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The Benzophenone-Amine Photoinitiator in Vinyl Polymerization

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SUMMARY

Fast spectroscopy experiments have been performed upon the photoinitiation process of a vinyl polymerization with the benzophenone-amine derivative system. The rate constants of the processes in the excited states have been determined. The results make it possible to discuss the rate constant of the polymerization and to deduce the efficiency of the initiating radicals.

1 - INTRODUCTION

In the perspective of a series dealing with the behaviour of the excited states of carbonyl compounds used as photoinitiators of radical chain polymerization *(eg.1)*, we report a time resolved spectroscopy investigation of the primary processes which occur in the combination benzophenone-amine derivative. Some interesting features can be drawn to discuss the results of the photopolymerization of methylmethacrylate (MMA) under steady state conditions.

2 - EXPERIMENTAL

Benzophenone (BP) and amine compounds were purchased from Fluka Corp. The vinyl monomer was washed with a solution of sodium carbonate, dried over calcium chloride and distilled under reduced pressure in the absence of oxygen.
For experiments with stationary irradiations, the solutions of MMA (5M) were deareated by N_2 bubbling. The samples were irradiated in rectangular cells using a 500 W high pressure mercury vapour lamp (suitable wavelenths were selected by a pass band filter centered around 360 nm). The incident light intensity was about 2.5×10^{16} phot. $cm^{-2}.s^{-1}$. at the sample and the concentration of the initiator was determined so as to obtain a fixed value of the optical density at 365 nm (typically 0.15).

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The conversion ratio of the monomer was deduced gravimetrically. The rate constant R_p of the polymerization was deduced from the linear part of the time-conversion curve.

The laser excitation source and the analyzing system have been described previously [2]. The excitation consists of a train of 6 pulses (200 ps FWHM, 10ns separated, obtained from a mode locked ruby laser. The incident energy density is about 50 $mJ.cm^{-2}$. at 347 nm.

3 - RESULTS AND DISCUSSION

a) Laser spectroscopy experiments

The generation of transient absorptions under laser excitation was investigated over the range 350-380nm. In a degassed benzenic solution, the well known triplet-triplet absorption is observed. The triplet lifetime is τ_T = 1.3μs and is dependent on the energy density of the excitation as mentioned previously [3]. In a benzene-THF mixture (0.6M) the absorptions of the triplet state and of the ketyl radical (fig.1) are recorded (the rate constant of the bimolecular quenching of the triplet state by THF is $4.2 \times 10^6 M^{-1}.s^{-1}$. at low [THF]).

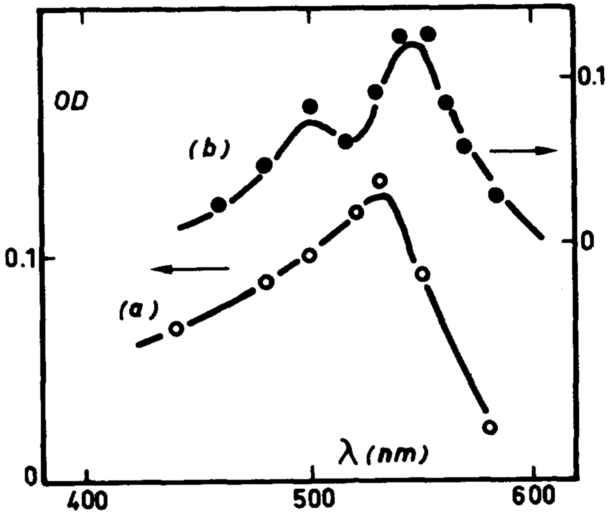

Fig.1 : Absorption spectra of the transients of benzophenone. (a) : triplet state in benzene. (b) : ketyl radical in THF.

In a benzene-amine mixture, the triplet state and the ketyl radical absorption are still observed. From the Stern-Volmer plots of fig.2, the rate constants of the bimolecular quenching of the benzophenone triplet state can be obtained (table 1). No evidence is found for an excited charge-transfer complex between benzophenone and the amine molecule of which the existence was postulated in previous works (4)(5).

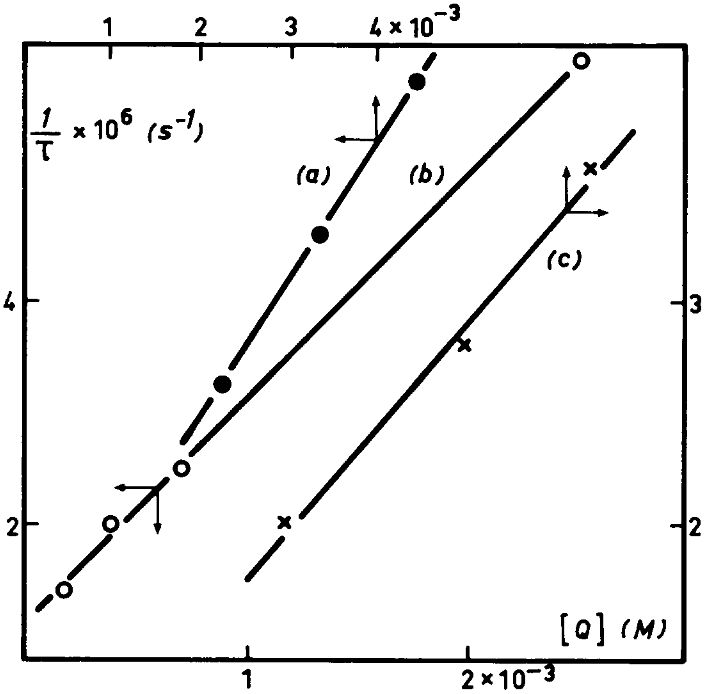

Fig.2 : Stern-Volmer plots of the reciprocal value of the triplet state lifetime as a function of the amine concentration : MDEA (a); BC (b) ; DABCO (c).

Amines	TEA	MDEA	DABCO	BC
$K_q \times 10^{-9} (M^{-1}.s^{-1}.)$	1,9	1,3	0,56	2

Table 1 : Bimolecular quenching rate constants of the triplet state of benzophenone by amines.TEA= triethylamine ;MDEA= methyldiethanolamine ;DABCO= diazobicyclooctane ;BC= methyl p-amino benzoate.

Addition of MMA leads to a decrease of the lifetime of the triplet ($K_q = 6.5 \times 10^7 M^{-1}.s^{-1}.$). No significant quenching of the ketyl radical is observed (the ketyl radical is known to interact very weakly with MMA [6] Thus, it is concluded that the amine-derived free radical is the initiating species of the polymerization (fig.3 shows the processes in the excited states.

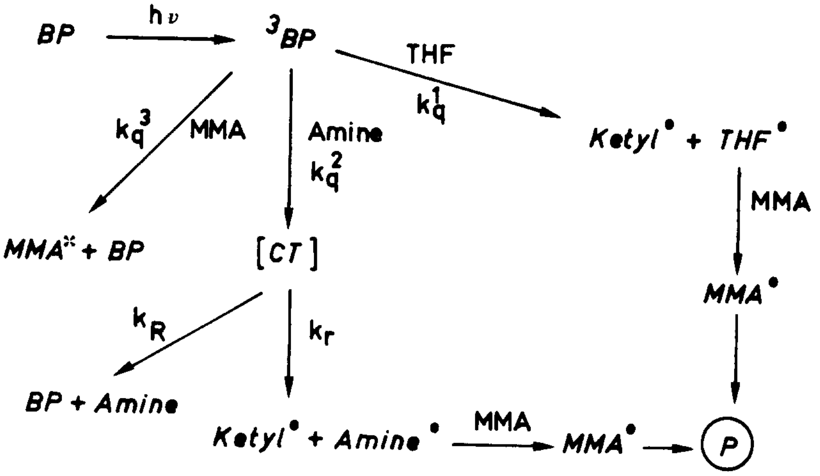

Fig. 3 : Processes involved in the excited states during the photoinitiation of the polymerization.

b) Steady state polymerization experiments

The rate constants R_p of the MMA polymerization, initiated by the system benzophenone-TEA were determined in terms of the TEA concentration, in the presence and in the absence of THF. By assuming the usual radical chain termination, R_p can be calculated. If α and β are the coefficients related to the efficiency of the initiation, the rate of the initiation R_i can be assumed to be a function of the initiating radicals:

$$R_i \propto \alpha\ [THF] + \beta[CH_3 - CH^{\bullet} - N(C_2H_5)_2]$$

Thus, the following equation holds :

$$R_p^2 = K[MMA]^2 \frac{1}{K_q^1[THF]+K_q^2[TEA]+K_q^3[MMA]} \left[\alpha K_q^1[THF]+\beta\frac{K_r K_q^2[TEA]}{K_r + K_d} \right]$$

with $K = k_p^2 k_t^{-1} 2.3 I_0 OD \phi_{ST}$ in absence of THF, the best fits were obtained with (fig.4) :

$$\frac{TEA}{R_p^2} = 31.2 \times 10^8 [TEA] + 5 \times 10^8 \quad \text{thus :} \quad \beta \frac{K_r}{K_r + K_d} = 2.7\ 10^{-3}$$

In the presence of THF ([THF]= 1M), the expected curve is accounted for by the equation :

$$R_p^2 = \frac{5.9[THF] + 0.29}{1.9 \times 10^9 [THF] + 3 \times 10^8}$$

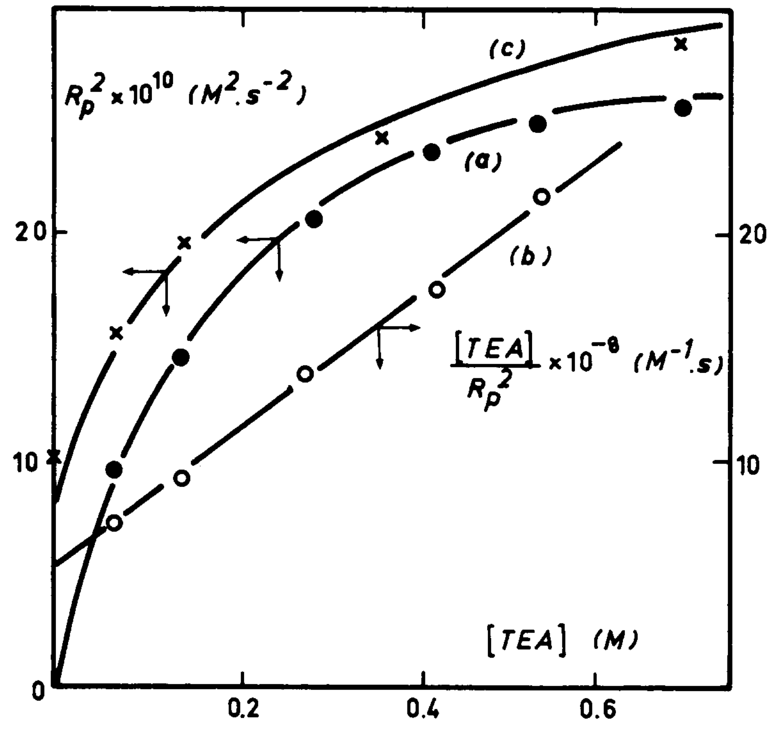

Fig.4 : Photopolymerization of MMA induced by the system benzophenone/TEA in benzene. [MMA]= 4.7M I_0= 2.5 x 10^{16}phot.cm^{-2}.s^{-1}. OD= 0.15 (λ= 365 nm).[THF]= 0 (curve(a) and (b)).[THF] = 1M experimental points (x) and calculated curves (c) (see text).

Fig.4 shows that a satisfactory agreement between the calculated and the experimental curve is obtained. Similar experiments have been carried out with the other amine derivatives. Table 2 summarizes the results. It can be outlined that the values of the coefficients are lying in the range (1- 5.5)x 10^{-3} and that β is at least equal to these values. One may remember that the initiation coefficient of the THF radical is higher (0.057 (7)).

Amine	$R_p \times 10^5 (M.s^{-1})$	$\beta \times \frac{K_r}{K_r+K_p}$
DABCO	2.5	3.5×10^{-3}
MDEA	5.0	5.5×10^{-3}
Triethanolamine	8.9	
DMBE	5.1	
TEA	3.45	2.6×10^{-3}
DMAB	3	
BC	2.1	0.96×10^{-3}

Table 2 : Rate of polymerization and initiation coefficient for the photopolymerization of MMA in benzene (4.7M) in presence of benzophenone (OD=0.15 at 365 nm) and amine (0.1M). Three amines cannot be studied by laser spectroscopy-DMBE = p.dimethylamino ethyl benzoate ; DMAB = p.dimethylamino benzaldehyde.

References

[1] J.P.FOUASSIER and A.MERLIN
J. of Photochem. 12, 17 (1980)
Canad.J. of Chem. 57, 2812 (1979)

[2] J.FAURE,J.P.FOUASSIER,D.J.LOUGNOT and R.SALVIN
Nouv. J. Chimie 1(1), 15, (1977)

[3] A.V.BUETTNER,J.DEDINAS
J.Phys. Chem. 75, 187, (1971)

[4] J.B.GUTTENPLAN,S.G.COHEN
Tetrahedron Lett. 2163 (1972)

[5] M.R.SANDNER,C.L.OSBORN,D.J.TRECKER
J.Polym. Sci. 3173 (1972)

[6] H.BLOCK,A.LEDWITH,A.R.TAYLOR
Polymer 2, 271, 1971

[7] A.MERLIN and J.P.FOUASSIER
Makromol. Chem. in press

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