Polymeric photoinitiators bearing side-chain benzoin methyl ether moieties: reactivity and excited-state processes

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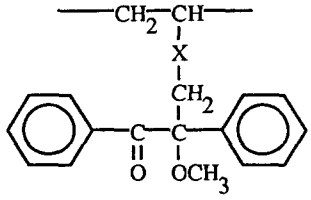
Polymeric photoinitiators based on benzoin methyl ether moieties are found to display higher activity, as compared with the corresponding low-molecular-weight structural models, in the ultra-violet-initiated polymerization of acrylic monomers both in solution and in film matrix. The yield of α cleavage in the high- and low-molecular-weight photoinitiators is quite similar, whereas a large difference is found in the efficiency of monomeric radical generation, which is much higher in the first system. A possible explanation for the different behaviour is suggested.

(Keywords: laser spectroscopy; photopolymerization; photocrosslinking; polymeric photoinitiators; benzoin ethers)

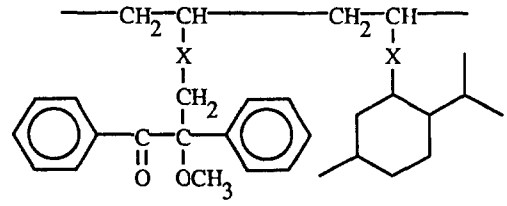
INTRODUCTION

Polymeric photoinitiators are attracting a great deal of interest in the area of u.v.-curable coatings for their ability to exhibit both non-yellowing and low-odour properties[1,2]. Moreover, in several cases, they also display a higher photoinitiation activity as compared with the corresponding low-molecular-weight analogues[3,4].

In polymeric systems bearing side-chain benzophenone moieties, the improvement of activity has to be mainly connected with an intramolecular hydrogen abstraction mechanism, as confirmed also by photophysical studies[5]. More recently, polymeric photoinitiators, operating via the much more efficient α-cleavage mechanism and based on side-chain benzoin methyl ether moieties, such as homopolymers of α-methylolbenzoin methyl ether acrylate (poly(MBA)) and α-vinyloxymethylbenzoin methyl ether (poly(MBVE)) as well as their copolymers with (−)-menthyl acrylate and (−)-menthyl vinyl ether (poly(MBA-*co*-MtA) and poly(MBVE-*co*-MtVE), respectively), have been reported to display higher photoinitiation activity in photocrosslinking of film matrix acrylic formulations as compared with their structural monomeric models[6].

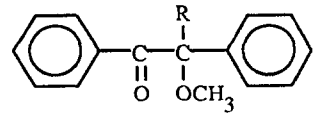


X = COO poly(MBA)
X = O poly(MBVE)



X = COO poly(MBA-*co*-MtA)
X = O poly(MBVE-*co*-MtVE)

In this context the present paper is devoted to the investigation of excited-state processes and reactivity of the above polymeric systems in solution polymerization of acrylic monomers. Low-molecular-weight models such as α-methylolbenzoin methyl ether acetate (MBAc), α-methylolbenzoin methyl ether 2-methylpropanoate (or isobutyrate) (MBI), benzoin methyl ether (BME), α-ethyloxymethylbenzoin methyl ether (MBEE) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) have been analogously studied in order to gain a better knowledge about the photophysical and photochemical pathways responsible for the observed improved efficiency of the polymeric photoinitiators.



R = H	BME
R = CH_2OCOCH_3	MBAc
R = $CH_2OCOCH(CH_3)_2$	MBI
R = $CH_2OC_2H_5$	MBEE
R = OCH_3	DMPA

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EXPERIMENTAL

Poly(MBA) having $\bar{M}_n = 12000$ and poly(MBA-*co*-MtA) with 51.6 mol% of MBA units and $\bar{M}_n = 32000$ were prepared by free-radical polymerization in benzene solution at 60°C, using azobisisobutyronitrile (AIBN) as initiator[7].

Poly(MBVE) and poly(menthyl vinyl ether) (poly (MtVE)) having $\bar{M}_n = 40500$ and 68000, respectively, as well as poly(MBVE-*co*-MtVE), with 81.3 mol% of MBVE units and $\bar{M}_n = 35400$, were prepared by cationic polymerization at −78°C using CH_2Cl_2 and $BF_3.Et_2O$ as solvent and initiator, respectively[7]. MBEE was synthesized by H_2/Pt hydrogenation of MBVE[7]. MBAc and MBI were prepared from α-methylolbenzoin methyl ether and the corresponding acyl chlorides in the presence of Et_3N, following the same procedure as for MBA[8].

BME and DMPA from Ciba-Geigy were supplied as purified laboratory samples.

Methyl methacrylate (MMA), methyl acrylate (MA), n-butyl acrylate (BA) and 1,6-hexanediol diacrylate (HDDA), commercially available from Aldrich, were purified as previously described[6,9].

The time evolution of photoinitiated polymerizations under nitrogen, carried out in film matrix of BA/HDDA equimolar mixtures under u.v. irradiation at 330 nm and in the presence of each photoinitiator (0.5 mol% of benzoin methyl ether moiety), were followed by microwave dielectrometry at 9.5 GHz as previously reported[6] (irradiation intensity was 53 W m^{-2}; the measurement method and apparatus have been fully described elsewhere[10]).

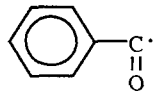
The photoinitiated polymerizations of MMA were also carried out in the presence of the different photoinitiators in degassed toluene solution (7 M, whose optical density is typically 0.1 at $\lambda = 366$ nm). The solutions were irradiated with light (filtered at $\lambda = 366$ nm) delivered by a mercury lamp HPK 125 W. Rates of polymerization in solution were evaluated from the percentage conversion–time curve, determined gravimetrically at low conversion. Relative rates of polymerization were also checked by dilatometry.

A full description of the time-resolved laser spectroscopy apparatus has been previously presented[11,12]. A short light pulse (3 ns) delivered by a YAG/Nd laser was used at $\lambda = 355$ nm.

RESULTS AND DISCUSSION

Laser excitation of both high- and low-molecular-weight benzoin methyl ether compounds in degassed toluene leads to a long-lived and weakly absorbing species (in the 400–500 nm region), which seems to decay according to second-order kinetics (*Figure 1*).

Owing to the well known α-cleavage process[13] that should occur in these molecules, the transient absorption looks like that already reported for BME in ref. 14 and is partly ascribed to the benzoyl radical:



However, the contribution of other radicals cannot be completely ruled out, which would explain why the kinetic treatment of the decay is not accurate. Triplet-state lifetimes τ_T of our samples, as previously

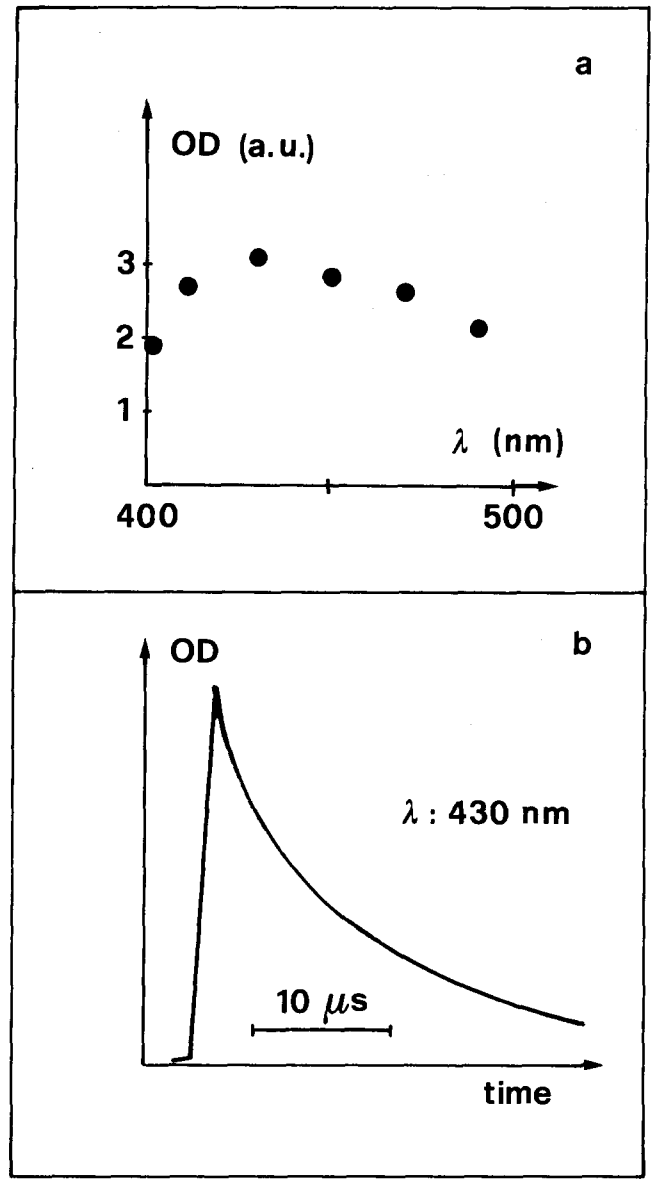


Figure 1 Typical absorption spectrum (a) and transient decay (b) of long-lived species in toluene solution after laser pulse irradiation of MBEE

reported in benzoin ether derivatives[15,16], cannot be directly measured because of their shortness. An estimation of τ_T of the triplet state T_1 can be made through an energy transfer experiment with 1-methylnaphthalene (MeN), which leads to the formation of the triplet state of MeN, with an absorption around 410 nm, according to:

$$T_1 + MeN \xrightarrow{k_{et}} S_0 + {}^3MeN$$

where S_0 represents the singlet ground state of the ketone and k_{et} is the bimolecular rate constant of the quenching of T_1 by MeN. A usual plot of the optical density OD_Q of ^{3}MeN as a function of the MeN concentration leads to the determination of τ_T if k_{et} is assumed to be 5×10^9 M^{-1} s^{-1}, as usually considered[17,18]:

$$\frac{1}{OD_Q} = K\left(1 + \frac{1}{k_{et}\tau_T[MeN]}\right)$$

where τ_T is the triplet-state lifetime in toluene of the benzoin derivative in the absence of MeN.

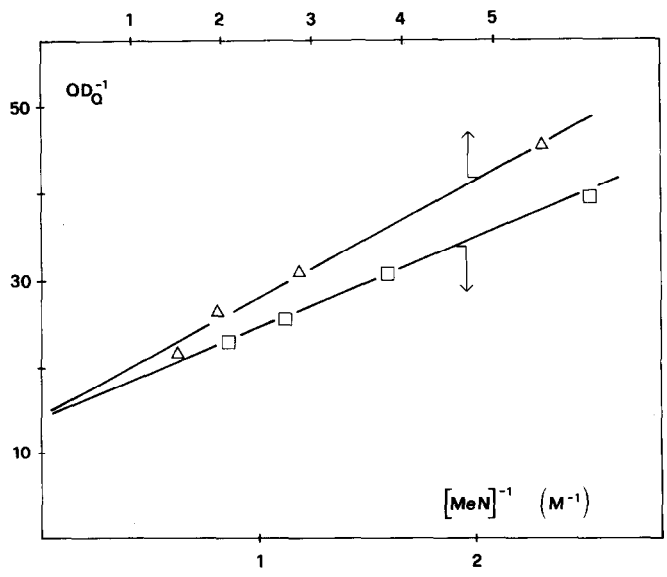


Figure 2 Plot of OD_Q vs. MeN concentration (see text) for poly(MBA) in degassed toluene, in the absence of monomer (△) and in the presence of 3.5 M MMA (□)

Table 1 Triplet-state lifetimes and rate constants of monomer quenching in toluene[a]

	$10^9\tau_T$ (s)	$10^9\tau'_T$ (s)		$10^{-8}k_q$ (M^{-1} s^{-1})	
		MMA	MA	MMA	MA
BME	<0.30	–	–	2[f]	–
DMPA[b]	<0.10	–	–	–	–
MBEE	0.60	0.40	0.40	2.4	1.8
MBI	0.35	0.20	0.15	5.5	5.4
MBAc	0.45	0.20	0.20	7.0	4.6
poly(MBVE)	0.60	0.30	0.25	4.7	3.7
poly(MBA)	0.60	0.25	0.20	6.6	5.2
MBEE/poly(MtVE)	0.55	–	–	–	–
poly(MBA-*co*-MtA)[c]	–	–	0.20	–	5.0
poly(MBVE-*co*-MtVE)[d]	–	–	0.20	–	5.0
HIPK[e]	1.40	0.30	–	2.5	–
HIPK-OL[e]	8.00	2.60	–	2.5	–

[a][MMA] = 3.5 M; [MA] = 5.6 M
[b]Value taken from ref. 13
[c]51.6 mol% of MBA units
[d]81.3 mol% of MBVE units
[e]Values taken from ref. 19
[f]Value taken from ref. 20

The above triplet-state lifetime is shortened in the presence of a monomer M. The same treatment used for a quenching experiment by MeN in toluene/M instead of toluene alone leads to a new T_1 lifetime τ'_T.

The rate constant k_q of the bimolecular quenching between T_1 and the monomer is easily calculated according to:

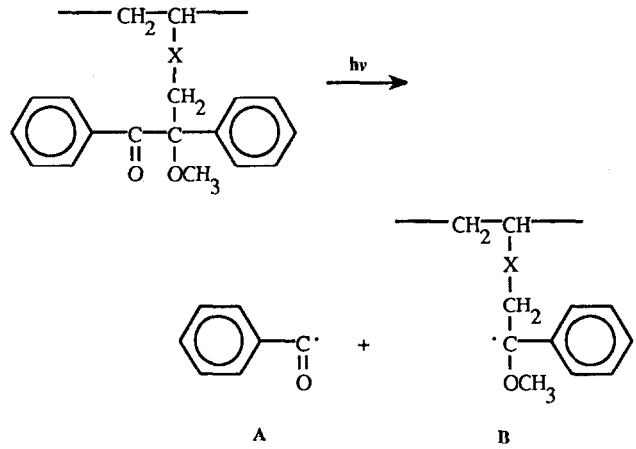
$$\frac{1}{\tau'_T} = \frac{1}{\tau_T} + k_q[M]$$

A typical plot for the energy transfer process is shown in *Figure 2* for poly(MBA).

Table 1 summarizes the values of τ_T, τ'_T and k_q for the high- and low-molecular-weight benzoin methyl ether derivatives in the presence of the monomer (either MMA or MA).

According to the data reported in *Table 1*, the rate constant of α cleavage in the absence of monomer, k_α, which is considered as the reciprocal value of τ_T, is very high for all the benzoin methyl ether compounds investigated, but slightly lower than that obtained for BME. No striking differences between the polymeric systems and the corresponding low-molecular-weight models are observed for τ'_T and k_q values, in the presence of MMA or MA (*Table 1*). In addition, by comparing poly(MBVE) and MBEE/poly(MtVE), the k_q value is quite similar (*Table 1*), when considering the benzoin methyl ether moiety as pendant from a polymer backbone or dispersed in a homopolymer, no typical effect of the environment being found.

The same holds true for the benzoyl radical, which appears in all the examined compounds as completely free in the medium. In fact, in the polymeric systems the α cleavage of the benzoin methyl ether moiety gives rise to a low-molecular-weight benzoyl radical (A) and a side-chain benzylic-type polymeric radical (B).



A more important effect was found[19] for τ_T when going from 2-hydroxy-2-methylpropiophenone (HIPK) to a polymeric compound bearing the same ketone moiety (HIPK-OL) (*Table 1*). The situation is different in the above-mentioned HIPK-OL, where the benzoyl radical is anchored to the polymer chain at the *para* position (in that case, the decay is faster and clearly first-order because of hydrogen abstraction reactions[19]).

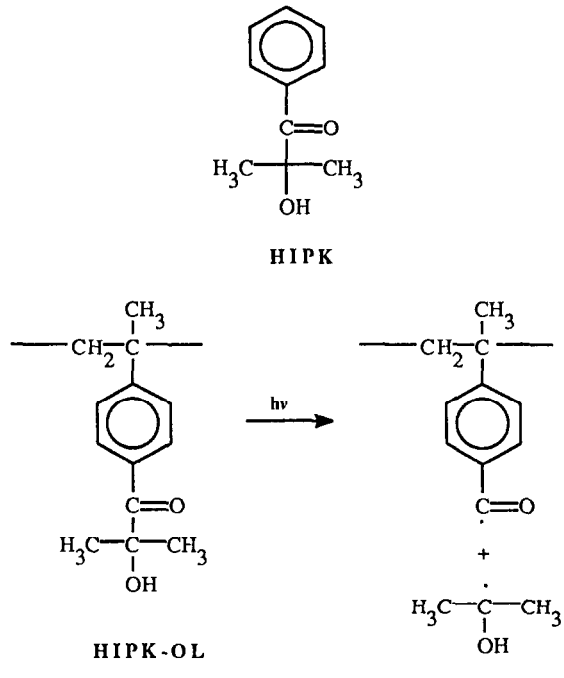


Table 2 Rate of polymerization (R_p) in arbitrary units, quantum yield of initiation (ϕ_i) in arbitrary units, yield of α cleavage (ϕ_α) and yield of initiating monomeric radicals generation (ϕ_{RM}) in arbitrary units for the polymerization of MMA (7 M) in toluene; yield of α cleavage (ϕ'_α) for the polymerization of MA (7 M) in toluene and rate (R_c) for the polymerization of an equimolar mixture HDDA/BA

	R_p[a]	ϕ_i[a]	ϕ_α	ϕ_{RM}	ϕ'_α	R_c[b] (s^{-1})
BME	1.40	1.96	>0.8	<2.45	–	–
DMPA	1.00	1.00	1.00	1.00	–	–
MBEE	0.80	0.64	0.50	1.28	0.60	10.1
MBI	0.75	0.56	0.45	1.24	0.45	–
MBAc	–	–	0.30	–	0.40	11.0
poly(MBVE)	1.20	1.44	0.35	4.11	0.40	12.8
poly(MBA)	1.80	3.24	0.25	12.96	0.30	20.2
HIPK[c]	1.00	1.00	0.28	3.57	–	–
HIPK-OL[c]	0.63	0.40	0.07	5.71	–	–
poly(MBA-*co*-MtA)	1.40	1.96	–	–	0.45	17.0
poly(MBVE-*co*-MtVE)	1.60	2.56	–	–	0.45	15.1

[a]The value for DMPA has been arbitrarily set to 1
[b]Calculated in film matrix by dielectrometric measurement; expressed as percentage of monomer to polymer conversion over time and calculated at the polymerization half-time
[c]Taken from ref. 19

Typical rates of polymerization R_p are reported in *Table 2*, relative to DMPA. Quantum yield of initiation ϕ_i for a polymerization process can be expressed from the rate of polymerization R_p by:

$$\phi_i = k' R_p^2$$

and yields of α cleavage ϕ_α can be calculated from:

$$\phi_\alpha = \frac{k_\alpha}{k_\alpha + k_q[M]}$$

where $k_\alpha = 1/\tau_T$. Values of R_p, ϕ_α and ϕ_i for the photoinitiated polymerization of MMA in toluene solution as well as of ϕ'_α for the corresponding polymerization of MA are reported in *Table 2*. The ϕ_α and ϕ'_α values for poly(MBA) and poly(MBVE) are appreciably lower than for the corresponding low-molecular-weight analogues MBAc or MBI and MBEE, respectively. Similar results are obtained also for poly(MBA-*co*-MtA) and poly(MBVE-*co*-MtVE), in terms of ϕ'_α values, even if the differences against the structural models are slightly smaller. On the basis of the above results, it would be expected that the polymeric photoinitiators display lower activity in the polymerization of acrylic monomers. On the contrary, poly(MBA) and poly(MBVE) and the corresponding copolymers show higher values of both ϕ_i and R_p in the u.v.-initiated polymerization of MMA in toluene solution (*Table 2*). The improvement of photoinitiation activity on the polymerization of MMA in toluene solution by the polymeric systems examined, as compared with the low-molecular-weight analogues MBI and MBEE, confirms our previous results obtained[6] also in film matrix, where a HDDA/BA equimolar mixture was used as curing formulation (see R_c values in *Table 2*).

Taking into account that ϕ_i can be expressed as:

$$\phi_i = k'' \phi_\alpha \phi_{RM}$$

where ϕ_{RM} represents the yield of initiating monomeric radicals generation in arbitrary units, it can be concluded that this last quantity is much higher in the polymeric systems than in the models (*Table 2*). The higher value of ϕ_{RM} in HIPK and HIPK-OL relative to DMPA has been already[19] accounted for by the presence of two initiating radicals (benzoyl and isopropyl radicals, the latter being more reactive than the former). In the case of polymeric systems based on benzoin methyl ether moieties, this behaviour can be attributed to the reduced mobility of the B radicals anchored to the polymer backbone, which prevents their mutual coupling reactions without appreciably affecting their capability to initiate the polymerization of acrylic monomers, as previously proposed when the u.v.-initiated polymerization of HDDA/BA equimolar mixture in film matrix was carried out[6].

CONCLUSIONS

Photophysical studies by laser flash photolysis of high- and low-molecular-weight benzoin methyl ether derivatives have allowed us to determine not only their triplet-state lifetime but also the relative quantum yields of initiation and polymerization rates of MMA in solution.

The results obtained clearly indicate that the polymeric photoinitiators display higher activity than the low-molecular-weight analogues, thus confirming our previous data on u.v.-initiated polymerization of acrylic formulations in film matrix.

The evaluation of the single steps of the initiation process in terms of relative quantum yields has allowed us to clarify the mechanism responsible for the activity improvement in the case of the polymeric systems. This performance enhancement has thus been attributed to a much higher yield of initiating monomeric radicals generation and may be tentatively explained by a reduced capability of the radicals anchored to the polymeric matrix to give coupling reactions; as a consequence the efficiency of monomeric radicals generation is increased.

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