 and 313 nm wavelengths were selected by a pass-band filter. The incident light intensity was about 10^{16} photons cm^{-2} s^{-1} at the sample. Two photodiodes allowed continuous recording of the light intensity in front of and behind the sample. After irradiation, the micellar solution was destroyed by THF and the polymer removed from the solution by diluting in acidified methanol with vigourous stirring. The conversion (%) was determined gravimetrically and R_p was calculated from the linear part of the time–conversion (%) curve. The molecular weights of the polymer were calculated from intrinsic viscosity measurements on 1% polymeric solutions in acetone, using the equation: $[\eta] = 0.0055 [M_v]^{0.75}$. Typical conversion–percentage time curves are reported in *Figure* 1. They show that high conversion can quickly be attained in the micellar system.

We measured the rate of the polymerization of MMA in presence of DMPA ($\lambda = 365$ nm) for various values of the incident light intensity. From the plot in *Figure* 2, we obtain a slope of ~0.5 which shows that $R_p \propto \sqrt{I_0}$. A plot of log R_p as a function of the optical density of the solution at 365 nm (log *OD*) leads to the conclusion that $R_p \propto \sqrt{OD}$. Thus, it appears that the law of the polymerization is similar to the one obtained in the case of a bulk polymerization initiated photochemically.

In bulk experiment[5], R_p can be expressed by the following formula, under conditions of low light absorption ($I_{abs} = 2.3\ I_0 \times OD$) and by assuming the usual radical chain termination:

$$R_p = A\sqrt{2.3 I_0 \varphi_i OD} \times [M]$$

where φ_i is the quantum yield of the initiation by radicals, *OD* the optical density of the sample at the wavelength of irradiation and *A* is a proportionality constant. In the

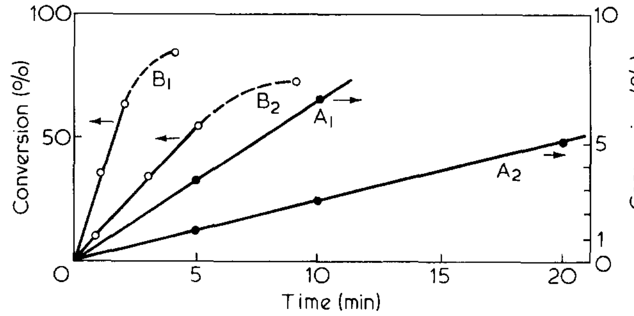

Figure 1 Conversion (%) as a function of time for the photopolymerization of MMA in bulk (A) and in micelle (B). Initiator, DMPA. (A_1) and (B_1), $\lambda = 313$ nm, $OD = 1.2$; (A_2) and (B_2), $\lambda = 365$ nm, $OD = 0.15$; I_0 ($\lambda = 365$ nm) $= 1.9 \times 10^{16}$ photons cm^{-2} s^{-1}; I_0 ($\lambda = 313$ nm) $= 2.9 \times 10^{16}$ photons cm^{-2} s^{-1}

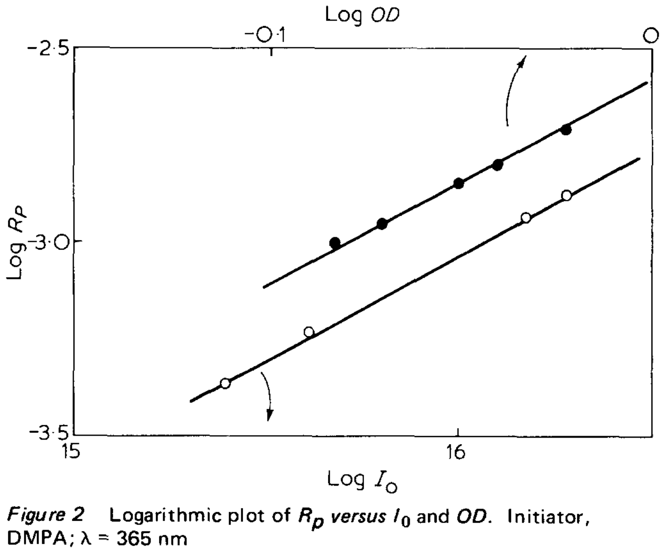

Figure 2 Logarithmic plot of R_p *versus* I_0 and *OD*. Initiator, DMPA; $\lambda = 365$ nm

0032-3861/80/1363-02$02.00

Table 1 Rate of polymerization (R_p), molecular viscometric weight, polydispersity for micellar photopolymerization of MMA photo-initiated by benzoin derivatives at λ = 365 nm. R_p values for the corresponding bulk polymerization. ϕ_m, ρ_m and $A\sqrt{\phi_i}$ values for polymerization in bulk and in micellar solutions.

ρ_m is defined by the ratio R_p/[initiator] and [initiator] is referred to the concentration of the initiator in the monomer phase. The R_p values are corrected to take into account the difference in the light intensity between the two sets of experiments (see *Table 1*); thus ρ_m represents the number of monomer units polymerized/the amount of initiator, under a fixed value of the light absorption. Incident light intensity: 1.9 x 10^{16} photons cm^{-2} s^{-1} (micellar polymerization) and 1.5 x 10^{16} photons cm^{-2} s^{-1} (bulk polymerization). Optical density of the sample, 0.15 at 365 nm. M_v was determined with samples at 50% conversion (except for experiment with PA where a 20% conversion sample was used)

	Micellar polymerization						Bulk polymerization			
Initiator	$R_p \times 10^5$ (M s^{-1})	$M_v \times 10^{-5}$ (g)	Poly-dispersity	ϕ_m	ρ_m (s^{-1})	$A\sqrt{\phi_i} \times 10$ ($M^{-1/2}$ $s^{-1/2}$)	$R_p \times 10^5$ (M s^{-1})	ϕ_m	ρ_m (s^{-1})	$A\sqrt{\phi_i} \times 10^3$ ($M^{-1/2}$ $s^{-1/2}$)
PA	25	9.3	1.9	22.7	–	–	5	5.1	–	18
DMPA	105	3.5	2.2	95.5	1.4	5.6	35	48.2	0.52	12
MPA	155	4.6	1.8	141	0.72	8.3	45.5	55.7	0.24	16
EPA	158	3.6	2.1	143.6	0.68	8.4	46	56.2	0.22	16
BZ	166	4.2	1.3	151	0.22	8.9	47	57.4	0.07	17
IPPA	173	3.7	1.7	152.3	1.04	9.2	46	56.2	0.31	16

Table 2 Rate of polymerization R_p and ϕ_m, $A\sqrt{\phi_i}$ and ρ_m for the polymerization in bulk and micellar solutions. I_0 = 1.9 x 10^{16} photons cm^{-2} s^{-1}. *OD* = 0.15 at 365 nm. Additive, 1% w/w of benzocaine. The calculation for ϕ_m is carried out for the same value of the absorbed energy (I_0 = 1.9 x 10^{16} photons cm^{-2} s^{-1}, *OD* = 0.15) by correcting the R_p values

	Micellar polymerization				Bulk polymerization			
Initiator	$R_p \times 10^5$ (M s^{-1})	ϕ_m	ρ_m (s^{-1})	$A\sqrt{\phi_i} \times 10$ ($M^{-1/2}$ $s^{-1/2}$)	$R_p \times 10^5$ (M s^{-1})	ϕ_m	ρ_m (s^{-1})	$A\sqrt{\phi_i} \times 10^3$ ($M^{-1/2}$ $s^{-1/2}$)
PA	32	29		1.7	5.4	5		48
DMPA	190	173	2.5	10	45	41.3	0.6	14
MPA	195	177	0.91	10	50	46.8	0.22	16
EPA	200	182	0.86	11	51	45.9	0.23	16
BZ	220	250	0.29	12	60	55.1	0.08	19
IPPA	215	195	1.29	12	62	56.9	0.37	20

bulk polymerization of MMA, $A = k_p/k_t^{1/2} = 0.06$ $M^{-1/2}$ $s^{-1/2}$. In the micellar polymerization, the experimental results lead to a similar expression (the problem, however may be in the value of the A constant).

The photopolymerization of MMA was then initiated by substituted benzoin derivatives. *Table* 1 shows the values of R_p, M_v and the polydispersity I (obtained from g.p.c. measurements). For comparison, the values of R_p for a photopolymerization in bulk are reported. We observe an enhancement of the rate of polymerization which is due to the expected micellar effect, since the two sets of experiments are conducted under almost the same conditions of light absorption. The efficiency scale of the different initiators observed in bulk polymerization is found again in the micellar polymerization.

If we defined the number of monomer units φ_m polymerized per quantum absorbed, values of $\varphi_m = 56$ and 141 ($I_0 = 1.9 \times 10^{16}$ photons cm^{-2} s^{-1}) are obtained for the polymerization in bulk and in micellar sytems photo-initiated by MPA (φ_m is expressed by $R_p/2.3 I_0 OD$, where R_p is related to the concentration of the monomer in bulk ([MMA] = 9.4 M) or in the aqueous phase).

By assuming the usual value $k_p/k_t^{1/2} = 0.06$ $M^{-1/2}$ $s^{-1/2}$, the quantum yield of initiation in bulk is $\varphi_i = 0.075$ ($\lambda = 365$ nm) which is in good agreement with the result ($\varphi_i = 0.1$) calculated from data of previous measurements[6]. The $A\sqrt{\varphi_i}$ coefficient is 0.016 $M^{-1/2}$ $s^{-1/2}$. In micellar systems, the value of the coefficient is higher than the value of the coefficient obtained in the bulk experiment ($A\sqrt{\varphi_i} = 0.83$ $M^{-1/2}$ $s^{-1/2}$).

The complete results are reported in *Table* 1; we point out that higher values (by a factor of 17) of R_p, φ_m and φ_p can be found if the micellar polymerization is considered as a microbulk polymerization ([MMA] = 9.4 M in the micellar system).

The φ_m values for the two sets of experiments are reported in *Table* 1 together with the values of ρ_m which represents the number of monomer units polymerized/the amount of initiator (under a fixed value of the light absorption). ρ_m is related to a practical efficiency of the initiator. The results show that DMPA appears as the most efficient initiator (ρ_m maximum) as mentioned, but DMPA does not lead to the highest efficiency in terms of quantum yield.

Addition of amine derivatives was shown to enhance the rate of polymerization. We used ethyl-4-aminobenzoate (benzocaine) which is water-insoluble. The results are reported in *Table* 2 both for bulk and micellar experiments.

By conducting the same type of experiment at 313 nm ($OD = 1.2$) we observe a weak decrease of $A\sqrt{\varphi_i}$ (for DMPA as initiator, $A\sqrt{\varphi_i}(\lambda = 313$ nm$) = 0.009$ $M^{-1/2}$ $s^{-1/2}$ in bulk; and $A\sqrt{\varphi_i}(\lambda = 313$ nm$) = 0.5$ $M^{-1/2}$ $s^{-1/2}$ in micellar polymerization) but an increase in the rate of polymerization R_p [$R_p(\lambda = 313$ nm$) = 328 \times 10^{-5}$ M s^{-1} and 100×10^{-5} M s^{-1} for micelle and bulk polymerization, respectively; $I_0 = 2.9 \times 10^{16}$ photons cm^{-2} s^{-1}.]

Table 3 shows the effect of an increase in acidity of the aqueous phase upon both the rate of polymerization and the quantum yield of initiation.

The results show that a high rate of polymerization can be attained in a micellar system compared with bulk

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})	2.9×10^{16}	2.9×10^{16}	2.9×10^{16}
R_p (M s^{-1})	247×10^{-5}	194×10^{-5}	190×10^{-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)*

J. C. Selwyn† and J. C. Scaiano
Division of Chemistry, National Research Council, Ottawa K1A 0R6, Canada

(*Received* 7 *August* 1980)

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

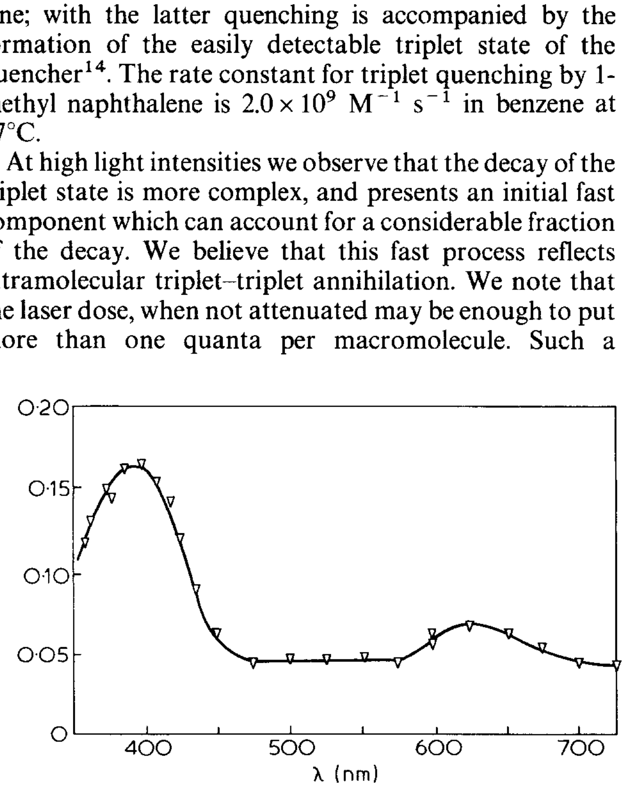

Figure 1 Transient spectrum observed immediately after laser excitation of a solution of PPMA in benzene at 27°C

---

* Issued as NRCC-00000
† NRCC Summer Student, 1980

0032-3861/80/1365-02$02.00