Polymeric photoinitiators having benzoin methyl ether moieties connected to the main chain by the benzoyl group and their activity for ultra-violet curable coatings

Luigi Angiolini, Daniele Caretti, Carlo Carlini* and Elena Corelli
Dipartimento di Chimica Industriale e dei Materiali, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

and Pier Angelo Rolla
Consorzio INFM, Dipartimento di Fisica, University of Pisa, Piazza Torricelli 2, 56100 Pisa, Italy
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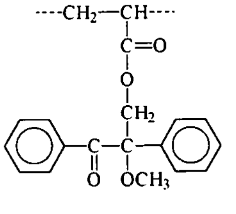
Homopolymers of 4-acryloyloxybenzoin methyl ether (ABME) and 4-acryloyloxy-α-methylbenzoin methyl ether (AMBE) [poly(ABME) and poly(AMBE)] as well as copolymers of AMBE with (−)-menthyl acrylate (MtA) and with different *N*,*N*-dialkylaminoethyl acrylates have been employed in the photoinitiated polymerization and crosslinking of a standard acrylic formulation for u.v. clear curable coatings. The photoinitiation activity of the above systems, detected by microwave dielectrometry, has been compared with that found for the corresponding low molecular weight structural models. The results clearly indicate that high and low molecular weight photoinitiators promote u.v. curing at a similar rate; however, a significant decrease of the induction period and hence an improved overall activity is found for the polymeric systems. An interpretation of the experimental findings, related to the behaviour of previously reported polymeric photoinitiators based on the benzoin methyl ether moiety, is also reported.

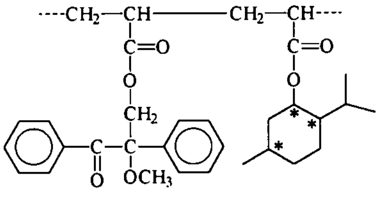
(Keywords: polymeric photoinitiators; u.v. curing of acrylic coatings; microwave dielectrometry)

INTRODUCTION

The homopolymer of α-methylolbenzoin methyl ether acrylate (MBA) and its copolymers with (−)-menthyl acrylate (MtA) [poly(MBA) and poly(MBA-*co*-MtA)s, respectively] are reported to behave as much more active photoinitiators than the corresponding low molecular weight structural models in the u.v. curing of acrylic clear coatings[1–3].



poly(MBA)

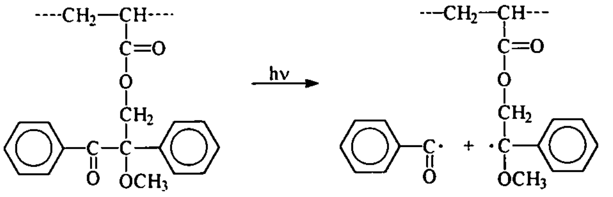


poly(MBA-*co*-MtA)s

This behaviour allowed us to suggest that, due to the well established[4–8] photo-α-cleavage of these systems, the polymer-bound α-methoxybenzyl primary radicals (*Scheme 1*), protected by the macromolecular coiling, are less prone to give coupling reactions with respect to the corresponding low molecular weight counterpart, the initiation process with the monomers being thus favoured[2].

Indeed, photophysical studies, combined with kinetic measurements of u.v. promoted methyl methacrylate polymerization by the above systems, clearly indicate[9] that the quantum yield of initiation is much higher in the case of the polymeric systems, despite their lower quantum yield of α-cleavage, as compared with the corresponding structural models.

Although studies on ^{14}C-labelled benzoin ethers presented evidence that the benzoyl and α-alkoxybenzyl primary radicals are equally effective in the polymerization of acrylates and methacrylates[10,11], evidence for a higher reactivity of the benzoyl radical with styrene has also been presented[12,13]. Therefore, it appeared of interest to prepare polymers bearing side chain benzoin methyl



Scheme 1

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*To whom correspondence should be addressed

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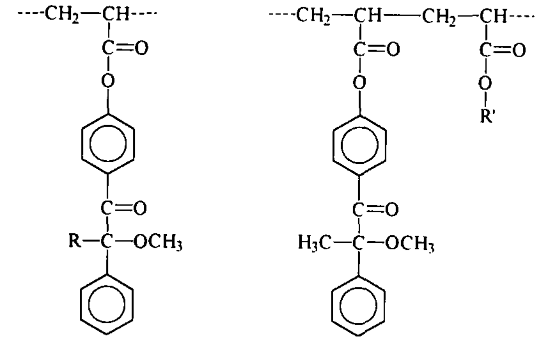
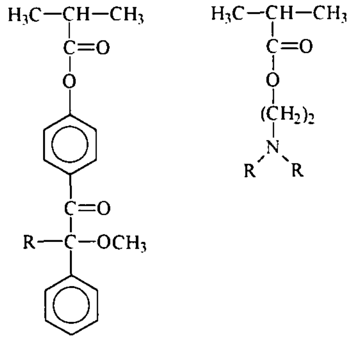
ether moieties anchored to the backbone through the benzoyl group, as the photocleavage would give rise in this case to polymer-bound benzoyl and low molecular weight α-alkoxybenzyl radicals, thus generating the opposite situation with respect to poly(MBA) and poly(MBA-*co*-MtA)s. In fact, differences of activity between these last systems and the proposed new series of polymeric photoinitiators could allow a better insight into the relative initiation activity of the two primary radical species. Moreover, the novel polymeric systems, as compared with 4-substituted benzoin ether low molecular weight models, could also provide evidence of the presence of a possible 'polymer effect' on the photoinitiation activity. In this regard, we have recently prepared[14] the homopolymer of 4-acryloyloxy-α-methylbenzoin methyl ether (AMBE) and its copolymers with MtA [poly(AMBE) and poly(AMBE-*co*-MtA)s, respectively]. An optically active comonomer was chosen in order to study the conformational properties in solution of the macromolecules by circular dichroism (c.d.) and hence obtain information about possible dipole–dipole interactions between side chain benzoin methyl ether moieties which in principle may affect the photoinitiation activity. On the basis of c.d. data, it was concluded[14] that poly(AMBE-*co*-MtA)s, although displaying a higher conformational rigidity with respect to poly(MBA-*co*-MtA)s, do not show significant interactions between lateral photosensitive moieties, thus suggesting that benzoin groups in both series behave as if isolated. In the present paper the synthesis of the homopolymer of 4-acryloyloxybenzoin methyl ether (ABME) [poly(ABME)] is also reported and its photoinitiation activity compared with that of poly(AMBE) and poly(AMBE-*co*-MtA)s with the aim also of investigating how this last property is affected by the presence of an alkyl group on the α-alkoxybenzyl moiety. Finally, the copolymers of AMBE with *N*,*N*-dialkylamino acrylates such as 2-(*N*,*N*-dimethylamino)ethyl acrylate (DMEA) and 2-(*N*,*N*-diethylamino)ethyl acrylate (DEEA) [poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA), respectively] have been also synthesized in order to study how the close vicinity of the benzoin methyl ether moieties to the tertiary amine groups may affect the photoinitiating activity of the above systems, as observed in the case of copolymers of MBA with different *N*,*N*-dialkylamino acrylates[15].



R = CH_3: poly(AMBE)
R = H: poly(ABME)

R' = menthyl: poly(AMBE-*co*-MtA)s
R' = $(CH_2)_2$-$N(CH_3)_2$: poly(AMBE-*co*-DMEA)
R' = $(CH_2)_2$-$N(C_2H_5)_2$: poly(AMBE-*co*-DEEA)

In this context the low molecular weight structural models 4-(2-methylpropionyloxy)-α-methylbenzoin methyl ether (PMBE)[14], 4-(2-methylpropionyloxy)benzoin methyl ether (PBME), 2-(*N*,*N*-dimethylamino)ethyl 2-methylpropanoate (DMEI)[15] and 2-(*N*,*N*-diethylamino)ethyl 2-methylpropanoate (DEEI)[15] have been also tested in u.v. curing experiments.



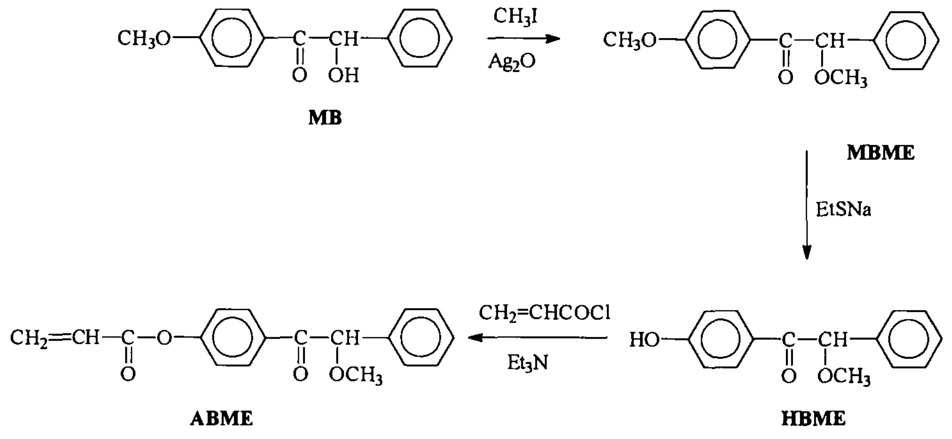
R = CH_3: PMBE
R = H: PBME

R = CH_3: DMEI
R = C_2H_5: DEEI

EXPERIMENTAL

Monomers

ABME. This was prepared starting from 4-methoxybenzoin (MB)[14,16], according to *Scheme 2*. According to a general procedure for the alkylation of alcohols[11], MB



Scheme 2

(0.1 mol) and CH_3I (0.36 mol) were added, in that order, at room temperature and under dry nitrogen, to a suspension in 150 ml of anhydrous tetrahydrofuran (THF) of freshly prepared Ag_2O (0.14 mol) (obtained by mixing equimolar amounts of aq. 1 M NaOH and $AgNO_3$ solutions, washing the precipitate with water, acetone, and dry diethyl ether in that order). The reaction mixture was refluxed under magnetic stirring for 1.5 h, cooled at room temperature and filtered. The solution, combined with the diethyl ether washings of the solid residue, was evaporated under vacuum to give an oily crude product which was purified by flash chromatography on silica gel, using chloroform as eluent. By the above procedure pure MBME was obtained in 64% yield as a yellow oil. ^1H n.m.r.: ($CDCl_3$) $\delta = 8.0$–7.9 ppm (m, 2H, aromatic protons *ortho* to the carbonyl group); 7.5–7.2 ppm (m, 5H, aromatic protons of the benzyl group); 6.9–6.8 ppm (m, 2H, aromatic protons *ortho* to the methoxy group); 5.5 ppm (s, 1H, –CH–); 3.8 ppm (s, 3H, CH_3–OPh); 3.4 ppm (s, 3H, C–OCH_3).

MBME (0.06 mol) was reacted, under nitrogen, with EtSNa (0.22 mol) in 900 ml of anhydrous DMF at the refluxing temperature for 4 h, according to a procedure adopted for the demethylation of aryl methyl ethers[17]. After cooling at room temperature, 400 ml of aq. 2 M HCl were added and the reaction mixture extracted with diethyl ether. The ethereal layer was repeatedly treated with aq. 1 M NaOH. The combined aqueous layers were then acidified with aq. HCl and finally extracted with diethyl ether. After drying on anhydrous Na_2SO_4, the solvent was removed under vacuum and the oily residue crystallized from cyclohexane to give pure HBME in 50% yield. ^1H n.m.r. ($CDCl_3$): $\delta = 8.0$–7.9 ppm (m, 2H, aromatic protons *ortho* to the carbonyl group); 7.5–7.2 ppm (m, 5H, aromatic protons of the benzyl group); 7.0–6.9 ppm (bs, 1H, OH); 6.8–6.7 ppm (m, 2H, aromatic protons *ortho* to OH group); 5.5 ppm (s, 1H, –CH–); 3.4 ppm (s, 3H, CH_3).

Acryloyl chloride (0.05 mol), dissolved in 10 ml of anhydrous diethyl ether, was dropped at 0°C into 100 ml of anhydrous diethyl ether containing 0.02 mol of HBME and 0.022 mol of triethylamine, under nitrogen and magnetic stirring. The reaction mixture was allowed to reach room temperature and then refluxed for 2 h. The time evolution of the reaction was followed by thin-layer chromatography (t.l.c.) on silica gel using a $CHCl_3/CH_3OH$ (9:1, v/v) as eluent. After cooling the reaction mixture was filtered, the ethereal solution evaporated to dryness and finally the residue purified by flash chromatography on silica gel, using $CHCl_3$ as eluent, to give pure ABME in 25% yield. ^1H n.m.r ($CDCl_3$): $\delta = 8.1$–8.0 ppm (m, 2H, aromatic protons *ortho* to the ketone group); 7.5–7.2 ppm (m, 5H, aromatic protons of the benzyl group); 7.2–7.1 ppm (m, 2H, aromatic protons *ortho* to the ester group); 6.7–6.6 and 6.1–6.0 ppm (2dd, 2H, $CH_2=$); 6.4–6.2 ppm (dd, 1H, $CH=$); 5.5 ppm (s, 1H, –CH–); 3.4 ppm (s, 3H, OCH_3). I.r. spectrum (cm^{-1}): 3080–3000, ν(C–H) (aromatic rings and vinyl group); 2931–2828, ν(C–H) (aliphatic); 1746, ν(C=O) (ester group); 1694, ν(C=O) (ketone group); 1634, ν(C=C) (vinyl group); 1598, ν(C=C) (aromatic rings); 1404, δ($CH_2=$) (scissoring, vinyl group); 984 and 905, δ($CH_2=$) (out-of-plane bendings, vinyl group); 847, δ(C–H) (1,4-disubstituted phenyl ring); 759 and 702, δ(C–H) (monosubstituted phenyl ring).

AMBE. AMBE was prepared as previously described in detail[14].

DMEA and DEEA. DMEA (Aldrich) and DEEA (Fluka) were distilled at reduced pressure under nitrogen just before use.

1,6-Hexanediol diacrylate (HDDA) and n-butyl acrylate (BA). The commercial products (Aldrich) were treated with aq. 5% KOH, washed with water, dried on anhydrous Na_2SO_4 and freshly distilled under nitrogen at reduced pressure (b.p. = 108°C/0.1 mbar and 44°C/15 mbar, respectively).

Model compounds

PBME. PBME was prepared starting from HBME and 2-methylpropionyl chloride, following the same procedure as reported for ABME. The crude product was purified by flash chromatography on silica gel using $CHCl_3$ as eluent and crystallized from ethanol to give pure PBME in 44% yield. ^1H n.m.r. ($CDCl_3$): $\delta = 8.1$–8.0 ppm (m, 2H, aromatic protons *ortho* to the ketone group); 7.5–7.3 ppm (m, 5H, aromatic protons of the benzyl group); 7.2–7.1 ppm (m, 2H, aromatic protons *ortho* to the ester group); 5.5 ppm (s, 1H, $C\underline{H}$–OCH_3); 3.4 ppm (s, 3H, OCH_3); 2.9–2.7 ppm [hept, 1H, $C\underline{H}(CH_3)_2$]; 1.4 ppm [d, 6H, $CH(C\underline{H}_3)_2$]. I.r. spectrum (cm^{-1}): 3090–3020, ν(C–H) (aromatic rings); 2977–2827, ν(C–H) (aliphatic); 1760, ν(C=O) (ester group); 1693, ν(C=O) (ketone group); 1599, ν(C=C) (aromatic rings); 1388 and 1346, δ(C–H) (bendings, geminal methyls of isopropyl group); 918, δ(C–H) (rocking, geminal methyls of isopropyl group); 862, δ(C–H) (1,4-disubstituted phenyl ring); 758 and 702, δ(C–H) (monosubstituted phenyl ring).

PMBE. PMBE was prepared as previously reported[14].

DMEI and DEEI. These compounds were prepared as previously described[15].

Radical initiator

2,2'-Azobisisobutyronitrile (AIBN). AIBN was recrystallized from ethanol just before use.

Polymerization experiments

Free radical homo- and copolymerizations were carried out at 60°C in dark-adapted glass vials using benzene as solvent and AIBN (0.5 wt% with respect to the monomers) as initiator. The components were introduced under nitrogen into vials submitted to several freeze–thaw cycles and sealed under high vacuum. After an appropriate period of time the reaction mixture was poured into a large excess of a non-solvent. For poly(ABME) as well as poly(AMBE) and poly(AMBE-*co*-MtA)s[14] methanol was used for this purpose. In the cases of poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA), as well as of poly(DMEA) and poly(DEEA)[15], petroleum ether was used as precipitating agent. The coagulated polymer was filtered, redissolved in chloroform and then reprecipitated with the non-solvent several times. The polymer was finally isolated by filtration, dried under vacuum and stored in a refrigerator in the dark.

The photoinitiated polymerization and crosslinking reactions were performed at 25°C, under nitrogen, by u.v.

irradiation at 330 nm (intensity 53 W m^{-2}) on a film matrix (0.2–0.3 mm) consisting of HDDA/BA equimolar mixtures containing 0.5 mol% of photoinitiator (in terms of benzoin methyl ether moieties). The time evolution of the photoinitiated curing process was followed by microwave dielectrometry at 9.5 GHz, in terms of ε'' (loss factor) of the reacting system, as previously reported[18]. The measurement method and the apparatus are fully described elsewhere[19,20].

Physicochemical measurements

^{1}H n.m.r. spectra were performed at 200 MHz in $CDCl_3$ solution on a Varian Gemini 200 spectrometer, using tetramethylsilane (TMS) as internal standard. I.r. measurements were recorded on a *FT*i.r. Perkin–Elmer 1750 spectrophotometer equipped with a Perkin–Elmer 7700 data station. Cast films on KBr discs or KBr pellets of the samples were used.

Average molecular weights of the polymers were evaluated by gel permeation chromatography (g.p.c.) measurements in $CHCl_3$ solution at 25°C, using high-pressure liquid chromatography (h.p.l.c.) (Waters Millipore 590 chromatograph equipped with a Waters model U6K injector and a Perkin–Elmer LC95 u.v. detector, using a TSK gel G4000HXL column). In the case of homopolymers of DMEA and DEEA as well as of their copolymers with AMBE, a Waters Ultrastyragel 500 Å column was employed. Monodisperse polystyrene samples were used for the calibration curve.

U.v. absorption measurements were carried out in $CHCl_3$ solution on a Kontron Instruments model UVICON 860 spectrophotometer, by using cell path lengths of 1 and 0.1 cm in the 400–300 and 300–240 nm regions, respectively. Concentrations of about 5×10^{-3} and 8×10^{-4} mol l^{-1} of benzoin methyl ether chromophore were used, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of the polymeric photoinitiators

Poly(AMBE) and poly(AMBE-*co*-MtA)s have been fully characterized elsewhere[14]. The relevant properties of the above polymeric products are reported in *Table 1*.

Homopolymerization of ABME and copolymerization of AMBE with DMEA and DEEA were performed by free radical initiation. ^{1}H n.m.r. and *FT*i.r. spectra well fit the expected structures. In fact, the absence in ^{1}H n.m.r. spectra of all the polymeric systems of signals in the 6.5–5.5 ppm region, related to the vinyl group, confirms that homo- and copolymerizations occurred by a polyaddition process involving only the acrylic functions. Accordingly, in the i.r. spectrum of poly(ABME) (*Figure 1*) no bands at 1634, 984 and 905 cm^{-1}, present in the corresponding monomer and connected with the vinyl group, are detectable. The absence in the i.r. spectra of poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) (*Figure 1*) of bands at 1625, 996 and 905 cm^{-1}, present

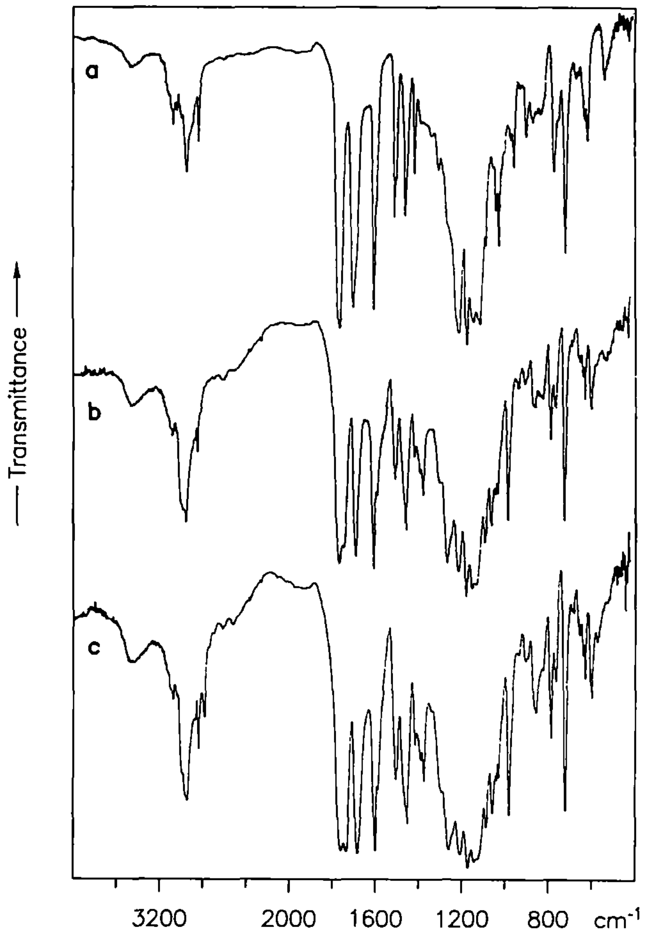


Figure 1 *FT*i.r. spectra of (a) poly(ABME), (b) poly(AMBE-*co*-DEEA) and (c) poly(AMBE-*co*-DMEA)

Table 1 Physical properties of poly(AMBE) and poly(AMBE-*co*-MtA)s

Sample	AMBE[a] co-units (mol%)	$\bar{M}_n^b$	U.v. absorption maxima[c]			
			$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
			λ_1	ε_1	λ_2	ε_2
Poly(AMBE)	100	21 900	341	219	253	12 500
Poly(AMBE-*co*-MtA)	79	33 400	340	219	254	14 100
	58	59 700	340	218	255	15 500
	43	43 100	340	215	255	14 400
	22	55 100	338	223	256	13 400
	15	46 800	338	209	257	12 700
PMBE	–	–	339	232	257	13 700

[a] Determined by ^{1}H n.m.r. analysis
[b] Determined by g.p.c.
[c] λ and ε are expressed in nm and l mol^{-1} cm^{-1}, respectively; ε is referred to one benzoin methyl ether moiety

in AMBE[14], and of analogous bands in the same regions, typical of the vinyl group in *N*,*N*-dialkylamino acrylates[15], also substantiates the above picture. Moreover, i.r. spectra of the copolymeric products show the contemporary presence of bands related to both AMBE and *N*,*N*-dialkylamino acrylate co-units. In particular, bands at 1735 and 1682 cm^{-1} (C=O stretching vibrations of ester and aromatic ketone groups, respectively, in the AMBE co-units) and at about 1757 and 1167 cm^{-1} (stretching vibration of the C=O ester group and of the C–N bond, respectively, in *N*,*N*-dialkylamino acrylate co-units) are present. The solubility of the above polymeric products in methanol, in contrast to the case for poly(AMBE)[14], clearly confirms that they consist of copolymer macromolecules. The copolymer composition has been determined by ^1H n.m.r. analysis by comparing the integrated area of the signals of the aromatic protons, related only to AMBE co-units, with the area of the signals of the aliphatic protons belonging to both AMBE and *N*,*N*-dialkylamino acrylate co-units. As reported in *Table 2*, in both poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) the content of AMBE co-units is slightly higher than in the corresponding feed, thus suggesting that AMBE is more reactive than the *N*,*N*-dialkylamino acrylate comonomers.

Poly(ABME) displays an average molecular weight ($\bar{M}_n$) higher that that reported for poly(AMBE) under the same polymerization conditions (*Table 1*)[14]. In contrast, poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) show very low values of $\bar{M}_n$ (*Table 2*) and have therefore to be considered as oligomers. This behaviour is in accordance with a pronounced tendency of the above *N*,*N*-dialkylamino acrylates to give transfer and/or termination reactions with the growing chain radicals, as previously observed in the copolymerization of the same amino acrylates with MBA, even if in these last systems, at comparable composition, slightly higher $\bar{M}_n$ values (in the 3700–4000 range) were obtained[15].

U.v. absorption spectra of poly(AMBE) and poly(AMBE-*co*-MtA)s show (*Table 1*) two bands centred at about 255 and 340 nm, related to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the aromatic chromophore and the ketone moiety, respectively[14]. The low molecular weight analogue PMBE, containing a single benzoin methyl ether moiety per molecule, displays substantially the same absorption spectrum[14] (*Table 1*). Taking into account that u.v. curing experiments are performed under light irradiation at 330 nm, only the $n \rightarrow \pi^*$ electronic transition is involved in the excitation process of the photoinitiators. In the above region poly(AMBE) and poly(AMBE-*co*-MtA)s show the same molar extinction coefficient ($\varepsilon \approx 220$), slightly lower than that found for PMBE. U.v. spectra of poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) show (*Table 2*) a band centred at 255 nm, associated with the $\pi \rightarrow \pi^*$ electronic transition of the benzene chromophore, and a broad shoulder in the region of the $n \rightarrow \pi^*$ electronic transition of the ketone group in the benzoin methyl ether moiety. Poly(ABME) and the corresponding low molecular weight model PBME display similar u.v. absorption spectra (*Table 2*). However, a hypsochromic shift of the $n \rightarrow \pi^*$ transition (about 10 nm), accompanied by a hyperchromic effect, is observed in both samples with respect to the homo- and copolymers of AMBE as well as to the corresponding structural model PMBE (*Tables 1* and *2*). This behaviour may be associated with the presence in the latter systems of a methyl on the α-alkoxybenzyl group of the benzoin methyl ether moiety.

Photoinitiation activity

Both high and low molecular weight benzoin methyl ether systems have been tested in the u.v. curing of the HDDA/BA equimolar mixture in film matrix, under the same conditions in terms of concentration of photoreactive moiety, light irradiation and thickness of the sample.

On the basis of the maximum polymerization rate values ($R_{c_{max}}$) reported in *Table 3*, poly(AMBE) and poly(AMBE-*co*-MtA)s display similar or slightly higher photoinitiation activity than that found for the corresponding low molecular weight analogue PMBE. Moreover, due to the longer induction period of the polymerization process (t_0) shown by PMBE, the polymeric photoinitiators display a significant higher overall activity, as indicated by the half-time values ($t_{1/2}$) of the curing process (*Table 3* and *Figure 2*). A slight

Table 2 Preparation[a] and properties of poly(ABME) as well as poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA)

	Feed			Polymer characterization					
	Benzoin ether (BE)					U.v. absorption maxima[e]			
						$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
Aminoacrylate monomer	Type	Mol%	Conv.[b] (%)	BE[c] units (mol%)	$\bar{M}_n$[d]	λ_1	ε_1	λ_2	ε_2
	ABME	100		100	62 000[f]	329	272	252	14 200
DMEA	AMBE	49.7	32	56	1 000[g]	340[h]	288	255	12 500
DEEA	AMBE	50.0	10	55	1 100[i]	340[h]	330	256	10 400
–	PBME	–	–	–	–	330	269	256	16 000

[a] Duration: 210–288 h

[b] Calculated as (wt of polymer/wt of comonomers) × 100

[c] Determined by ^1H n.m.r.

[d] Determined by g.p.c.

[e] λ and ε are expressed in nm and $l\ mol^{-1}\ cm^{-1}$, respectively; ε is referred to one benzoin methyl ether moiety

[f] $\bar{M}_w/\bar{M}_n = 2.7$

[g] $\bar{M}_w/\bar{M}_n = 2.6$

[h] Shoulder

[i] $\bar{M}_w/\bar{M}_n = 2.8$

Table 3 Kinetic parameters determined by microwave dielectrometry for u.v. curing of HDDA/BA equimolar mixtures in the presence of low and high molecular weight 4-substituted benzoin methyl ethers[a]

Photoinitiator	Benzoin methyl ether moiety (mol%)	$R_{c_{max}}$[b] (s^{-1})	$R_{c_{1/2}}$[c] (s^{-1})	$t_{1/2}$[d] (s)	t_0[e] (s)
Poly(AMBE)	100	8.3	7.8	9.7	3.3
Poly(AMBE-*co*-MtA)	79	9.7	8.8	10.0	4.2
	58	7.9	7.5	11.0	4.4
	43	10.0	9.6	7.7	2.5
	22	8.6	8.0	10.2	4.0
	15	8.0	7.3	10.4	3.5
PMBE	100	8.0	7.6	13.6	7.1
Poly(ABME)	100	10.4	9.8	8.1	2.9
PBME	100	11.4	10.5	9.6	5.2

[a] Concentration of the photoinitiator: 0.5 mol% of benzoin methyl ether moiety with respect to the HDDA/BA mixture; irradiation intensity at 330 nm: 53 W m^{-2}

[b] Maximum polymerization rate, expressed as percentage of monomers to polymer conversion per second

[c] Polymerization rate expressed as above and determined at the half-time of the process

[d] Half-time of the polymerization process

[e] Induction period of the polymerization process

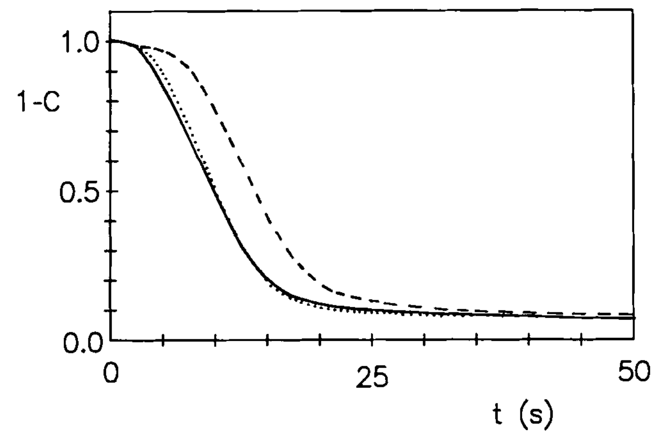


Figure 2 Residual monomers concentration (1-C) *versus* time in the u.v. curing in film matrix of the HDDA/BA equimolar mixture in the presence of (——) poly(AMBE), (········) poly(AMBE-*co*-MtA) with 79 mol% of AMBE co-units and (------) PMBE

Table 4 Kinetic parameters determined by microwave dielectrometry for u.v. curing of HDDA/BA equimolar mixtures in the presence of low and high molecular weight 4-substituted and unsubstituted benzoin methyl ethers[a]

Photoinitiator	Benzoin methyl ether moiety (mol%)	$R_{c_{max}}$[b] (s^{-1})	t_0[c] (s)
Poly(AMBE)	100	8.3	3.3
Poly(ABME)	100	10.4	2.9
Poly(MBA)	100	17.0	2.3
Poly(AMBE-*co*-MtA)	79	9.7	4.2
Poly(MBA-*co*-MtA)	79	17.6[d]	3.6
PMBE	100	8.0	7.1
PBME	100	11.4	5.2
MBI	100	12.0	2.8

[a–c] See footnotes to *Table 3*

[d] $R_{c_{1/2}}$ value

[e] α-Methylolbenzoin methyl ether 2-methylpropanoate

improvement of photoinitiating activity is obtained in the case of poly(ABME) with respect to poly(AMBE), having a methyl group inserted into the α-alkoxybenzyl moiety. An analogous effect is observed by comparing the photoinitiation activity of PBME and PMBE, as indicated by their $R_{c_{max}}$ values (*Table 3*). Poly(ABME) displays a slightly lower activity than PBME. However, due to the longer t_0 value given by PBME, the polymeric system in this case also shows improved overall photoinitiation efficiency. Taking into account all the above data, it may be concluded that, when the benzoin methyl ether moiety is anchored to the polymer backbone through the *para* position of the benzoyl group, the macromolecular coiling does not seem appreciably to affect the rate of the u.v. curing process, only a shortening of the induction period being observed, as compared with the low molecular weight analogues. The slightly higher efficiency of poly(ABME) and PBME with respect to poly(AMBE) and PMBE may be related to the larger ε value of the former systems at the irradiation wavelength.

When these kinetic data are compared with those previously reported[2,9] under the same conditions for poly(MBA) and poly(MBA-*co*-MtA)s, where the benzoin methyl ether moiety is connected to the main chain through the α-alkoxybenzyl group, as well as with the corresponding low molecular weight structural model MBI (*Table 4*), the following main observations can be made:

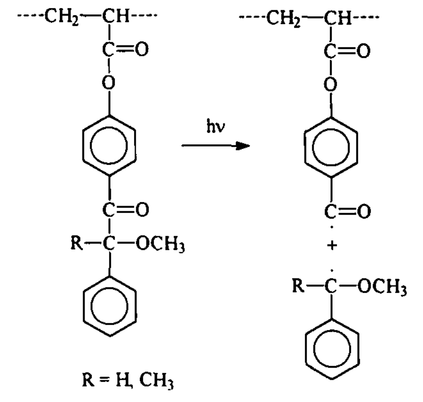
- The presence of an ester group bound to the 4-position of the benzoin methyl ether moiety through the oxygen atom, reduces in general the photoinitiating activity in both low and high molecular weight systems.
- The above detrimental effect is, however, higher in the polymeric systems than in the low molecular weight analogues.

This last statement can be tentatively explained as follows: the higher photoinitiation activity of poly(MBA) and poly(MBA-*co*-MtA)s with respect to MBI, as mentioned in the Introduction, was interpreted[2,9] assuming that the polymer-bound α-alkoxy benzyl primary radicals, owing to the macromolecular coiling, are more prone than the corresponding low molecular weight models to initiate polymerization rather than to give coupling reactions, thus increasing substantially the initiation quantum yield (Φ_i) of the polymerization process. The higher values of Φ_i for the polymeric systems were deduced from experimental R_p values according to equation (1)[21,22]:

$$R_p = (2.303\Phi_i \varepsilon c l I_o)^{1/2} k_p k_t^{-1/2} [M] \qquad (1)$$

where k_p and k_t represent the propagation and termination rate constants, respectively, l is the light path length, ε and c are the molar extinction coefficient and concentration of the photoinitiator, respectively, I_o is the incident light intensity at 330 nm and [M] is the molar monomer concentration. The above evaluation was made assuming that all these quantities are constant and equal for low and high molecular weight photoinitiators, thus reducing equation (1) to equation (2):

$$R_p = K\Phi_i^{1/2} \qquad (2)$$



Scheme 3

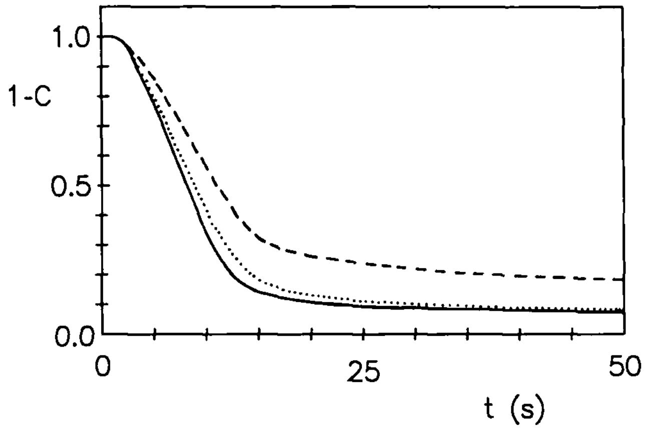


Figure 3 Residual monomers concentration (1-C) *versus* time in the u.v. curing in film matrix of the HDDA/BA equimolar mixture in the presence of (——) PMBE/DMEI 56/44 (mol/mol), (⋯⋯) poly(AMBE)/poly(DMEA) 56/44 (mol/mol) and (------) poly(AMBE-*co*-DMEA) with 56 mol% of AMBE co-units

If we assume, however, that the polymer-bound α-alkoxybenzyl primary radicals, owing to the steric hindrance of the backbone, reduce their termination capability towards the growing chain radicals, a lower value of k_t is obtained as compared with the structural models. This implies that the higher experimental value of R_p in the polymeric systems may be caused by a lower value of k_t according to equation (1). This picture is consistent with the assumption that benzoyl primary radicals are more active as initiating agents than α-alkoxybenzyl primary radicals, the latter being more prone to give termination reactions. Indeed, the higher photoinitiation activity of copolymers of methyl acrylate and methyl methacrylate with α-methylolbenzoin methyl ether and α-methylolbenzoin acrylates and methacrylates, with respect to the corresponding low molecular weight models, has been recently[23,24] explained on the basis of a reduced termination efficiency by the polymer-bound benzyl-type primary radicals, due to the shielding of the main chain. This hypothesis also fits quite well the experimental data obtained with poly(AMBE), poly(ABME) and poly(AMBE-*co*-MtA)s against their corresponding low molecular weight models. In fact, in contrast to what occurred in the previous system, this novel series of polymeric photoinitiators, upon α-photocleavage, gives low molecular weight α-alkoxybenzyl and polymer-bound benzoyl primary radicals (*Scheme 3*) having similar reactivity to that found with low molecular weight models. Indeed, free and polymer-bound benzoyl primary radicals may promptly react with readily diffusing acrylic monomers, giving rise to initiation processes, whereas the low molecular weight α-alkoxybenzyl primary radicals have, obviously, the same termination efficiency in both systems. The results obtained in the HDDA/BA u.v. curing by the copolymers of AMBE with *N*,*N*-dialkylamino acrylates are also in good agreement with the proposed picture and nicely confirm the role of the benzoyl radical as the most effective initiating species. Indeed, the lower $R_{c_{max}}$ values, obtained with poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) with respect to the corresponding mixtures of both homopolymers and low molecular weight models (see for instance *Figure 3*) (*Table 5*), can be easily explained by considering that in the copolymeric systems the polymer-bound benzoyl primary radicals are more prone to react (*Scheme 4*) with the neighbouring tertiary amino groups, thus giving rise to polymer-bound amino-derived

Table 5 Kinetic parameters determined by microwave dielectrometry for u.v. curing of HDDA/BA equimolar mixtures in the presence of poly(AMBE-*co*-DMEA) and poly(AMBE-*co*-DEEA) and the corresponding low molecular weight model compounds[a]

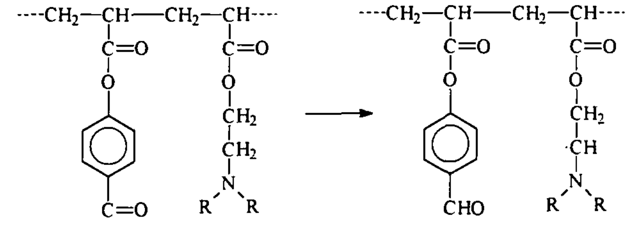
Photoinitiator	Benzoin methyl ether moiety (mol%)	$R_{c_{max}}$[b] (s^{-1})	$R_{c_{1/2}}$[c] (s^{-1})	$t_{1/2}$[d] (s)	t_o[e] (s)
Poly(AMBE-*co*-DMEA)	56	6.6	6.2	10.6	2.6
Poly(AMBE)/poly(DMEA)	56	8.6	8.3	8.8	2.8
PMBE/DMEI	56	9.4	8.9	7.9	2.3
Poly(AMBE-*co*-DEEA)	55	6.2	4.8	11.4	0.8
Poly(AMBE)/poly(DEEA)	55	7.8	7.5	10.0	3.3
PMBE/DEEI	55	7.4	7.2	9.5	2.5

[a–e] See footnotes to *Table 3*

Table 6 Kinetic parameters determined by microwave dielectrometry for u.v. curing of HDDA/BA equimolar mixtures in the presence of copolymers of 4-substituted and unsubstituted benzoin methyl ethers with *N*,*N*-dialkylamino acrylates[a]

Photoinitiator	Benzoin methyl ether co-units (mol%)	$R_{c_{max}}$[b] (s^{-1})	$t_{1/2}$[c] (s)	t_0[d] (s)
Poly(AMBE-*co*-DMEA)	56	6.6	10.6	2.6
Poly(MBA-*co*-DMEA)	44	17.0	3.9	0.5
Poly(AMBE-*co*-DEEA)	55	6.2	11.4	0.8
Poly(MBA-*co*-DEEA)	52	17.0	4.9	1.5

[a–d] See footnotes to *Table 3*



Scheme 4

free radicals, which are known[25] to display lower reinitiation capability, with a reduction of the overall initiation efficiency.

This phenomenon takes place to a lesser extent when mixtures of low molecular weight structural models PMBE/DMEI and DEEI (*Table 5*) are employed, as the tertiary amino groups may equally react with benzoyl and α-alkoxybenzyl primary radicals. The general increase of activity on passing from low and high molecular weight systems containing diethylamino moieties to the corresponding dimethylamino derivatives (*Table 5*) can be related to the lower hydrogen-donating power of the latter groups towards the initiating benzoyl primary radicals. Accordingly, poly(AMBE)/poly(DMEA) and poly(AMBE)/poly(DEEA) exhibit higher photoinitiating activity, with respect to the corresponding copolymers, as the tertiary amino moieties have a reduced interaction capability towards the polymer-bound benzoyl primary radicals, the two species being located on distinct macromolecules.

A decrease of the induction period (t_0) is observed for the amine-containing copolymers with respect to poly(AMBE-*co*-MtA) having similar composition (*Tables 3* and *5*). These findings may be attributed to the consumption of traces of oxygen present in the acrylic formulation by the amino-derived radicals through a chain reaction mechanism involving peroxy radicals and further adjacent side-chain amino groups, as previously proposed for copolymers of MBA with the same *N*,*N*-dialkylamino acrylates[15].

If the photoinitiation activity of AMBE/*N*,*N*-dialkylamino acrylate copolymers is compared with that previously obtained[15] with the corresponding MBA copolymers (*Table 6*), a remarkable reduction is observed in the former systems. Moreover, poly(MBA-*co*-DMEA) and poly(MBA-*co*-DEEA) are[15] more active than the corresponding mixtures of homopolymers as well as of the low molecular weight models, in contrast to what occurs for the AMBE/*N*,*N*-dialkylamino acrylate copolymers. All these data are consistent with the above interpretation that in the MBA/*N*,*N*-dialkylamino acrylate copolymers the tertiary amino groups preferentially react with the polymer-bound α-alkoxybenzyl primary radicals.

CONCLUSIONS

On the basis of the reported data the following concluding remarks can be made:

- Novel homo- and copolymers bearing side-chain benzoin methyl ether moieties connected to the main chain by the *para* position of the benzoyl group have been synthesized and fully characterized.
- The photoinitiation activity of all the above polymeric systems in the u.v. curing of acrylic formulations for clear coatings is shown to be lower than that previously observed for polymeric photoinitiators where the side-chain benzoin methyl ether moieties were attached to the backbone through the α-alkoxybenzyl group. Moreover, in contrast to the latter systems, no substantial enhancement of activity is observed with respect to the corresponding low molecular weight model compounds.
- All the results obtained in the present paper and the data previously reported support the hypothesis that benzoyl primary radicals are more active as initiating agents than the α-alkoxybenzyl primary radicals, these last being more prone to give termination reactions.

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