

Polymeric photoinitiators having benzoin methylether moieties connected to the main chain through the benzyl aromatic ring and their activity for ultraviolet-curable coatings

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Abstract

New polymeric UV photoinitiators, bearing the benzoin methyl ether moiety linked to the side chain through the 4' position, were synthesized by radical homopolymerization of the corresponding monomers, 4'-methacryloyloxy benzoin methyl ether and 4'-methacryloyloxy α -methyl benzoin methyl ether, prepared in turn after a thorough investigation of synthetic methods. For comparison, low molecular weight structural models of the repeating co-units of the polymers having the pivaloyloxy group linked to the 4' position of the benzoin methyl ether moiety were also prepared. All polymeric and model compounds were fully characterized and employed in the photoinitiated polymerization and crosslinking of a standard acrylic formulation for clear UV curable coatings. The photoinitiating activity of these systems, measured by microwave dielectrometry, indicates a higher cure fastness for the model compounds with respect to the corresponding polymeric derivatives, and such a behaviour is tentatively interpreted in terms of the fragmentation mechanism of the benzyl methyl ether radicals formed on α -photocleavage of the benzoin moiety. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymeric photoinitiators; 4'-Methacryloyloxy benzoin methyl ether; 4'-Methacryloyloxy α -methyl benzoin methyl ether

1. Introduction

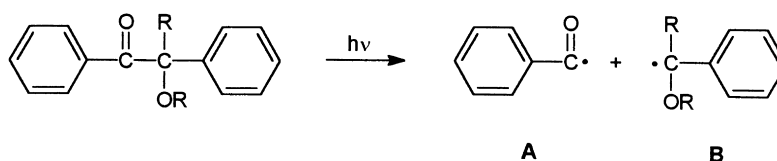
Since many years, benzoin ether derivatives have been well known as efficient UV radical photoinitiators for polymerization and crosslinking of mono- and multi-functional unsaturated monomers. They were applied to various UV-polymerizable systems in several fields, such as surface protecting coatings, photoresists and adhesives [1–7]. Studies concerning the photochemical mechanism of fragmentation have led to the conclusion that a Norrish type I cleavage takes place upon irradiation, to produce benzoyl (**A**) and α -alkoxybenzyl (**B**) primary radicals (Scheme 1) [8–13].

Although studies on ¹⁴C-labelled benzoin ethers suggested that radicals **A** and **B** are equally effective in both initiation and hydrogen-abstraction processes in the photoinitiated polymerization of acrylates and methacrylates [14,15], evidence of a higher reactivity of **A** benzoyl radicals has also been put forward [4,16].

Our earlier experience, derived from investigating the photoinitiating activity of polymeric photoinitiators (PP),

bearing the benzoin methylether moiety linked to the side chain of the acrylic backbone, appeared to suggest that **A** radicals are more active as initiating species than the α -methoxybenzyl radicals **B**, involved mainly in the termination reactions [17,18]. Indeed, the photoinitiating activity of PP derived from α -methylolbenzoin methyl ether acrylate [poly(MBA)] [19], giving rise upon irradiation to the low molecular weight (LMW) benzoyl radical **A** and the polymer-bound α -alkoxybenzyl radical **B'** (Scheme 2a), was found to be higher in the polymerization and crosslinking of a standard acrylic formulation than that afforded by the homopolymers of 4-acryloyloxy- α -methyl benzoin methyl ether [poly(AMBE)] or of 4-acryloyloxy benzoin methyl ether [poly(ABME)] [20], producing the reverse situation represented by the formation of a polymer-bound benzoyl radical **A'** and a LMW α -alkoxybenzyl radical **B** (Scheme 2b). This result was attributed to a reduced capability by radicals **B'** to give termination reactions, due to the steric hindrance by polymer coiling, thus giving rise to an overall higher activity of poly(MBA). A decrease of chain termination efficiency in α -methylol benzoin methyl ether polyacrylates and polymethacrylates [21], or in oligomeric epoxy and urethane resins bearing benzoin alkyl ether

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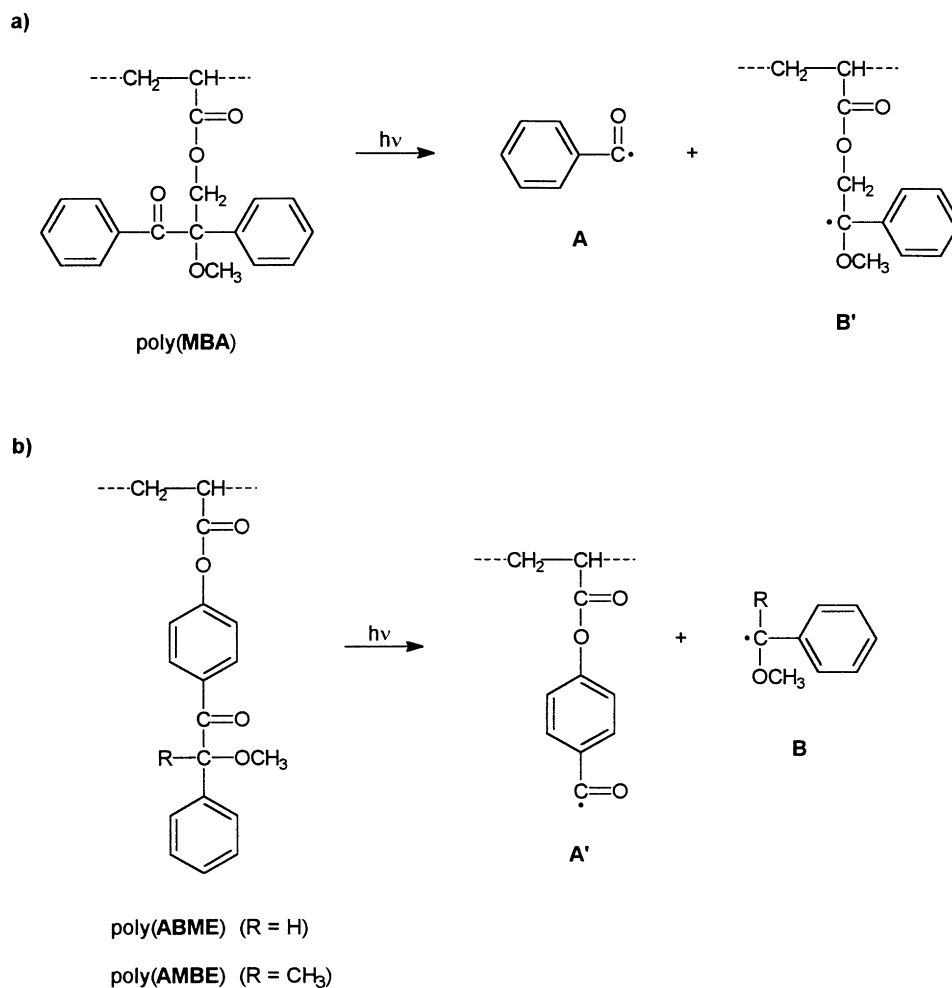


Scheme 1.

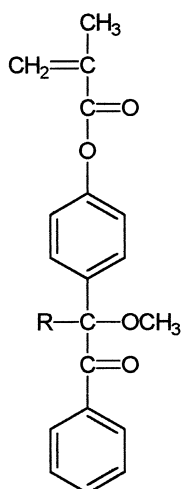
end groups [22] was similarly attributed to the shielding of radicals **B'** by the polymer chain which prevents termination reactions by radical–radical combination.

However, the photoinitiating activity of poly(AMBE) or poly(ABME) would be better compared by checking a polymeric system bearing the photosensitive groups at a comparable distance from the backbone, as the primary **B'** radical derived from the photofragmentation of poly(MBA) is apparently closer to the main chain than the **A'** radical derived from poly(AMBE) or poly(ABME). In this context, it appeared interesting to synthesize a PP bearing the α -alkoxybenzyl ring of the benzoin moiety linked to the main chain at position 4' in order to be

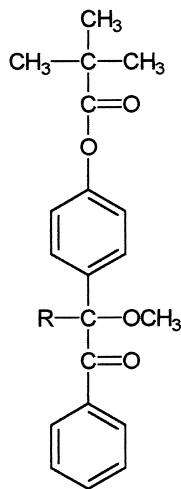
directly comparable with poly(AMBE) and poly(ABME), having the benzoyl ring connected to the backbone at position 4. Therefore, novel monomers, such as 4'-methacryloyloxy benzoin methyl ether (MHBM) and 4'-methacryloyloxy α -methyl benzoin methyl ether (MMBM), were prepared and submitted to radical polymerization to give the corresponding homopolymers poly(MHBM) and poly(MMBM). The LMW model compounds 4'-pivaloyloxy benzoin methyl ether (PHBM) and 4'-pivaloyloxy α -methyl benzoin methyl ether (PMBM) have also been prepared in order to observe possible differences in photoinitiating activity with respect to the polymeric derivatives.



Scheme 2.



MHBM (R = H)

MMBM (R = CH₃)

PHBM (R = H)

PMBM (R = CH₃)

2. Experimental

2.1. Materials

Solvents and reagents were purified or dried according to the reported procedures [23], methacryloyl chloride (Aldrich) and pivaloyl chloride (Aldrich) were distilled under inert atmosphere just before use. Hexanediol diacrylate (HDDA) and *n*-butyl acrylate (BA) were washed first with aq. 5% KOH, followed by water, and then dried over Na₂SO₄, distilled under reduced pressure, and finally stored under inert atmosphere in the refrigerator.

2.2. Monomers

MHBM was prepared from 4'-hydroxy benzoin methyl ether (HBM), which in turn can be obtained as follows: 4-hydroxy benzaldehyde dimethylacetal [24] (136 mmol) was taken in 50 ml of dry DMF and allowed to react with *tert*-butyl dimethylsilyl chloride (160 mmol) in the presence of imidazole (338 mmol) at 35°C for 5 h under stirring and inert atmosphere, according to the procedure reported [25] for a similar reaction. Then, 20 ml of 5% aq. NaHCO₃ was poured into the reaction mixture and the resulting suspension extracted with ethyl ether. After a few washings of the ethereal solution with 1 M NaOH, and drying (Na₂SO₄), the solvent was evaporated under reduced pressure and the crude product subjected to distillation (b.p. 150°C at 2 mbar) to give 4-*tert*-butyl dimethylsilyloxy benzaldehyde dimethylacetal **1** (R = *tert*-BuMe₂Si) with 69% yield.

¹H NMR: 7.3 (d, 2H, arom. in position 2), 6.8 (d, 2H, arom. in position 3), 5.3 (s, 1H, CH), 3.3 (s, 6H, OCH₃), 1.0 (s, 9H, CCH₃), 0.2 (s, 6H, SiCH₃) ppm.

FTi.r.: 3098–3037 (ν_{CH} arom.), 1610 (ν_{C=C} arom.), 915 (ν_{SiOC} arom.) cm⁻¹.

The cyanohydrin **2** (R = *tert*-BuMe₂Si) was prepared by pouring 12 ml (96 mmol) of trimethyl silyl cyanide in methylene dichloride (10 ml) to a solution of **1** (88 mmol) in dry THF (90 ml) at -78°C under stirring and inert atmosphere. Then, trimethylsilyl triflate (0.5 ml) was added and the mixture kept for 1 h at -78°C and left to approach the room temperature in 1 h. Pyridine (3 ml) was finally added and the mixture poured into 5% aq. NaHCO₃ (150 ml). Product **2** was extracted with methylene dichloride and obtained (99% yield) after drying (Na₂SO₄) and evaporation under reduced pressure of the methylene dichloride solution.

¹H NMR: 7.3 (d, 2H, arom. in position 2), 6.9 (d, 2H, arom. in position 3), 5.1 (s, 1H, CH), 3.5 (s, 3H, OCH₃), 1.0 (s, 9H, CCH₃), 0.2 (s, 6H, SiCH₃) ppm.

FTi.r.: 3064–3038 (ν_{CH} arom.), 1609 (ν_{C=C} arom.), 912 (ν_{SiOC} arom.) cm⁻¹. The band connected to the stretching vibration of the nitrile group was hardly visible in the spectrum, due to the remarkable reduction of its intensity caused by the presence of the electron attracting oxygen atom linked to the α position [26].

4'-*tert*-butyl dimethylsilyloxy benzoin methyl ether **3** was prepared by pouring, under inert atmosphere, cyanohydrin **2** (18 mmol) in dry benzene (25 ml) to a solution cooled at 0°C of phenyl magnesium bromide derived from magnesium turnings (40 mmol) and bromobenzene (36 mmol) in dry THF (35 ml). Before the addition of **2**, about 2/3 of the THF solution of the Grignard reagent was evaporated under vacuum and replaced by an equal volume of dry benzene in order to improve the reactivity of the reagent [27]. The reaction mixture was then refluxed for 1 h and finally treated with 4% aq. HCl (400 ml) under stirring. The organic material was extracted with ethyl ether and the ethereal solution dried (Na₂SO₄) and evaporated to dryness to give crude **3** (80% yield) which was then submitted to the subsequent reaction without further purification.

The deprotection of **3** to HBM was carried out by pouring **3** in THF (100 ml) at room temperature, under strong stirring, to a buffered solution (pH = 5) obtained from 0.1 M sodium fluoride (36.45 ml) and 0.1 M hydrogen fluoride (1.05 ml). The progress of the reaction was monitored by thin layer chromatography (eluent chloroform/methanol 9:1 v/v) as long as the starting material was completely consumed (12 h). After evaporation under reduced pressure of most part of the solvent, the mixture was extracted with ethyl ether and the ethereal solution repeatedly washed with 1 M NaOH in order to dissolve the phenolic product. The aqueous solution was finally made acidic with conc. HCl and extracted again with ethyl ether. After drying (Na₂SO₄), the ethereal solution gave the crude HBM which was purified further by crystallization from ethanol/water (32% yield, m.p. 133°C).

¹H NMR: 7.9 (d, 2H, arom. in position 2), 7.5 (m, 1H, arom. in position 4), 7.4 (m, 2H, arom. in position 3), 7.3 (d, 2H, arom. in position 2'), 6.8 (d, 2H, arom. in position 3'), 5.5 (s, 1H, CH), 4.4 (bs, 1H, OH), 3.4 (s, 3H, OCH₃) ppm.

Table 1
Physical properties of poly(MHBM), PHBM, poly(MMBM) and PMBM

Sample	Yield (%) ^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	UV absorption maxima ^c			
				$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
				λ_1	ϵ_1	λ_2	ϵ_2
Poly(MHBM)	25 ^d	17 000	2.1	325 (sh)	760	251	11 400
PHBM	—	—	—	327	450	249	15 900
Poly(MMBM)	29 ^e	20 800	1.4	325 (sh)	360	251	13 600
PMBM	—	—	—	334	140	249	13 400

^a Calculated as (wt. of polymer/wt. of monomer) \times 100.

^b Determined by GPC.

^c In CHCl_3 solution; λ and ϵ are expressed in nm and $l \text{ mol}^{-1} \text{ cm}^{-1}$, respectively; ϵ is referred to one benzoin methyl ether repeating unit for polymeric derivatives; sh: shoulder.

^d Reaction duration 48 h.

^e Reaction duration 80 h.

FTi.r.: 3340 (ν_{OH}), 3068–3028 (ν_{CH} arom.), 1678 (ν_{CO}), 1599 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .

MHBM was prepared from HBM and methacryloyl chloride in the presence of triethylamine according to the reported procedure [20]. The crude product was purified by crystallization from 95% ethanol (35% yield, m.p. 81°C).

¹H NMR: 8.0 (d, 2H, arom. in position 2), 7.5 (m, 3H, arom. in position 4 and 2'), 7.4 (m, 2H, arom. in position 3), 7.1 (d, 2H, arom. in position 3'), 6.3 and 5.7 (2d, 2H, $\text{CH}_2=$), 5.5 (s, 1H, CH), 3.4 (s, 3H, OCH_3), 2.0 (s, 3H, CCH_3) ppm.

FTi.r.: 3065 (ν_{CH} arom.), 1730 (ν_{CO} ester), 1693 (ν_{CO} ketone), 1636 ($\nu_{\text{C=C}}$ methacr.), 1596 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .

MMBM was obtained from 4'-hydroxy α -methyl benzoin methyl ether (MBM), produced in turn from 4'-tert-butyl dimethylsilyloxy benzoin methyl ether **3** as follows:

4'-tert-butyl dimethylsilyloxy benzoin methyl ether **3** (17.6 mmol), previously purified by column chromatography (SiO_2 , eluent ethyl ether/petroleum ether 1:1 v/v), in dry THF (100 ml) was added to a suspension of KH (22 mmol) in dry THF (10 ml) under stirring and inert atmosphere at room temperature. The mixture was allowed to react for 0.5 h, then CH_3I (25 mmol) was dropped into the suspension and the reaction left to proceed for 2 h. Water was then cautiously added under stirring as long as the gas evolution terminated and the reaction product extracted with methylene dichloride. After drying (Na_2SO_4) and evaporation of the solvent under reduced pressure, the crude product was submitted to purification by column chromatography (SiO_2 , eluent benzene/ethyl acetate 20:1 v/v) to give pure 4'-tert-butyl dimethylsilyloxy α -methyl benzoin methyl ether **8** (97% yield).

¹H NMR: 7.9 (d, 2H, arom. in position 2), 7.5 (m, 1H, arom. in position 4), 7.4 (m, 2H, arom. in position 3), 7.3 (d, 2H, arom. in position 2'), 6.8 (d, 2H, arom. in position 3'), 3.4 (s, 3H, OCH_3), 1.7 (s, 3H, $\alpha\text{-CH}_3$), 0.9 (s, 9H, CCH_3), 0.2 (s, 6H, SiCH_3) ppm.

FTi.r.: 3061–3050 (ν_{CH} arom.), 1694 (ν_{CO}), 1605 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .

The deprotection of **8** by HF/NaF, performed as described before for HBM, gave MBM (30% yield) as a viscous oil after purification by column chromatography (SiO_2 , eluent chloroform/methanol 10:1 v/v).

¹H NMR: 8.0 (d, 2H, arom. in position 2), 7.5 (m, 1H, arom. in position 4), 7.4 (m, 2H, arom. in position 3), 7.5 (d, 2H, arom. in position 2'), 7.0 (d, 2H, arom. in position 3'), 5.1 (bs, 1H, OH), 3.3 (s, 3H, OCH_3), 1.7 (s, 3H, $\alpha\text{-CH}_3$) ppm.

FTi.r.: 3381 (ν_{OH}), 3068 (ν_{CH} arom.), 1681 (ν_{CO}), 1596 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .

MMBM was prepared from MBM and methacryloyl chloride in the presence of triethylamine according to the reported procedure [20]. The crude product was purified by crystallization from 95% ethanol (45% yield, m.p. 73°C).

¹H NMR: 7.9 (d, 2H, arom. in position 2), 7.4 (m, 3H, arom. in positions 4 and 2'), 7.3 (m, 2H, arom. in position 3), 7.1 (d, 2H, arom. in position 3'), 6.3 and 5.7 (2d, 2H, $\text{CH}_2=$), 3.3 (s, 3H, OCH_3), 2.0 (s, 3H, $=\text{CCH}_3$), 1.7 (s, 3H, $\alpha\text{-CH}_3$) ppm.

FTi.r.: 3064 (ν_{CH} arom.), 1740 (ν_{CO} ester), 1682 (ν_{CO} ketone), 1638 ($\nu_{\text{C=C}}$ methacr.), 1595 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .

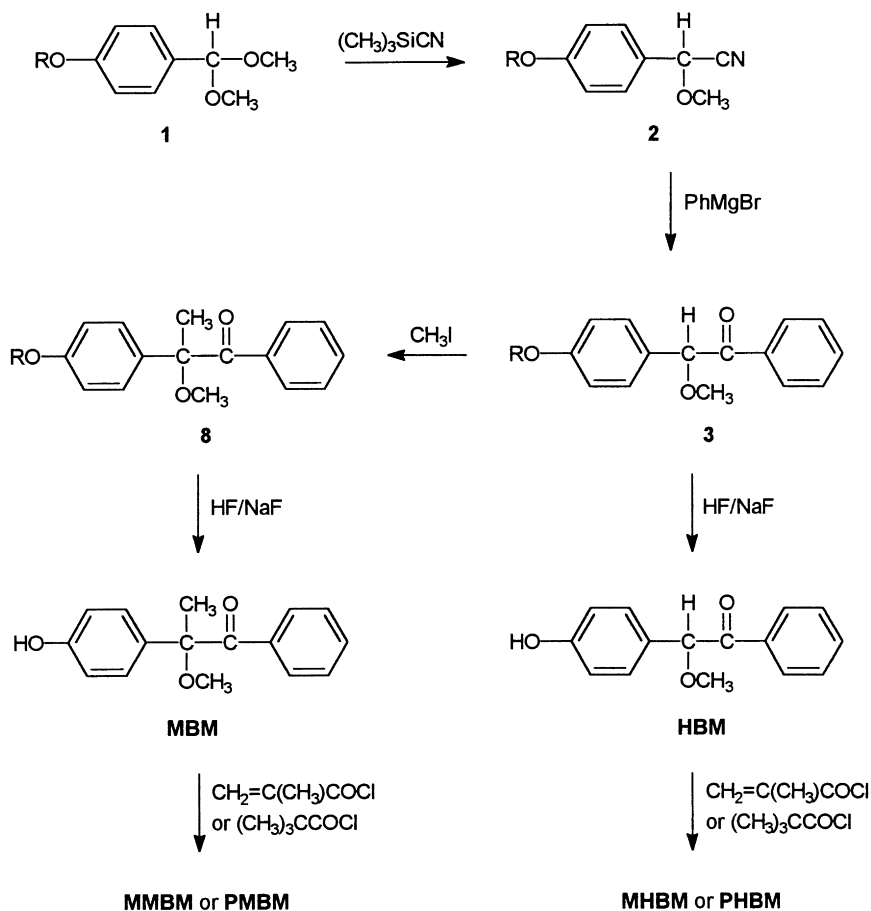
2.3. Low-molecular-weight model compounds

PHBM and PMBM were prepared by reaction of HBM and MBM, respectively, with pivaloyl chloride in the presence of triethylamine according to the reported procedure [20].

PHBM was obtained (40% yield) after crystallization from 95% ethanol, m.p. 90°C.

¹H NMR: 8.0 (d, 2H, arom. in position 2), 7.5 (m, 3H, arom. in positions 4 and 2'), 7.4 (m, 2H, arom. in position 3), 7.1 (d, 2H, arom. in position 3'), 5.5 (s, 1H, CH), 3.4 (s, 3H, OCH_3), 1.3 (s, 9H, CCH_3) ppm.

FTi.r.: 3070 (ν_{CH} arom.), 1735 (ν_{CO} ester), 1688 (ν_{CO} ketone), 1595 ($\nu_{\text{C=C}}$ arom.) cm^{-1} .



Scheme 3.

PMBM was obtained (38% yield) after crystallization from 95% ethanol, m. p. 79°C.

¹H NMR: 7.9 (d, 2H, arom. in position 2), 7.4 (m, 3H, arom. in positions 4 and 2'), 7.3 (m, 2H, arom. in position 3), 7.0 (d, 2H, arom. in position 3'), 3.3 (s, 3H, OCH₃), 1.7 (s, 3H, α-CH₃), 1.3 (s, 9H, CCH₃) ppm.

FTi.r.: 3075 (ν_{CH} arom.), 1745 (ν_{CO} ester), 1680 (ν_{CO} ketone), 1596 (ν_{C=C} arom.) cm⁻¹.

2.4. Polymers

The homopolymers, poly(MHBM) and poly(MMBM), were prepared in glass vials at 60°C using 2,2'-azo-bis-isobutyronitrile (AIBN) (1% w/w with respect to monomers) as thermal radical initiator and benzene as solvent (monomer concentration 10% w/v). The reaction mixture was submitted to several freeze-thaw cycles before closing the vial under high vacuum. After a suitable time, the polymerization was stopped by pouring the reaction mixture into a large excess of petroleum ether. The precipitated polymer was repeatedly dissolved in chloroform and precipitated

again in petroleum ether or methanol, then filtered, dried under vacuum and stored in the dark. Relevant properties of the polymeric products are reported in Table 1.

Poly(MHBM) was obtained (25% yield) after 48 h of reaction.

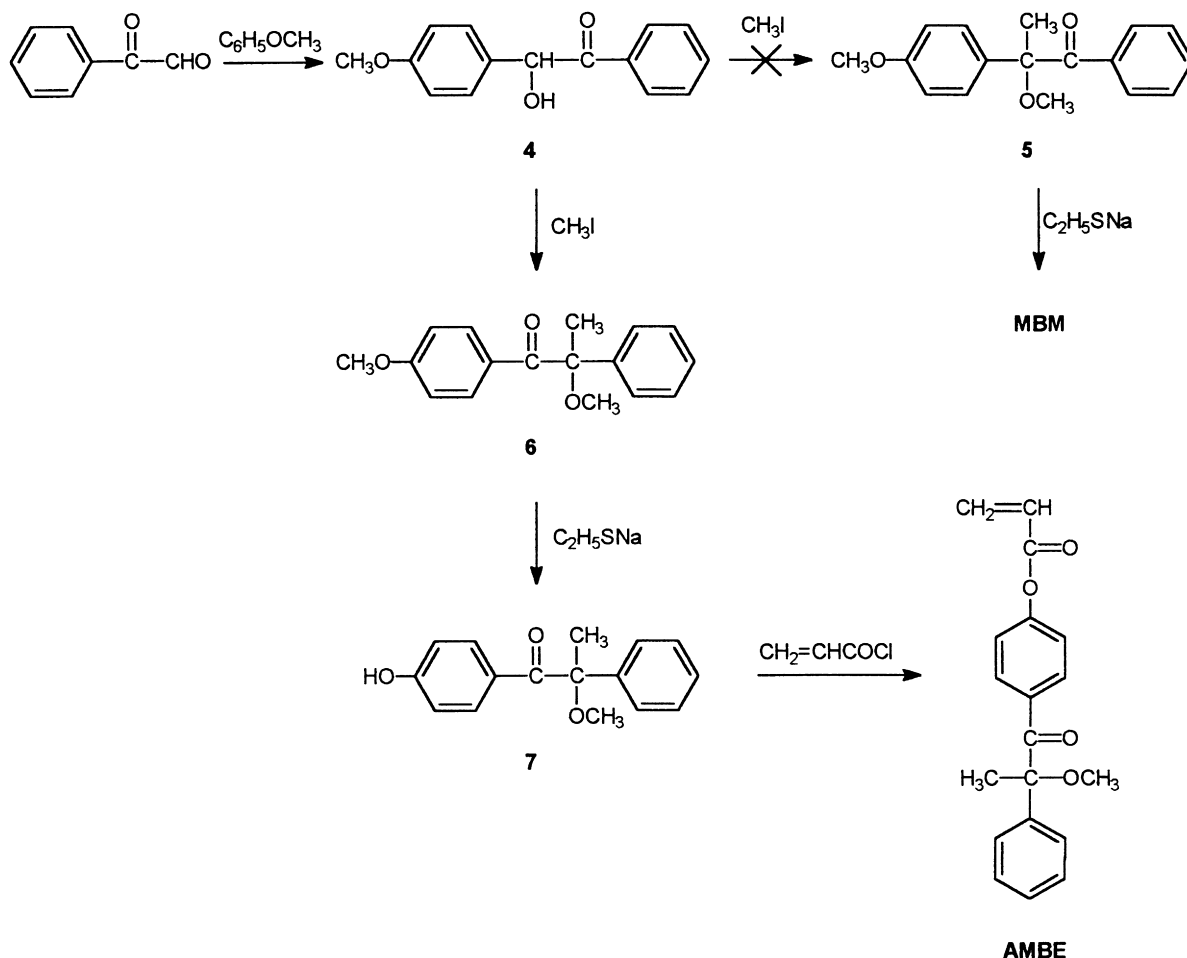
¹H NMR: 8.1–7.8 (bm, 2H, arom. in position 2), 7.6–7.2 (bm, 5H, arom. in positions 3, 4 and 2'), 7.2–6.8 (bm, 2H, arom. in position 3'), 5.6–5.4 (bs, 1H, CH), 3.4–3.2 (bs, 3H, OCH₃), 2.5–1.9 (bm, 2H, CH₂), 1.6–1.1 (bm, 3H, chain CH₃) ppm.

FTi.r.: 3071 (ν_{CH} arom.), 1747 (ν_{CO} ester), 1693 (ν_{CO} ketone), 1597 (ν_{C=C} arom.) cm⁻¹.

Poly(MMBM) was obtained (29% yield) after 80 h of reaction.

¹H NMR: 8.0–7.8 (bm, 2H, arom. in position 2), 7.5–7.2 (bm, 5H, arom. in positions 3, 4 and 2'), 7.1–6.9 (bm, 2H, arom. in position 3'), 3.4–3.2 (bs, 3H, OCH₃), 2.5–2.0 (bm, 2H, CH₂), 1.9–1.0 (bm, 6H, α-CH₃ and chain CH₃) ppm.

FTi.r.: 3064 (ν_{CH} arom.), 1751 (ν_{CO} ester), 1682 (ν_{CO} ketone), 1597 (ν_{C=C} arom.) cm⁻¹.



Scheme 4.

2.5. Physicochemical measurements

NMR spectra were recorded at 300 MHz on a Varian Gemini 300 spectrometer using CDCl_3 solutions and tetramethylsilane as internal standard.

FTi.r. spectra were carried out on a Perkin–Elmer 1750 spectrophotometer equipped with a Perkin–Elmer 7700 data station. The samples were prepared either as cast films on KBr discs or as KBr pellets.

UV absorption spectra in CHCl_3 solution were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. The spectral regions 400–300 and 300–230 nm were investigated using cell pathlengths of 1.0 and 0.1 cm, and concentrations of about 1×10^{-3} and $5 \times 10^{-4} \text{ mol l}^{-1}$, in terms of benzoin repeating units for the polymeric derivatives, respectively. The molar extinction coefficient (ϵ) values are expressed as $\text{l mol}^{-1} \text{ cm}^{-1}$.

Mass spectra were recorded using a VG 7070E spectrometer equipped with an electron impact ionization device.

The average molecular weights of the polymeric samples were determined in THF solution by GPC on a Waters 590 chromatograph equipped with a UV detector operating at

254 nm and a Phenogel column. Monodisperse polystyrene standards were used for calibration.

Melting point determinations were performed with glass capillaries on a Buchi 510 apparatus.

The photoinduced polymerization and crosslinking reactions were performed at 25°C , under nitrogen atmosphere, by UV irradiation at 330 nm (53 W m^{-2}) on a 0.2 mm thick film matrix constituted by a HDDA/BA equimolar mixture containing 0.5 mol% of photoinitiator in terms of benzoin moieties. The time evolution of the curing process was followed by microwave dielectrometry at 9.5 GHz in terms of the imaginary part of the dielectric constant ϵ'' (loss factor) of the reacting system, as previously reported [28]. Method and apparatus are described in detail elsewhere [29].

3. Results and discussion

3.1. Synthesis and characterization of monomers, model compounds and polymers

To obtain MHBM and MMBM, it was necessary to

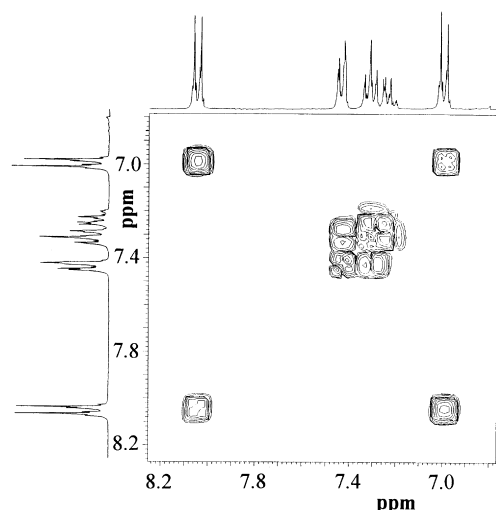


Fig. 1. COSY spectrum of 4-hydroxy α -methyl benzoin methyl ether 7.

prepare the phenolic intermediates HBM and MBM, respectively, representing the precursors to be submitted to the final reaction with methacryloyl chloride (Scheme 3). They were also intermediates suitable for the preparation of model compounds, such as PHBM and PMBM through an analogous reaction with pivaloyl chloride.

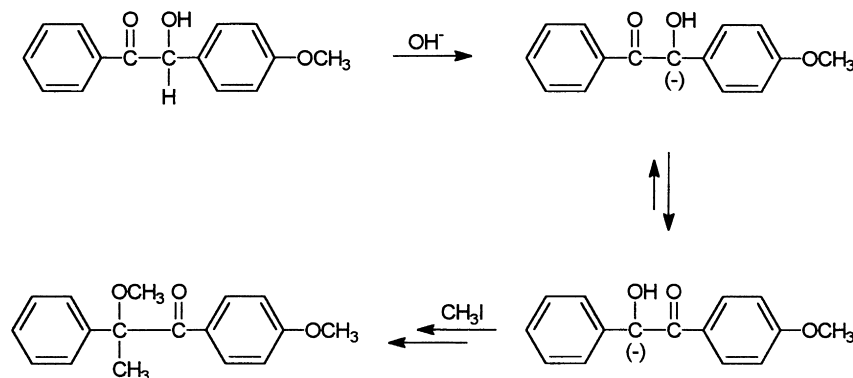
The synthesis of HBM is reported in the literature [30] to take place starting from the *tert*-butyldimethylsilyl-protected *p*-hydroxy benzaldehyde dimethylacetal **1** ($R = \text{tert-BuMe}_2\text{Si}$) (Scheme 3) through the corresponding cyanohydrin **2** ($R = \text{tert-BuMe}_2\text{Si}$), followed by Grignard reaction with PhMgBr to give the benzoin methyl ether derivative **3** ($R = \text{tert-BuMe}_2\text{Si}$) and by a final deprotection from the trialkylsilyl group. Thus, the above pathway was followed, and several changes introduced in order to improve the yields (see Section 2). The dimethyl acetal **1** ($R = \text{tert-BuMe}_2\text{Si}$) was prepared by acetalization of *p*-hydroxy benzaldehyde with acidic methanol, followed by functionalization with *tert*-butyldimethylsilyl chloride. The subsequent step of cyanohydrin formation gave a very satisfactory yield when carried out by addition of cyanotrimethylsilane in the presence of trimethylsilyl triflate, used

as catalyst for several nucleophilic replacement reactions in aprotic media [31]. The deprotection of hydroxy group in the 4' position of **3** in order to obtain HBM was performed using sodium fluoride/hydrofluoric acid, which appears quite an effective desilylating agent [32].

The synthesis of MBM is not reported in the literature and was initially planned to be prepared in few steps by simultaneous C- and O-methylation with methyl iodide [33] of 4'-methoxy benzoin **4** (Scheme 4), obtainable in turn from phenylglyoxal and anisole [34], to give the α -methyl methyl ether **5**, and finally MBM by deprotection of the aromatic methyl ether with sodium thioethoxide in DMF [35,36].

However, the product obtained from the methylation reaction was found to be constituted exclusively by the 4-methoxy- α -methyl benzoin methyl ether **6**, isomeric with the expected 4'-methoxy- α -methylbenzoin methyl ether derivative **5**. This occurrence was proved by the absence in the mass spectrum of the obtained material of the fragment having m/z 105 (benzoyl fragment derived from the expected product **5**), and the presence of a peak at m/z 135 (*p*-methoxy benzoyl fragment) derived from cleavage of the isomer **6**. A confirmation of this finding came from the subsequent demethylation of the aromatic methoxy group with thioethoxide [35,36], followed by acrylation with acryloyl chloride, which afforded the product identical to AMBE that was previously [20] synthesized through the intermediate **7**. The bidimensional COSY analysis of the phenolic product **7** indeed showed the typical pattern of the *p*-substituted benzoyl ring with the presence of only one proton–proton coupling between the lowest field protons at 8.0 ppm, located in the *o*-position to carbonyl group, and the *meta* protons adjacent to the hydroxy group, located at 7.0 ppm (Fig. 1).

Isomerization of unsymmetrical 4'-substituted benzoin to the 4-substituted derivatives under alkaline conditions is reported to occur partially in the presence of ethanolic potassium hydroxide at room temperature for three days [37], or by heating with ethanolic potassium cyanide for half an hour [38]. However, under our conditions (methyl iodide in dimethylsulfoxide in the presence of potassium hydroxide), the isomerization took place quantitatively at



Scheme 5.

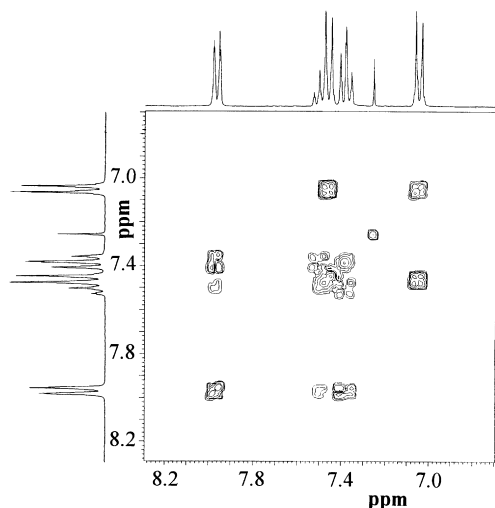


Fig. 2. COSY spectrum of 4'-hydroxy α -methyl benzoin methyl ether (MBM).

room temperature after only one hour, favoured by the electron donating methoxy group of **4**, which promotes the displacement of the tautomeric equilibrium towards the 4-substituted isomeric derivative, as depicted in Scheme 5. It is, in fact, reported that under alkaline conditions the equilibrium between isomeric unsymmetrical benzoin is shifted towards the form in which the carbonyl group is adjacent to the phenyl ring with the more electron-donating substituent [39]. A mechanism involving the simultaneous transposition of both the aromatic rings, leading to the more stable isomer has also been proposed [40]. Even the adoption of milder methylation conditions, such as methyl iodide in THF in the presence of silver oxide [41] or diazomethane in the presence of fluoboric acid in methylene dichloride [42], invariably produced a hardly separable mixture of isomers **5** and **6**.

In order to prevent isomerization during the methylation reaction, a precursor possessing the benzoin aliphatic hydroxy group already under the form of methylether was

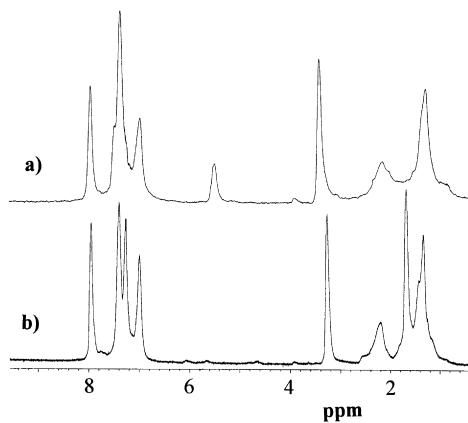


Fig. 3. ^1H NMR spectra in chloroform solution of poly(MHBM) (a), and poly(MMBM) (b).

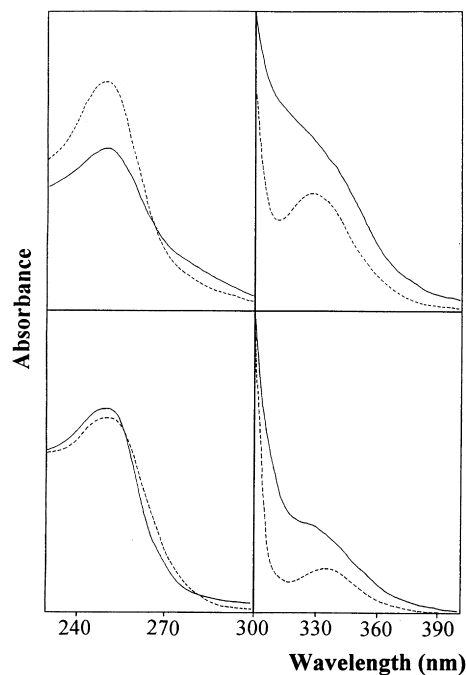


Fig. 4. UV spectra in chloroform solution of: PHBM (dotted line) and poly(MHBM) (full line) (upper spectra), PMBM (dotted line) and poly(MMBM) (full line) (lower spectra). Band intensities at the right hand side of the figure are magnified.

used. Thus, the synthetic route of Scheme 3 was again followed, starting from anisaldehyde dimethylacetal **1** ($R = \text{Me}$) through **3** ($R = \text{Me}$) [30]. In this case, the methylation step did not indeed afford any isomerization, thus allowing us to obtain the desired α -methylated benzoin methyl ether **8** ($R = \text{Me}$). However, the subsequent demethylation of the aromatic hydroxy group with thioethoxide in DMF afforded an unsatisfactory yield (10%) of MBM, although the method employed [35,36] was successful in previous syntheses [20]. This may be attributed to the absence in **8** of electron attracting groups in the *para* position with respect to the aromatic methoxy group favouring the methyl displacement. With the aim to improve the overall yield of the synthesis, the *tert*-butyl-dimethylsilyl group was then adopted as a protecting agent of the aromatic hydroxy group, this moiety being reported as sufficiently stable and readily removable under acidic conditions in the presence of fluoride anions [30]. Thus, the same route adopted for HBM was followed up to the common intermediate **3** ($R = \text{tert-BuMe}_2\text{Si}$), which was subsequently methylated to **8** ($R = \text{tert-BuMe}_2\text{Si}$), and finally deprotected with HF/NaF to MBM in acceptable yield (see Section 2). The COSY spectrum confirmed the expected structure of MBM (Fig. 2).

Treatment of HBM and MBM with methacryloyl chloride in the presence of triethylamine according to known procedures [20] gave finally the monomers MHBM and MMBM. The model compounds, PHBM and PMBM, were similarly prepared by reaction of HBM and MBM

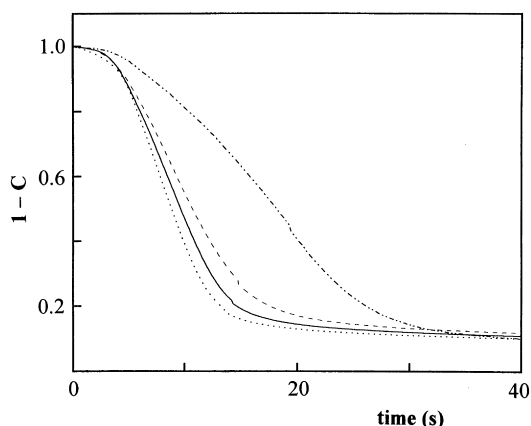


Fig. 5. Fraction of residual monomers ($1 - C$) versus time in the UV curing of HDDA/BA equimolar mixture in the presence of PHBM (dashed line), poly(MHBM) (dotted line), PMBM (full line) and poly(MMBM) (dashed-dotted line).

with pivaloyl chloride. IR and ^1H NMR characterizations were in agreement with the proposed structures (see Section 2).

The polymerization of MHBM and MMBM was carried out under radical conditions by using AIBN as a thermal initiator. The resulting polymers were isolated and purified by repeated precipitations and characterized by average molecular weight, ^1H NMR, IR and UV spectrophotometry. The occurrence of polymerization was confirmed by the absence in the ^1H NMR spectra (Fig. 3) of the resonances at 6.3 and 5.7 ppm, related to the unsaturated methacrylic protons, as well as by the disappearance in the IR spectra of the absorption band located around 1640 cm^{-1} , connected to the methacrylic double bond. As expected, an increase of the ester stretching frequency was observed on passing from the monomeric derivatives to the models or the polymers, due to the diminished electron delocalization originated by the polymerization of the methacrylic double bond (see Section 2).

As reported in Table 1, the \bar{M}_n values were in the same range as those obtained for poly(MBA) [43] and poly(AMBE) [44], with similar polydispersities.

Table 2

Kinetic parameters determined by microwave dielectrometry from the UV curing of a HDDA/BA equimolar mixture in the presence of polymeric and LMW benzoin methyl ether photoinitiators^a

Photoinitiator	$R_{c1/2}$ (s^{-1}) ^b	$t_{1/2}$ (s) ^c	t_0 (s) ^d
Poly(MHBM)	9.2	10.9	3.6
PHBM	11.0	9.1	3.6
Poly(MMBM)	5.5	18.2	4.0
PMBM	10.2	9.8	3.6

^a Photoinitiator concentration: 0.5 mol% of benzoin methyl ether moiety in the HDDA/BA mixture; irradiation intensity at 330 nm: 53 W m^{-2} .

^b Polymerization rate expressed as per cent conversion of monomers to polymers per second, determined at half-time of the process.

^c Half-time of the polymerization process.

^d Induction period of the polymerization process.

The UV spectra of polymers and model compounds (Table 1) exhibited two absorption maxima centered at about 250 and 330 nm in the spectral region between 230 and 400 nm, related to the lowest energy $\pi \rightarrow \pi^*$ electronic transition and to the $n \rightarrow \pi^*$ transition of the aromatic chromophore and the ketone moiety, respectively [45], with the band at a higher wavelength appearing as a shoulder of the more intense signal located at about 250 nm in the spectra of polymeric derivatives (Fig. 4). As a consequence, the molar extinction coefficient ϵ at 325 nm, related to the $n \rightarrow \pi^*$ transition, appears to be higher for poly(MHBM) and poly(MMBM) as compared to the corresponding model compounds (Table 1). It is also worth noting that while poly(MMBM) and PMBM exhibit ϵ values that are similar to those previously observed for poly(AMBE) ($\epsilon_{253} = 12\,500$; $\epsilon_{341} = 219$) and PMBE ($\epsilon_{257} = 13\,700$; $\epsilon_{339} = 232$) [20], poly(MHBM) displays lower and higher ϵ_{max} values than poly(AMBE) ($\epsilon_{252} = 14\,200$; $\epsilon_{329} = 272$) [20] for the bands at 251 and 325 nm, respectively.

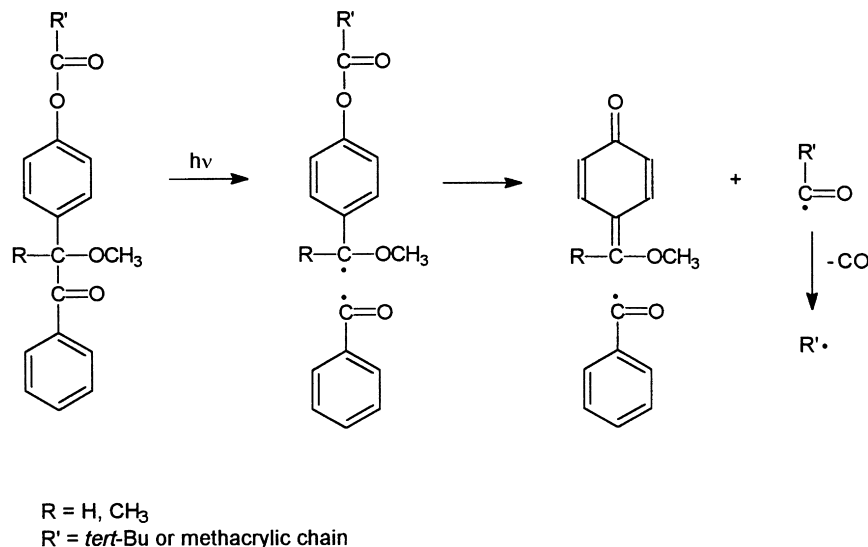
Considering that the UV curing experiments involving the aforementioned photoinitiators are performed under light irradiation at 330 nm, and that the $n \rightarrow \pi^*$ electronic transition should only undergo the excitation process, one would expect a higher amount of light absorption by poly(MMBM) and poly(MHBM) with respect to the corresponding models, as well as with respect to poly(AMBE) and poly(AMBE), in the photocrosslinking of the acrylic formulation.

3.2. Photoinitiating activity of model compounds and polymers

The photoinitiating activity of both polymers and model compounds was evaluated in the UV curing of an equimolar mixture HDDA/BA in film matrix, under inert atmosphere and constant conditions, in terms of molar concentration of photoreactive moiety, sample thickness, light irradiation and temperature. The crosslinking process was followed by measuring the monomer conversion C (Fig. 5) with time, thus allowing us to calculate the induction time, polymerization rate and the residual amount of monomers at the end of the process. Table 2 reports the obtained experimental kinetic parameters.

The following considerations can be drawn from the experimental data:

- Model compounds exhibit higher activity than the corresponding polymers, although they have less light absorbance at the irradiation wavelength (Table 1). In particular, while PHBM has a slightly better activity than poly(MHBM), PMBM is remarkably more active than poly(MMBM). This is confirmed by the $t_{1/2}$ values (Table 2). The induction times appear to be substantially similar for all the investigated samples. The absence of a positive “polymer effect” with this type of photoinitiators would, therefore, indicate that the benzyl radical which is



Scheme 6.

formed on α -photocleavage of the benzoin moiety does not play a role of chain termination species, as in this case the polymeric sample would allow a higher activity than that in the model compound, with the steric bulkiness of the polymeric chain hindering the recombination reaction between radicals. Therefore, in order to explain these results, an active role in the initiation should be invoked for the benzyl radicals also, with the steric hindrance of polymer coiling justifying the lower activity of polymer-bound benzyl radicals as compared to those derived from the model.

However, an alternative explanation could be tentatively put forward based on the presence of the ester group in the *para* position of the benzyl ring. In addition to the usual electron delocalization allowed by the aromatic moiety, the benzyl radical could evolve by further

fragmentation resulting in the formation of a stable product having a quinoid structure, and an aliphatic acyl radical, or eventually an alkyl radical by further loss of carbon monoxide, as depicted in Scheme 6. Thus, the polymer-bound radical species could possess a lower initiating activity, due to steric hindrance, than that of the radicals derived from the model compounds. As a consequence, the overall activity would be improved in PHBM and PMBM with respect to the PP. Although in the absence of experimental evidence confirming the reaction path of Scheme 6 (the assessment of the existence of fragmentation products derived from a few milligrams of initiator employed in each run in the crosslinked material is experimentally difficult) the aforementioned hypothesis appears to be reasonable and could explain the behaviour observed with these 4'-substituted benzoin systems.

- The α -methylated derivatives, poly(MMBM) and PMBM, display a lower photoinitiating activity than the corresponding un-methylated compounds. This can be attributed to the lower absorptivity of light at the irradiation wavelength (Table 1). A similar result was also previously [20] observed for poly(AMBE) and PMBE with respect to poly(ABME) and PBME.
- The comparison with previous data (Table 3) obtained from PP bearing the benzoin methyl ether moiety connected to the main chain through the benzoyl aromatic ring, indicates that poly(MHBM) and PHBM exhibit a photoinitiating activity very similar to poly(ABME) and PBME, whereas poly(MMBM) and PMBM are less and more active, respectively, than poly(AMBE) and PMBE. It cannot be excluded that the aforementioned hypothesized fragmentation mechanism plays an important role in affecting the activity of the 4'-substituted benzoin methyl ether moieties possessing the α -methyl group linked to the benzyl moiety. In

Table 3

Kinetic parameters determined by microwave dielectrometry from the UV curing of a HDDA/BA equimolar mixture in the presence of polymeric and LMW benzoin methyl ether photoinitiators reported in the literature^a

Photoinitiator	$R_{c1/2}$ (s ⁻¹) ^b	$t_{1/2}$ (s) ^c	t_0 (s) ^d	Ref.
Poly(ABME)	9.8	8.1	2.9	[20]
PBME	10.5	9.6	5.2	[20]
Poly(AMBE)	7.8	9.7	3.3	[20]
PMBE	7.6	13.6	7.1	[20]
Poly(MBA)	17.0	5.6	2.3	[43]
MBI	12.0	7.0	2.8	[43]

^a Photoinitiator concentration: 0.5 mol% of benzoin methyl ether moiety in the HDDA/BA mixture; irradiation intensity at 330 nm: 53 W m⁻². PBME: 4-pivaloyloxy benzoin methyl ether; PMBE: 4-pivaloyloxy- α -methyl benzoin methyl ether; MBI: α -methylol benzoin methyl ether isobutyrate.

^b Polymerization rate expressed as per cent conversion of monomers to polymers per second, determined at half-time of the process.

^c Half-time of the polymerization process.

^d Induction period of the polymerization process.

conclusion, however, poly(MBA) appears to display the best performance among these PP bearing the benzoin methyl ether moiety in the side chain.

4. Conclusions

The synthesis of PP by radical homopolymerization of new methacrylic monomers bearing the benzoin methyl ether moiety linked to the carboxy group through the *para* position of the benzyl ring was performed. Contrary to the expectation, these systems display a lower photoinitiating activity with respect to that of the corresponding LMW models in the UV curing of the acrylic equimolar formulation HDDA/BA, suggesting the possibility of a role other than that of chain terminating species by the benzyl radicals formed upon α -photocleavage, as previously proposed. However, the possibility of further fragmentation of these benzyl radicals exists, which would explain the results obtained. Among the PP investigated in the present and previous research, the system constituted by benzoin methyl ether moieties linked to the main chain through the α -methylol group still maintains the best performance in terms of curing fastness and induction time.

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