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The synthesis and characterization of some polymeric Type-1 photoinitiators based on α-hydroxymethylbenzoin and α-hydroxymethylbenzoin methyl ether

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Abstract

The acrylic and methacrylic esters of α-hydroxymethylbenzoin and α-hydroxymethylbenzoin methyl ether, respectively, are synthesized and thermally copolymerized with methyl acrylate and methyl methacrylate using a chain transfer agent in some cases to control the molecular weight of the copolymers. The products are characterized by ^{1}H NMR spectroscopy and UV-absorption spectroscopy. Certain copolymers exhibited hyperchromism. The photodecomposition of the copolymers in the presence of suitable radical trapping agents shows their potential as photoinitiators.

Keywords: α-Hydroxymethylbenzoin (meth)acrylate; Polymeric Type-I photoinitiators

1. Introduction

Interest has grown in the design and use of polymerizable and polymeric photoinitiators for a number of reasons, the main one being the desire to reduce the number of low molecular weight migratable species. Thus, various established photoinitiators have been provided with polymerizable groups at different positions of the molecules, possibly leading to different reactivities of the copolymers obtained from them as was extensively outlined in a recent review [1].

Our strategy is based upon the design of polymeric photoinitiators of which reactive radicals are being cleaved from the polymer backbone and may therefore be expected to initiate the polymerization in a similar way as the corresponding low molecular weight photoinitiators. This approach implies the synthesis of Type-1 photoinitiator moieties attached onto a polymer backbone through a spacer group, in principle without affecting the original chromophore of the photoinitiator and as a consequence the nature of its excited state involved in the photofragmentation. To this end the acrylic and methacrylic esters of α-hydroxymethylbenzoin and α-hydroxymethylbenzoin methyl ether are selected.

In the present communication the syntheses of these esters, their copolymerization with methyl acrylate and methyl methacrylate, and the characterization of the copolymers are described. Radical trapping agents such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) and 1,1-di(*p*-tolyl)ethylene (DTE), respectively, are used to characterize the radicals produced upon photolysis of the copolymers.

2. Experimental details

2.1. Physicochemical measurements

^{1}H NMR spectra were recorded on a Jeol JNM-PMX (100 MHz) and a Bruker WH-270 spectrometer, respectively, using tetramethylsilane ($\delta = 0$) as internal standard. IR spectra were recorded on a Perkin-Elmer 983 G spectrophotometer. UV spectra were recorded on a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer.

Melting points were determined with a Griffin melting point apparatus (Number P 1158). Molecular weights of the copolymers were determined by GPC analyses carried out using a Waters Associates instrument with a 254 nm UV detector. The P.L.1000 polystyrene/divinylbenzene column (Polylabs, UK) was eluted with tetrahydrofuran at a flow rate of 1 ml min^{-1}. A narrow standards calibration curve was used.

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2.2. Materials

α-Hydroxymethylbenzoin, m.p. 85.6–86.1°C, was available from a previous study [2]. Benzoin methyl ether, m.p. 47.1–47.4°C, was available from a previous study [3]. All reagents not specifically mentioned were obtained from Aldrich and were used without further purification. 2,2,6,6-Tetramethylpiperidino benzoate **4** [4], 2,2,6,6-tetramethyl-1-piperidyloxymethyl phenyl ketone **5** [5], 1-hydroxy-2,2,6,6-tetramethylpiperidine **6** [5], and DTE [6] were available from previous studies.

2.3. Syntheses

α-Hydroxymethylbenzoin methyl ether was synthesized from benzoin methyl ether and paraformaldehyde as described for α-hydroxymethylbenzoin [2], m.p. 72.5–73.5°C after recrystallization from toluene/hexane (reported 72–73°C [7]).

^{1}H NMR ($CDCl_3$): $\delta = 8.0$–7.8 (m, 2H, 2×*o*-benzoyl); 7.5–7.0 (m, 8H, arom.); 4.5, 4.1 (dd, $J = 13$ Hz, 2H, –CH_2O–); 3.3 (s, 3H, –OCH_3).

$C_{16}H_{16}O_3$ (256.31): Calcd.: C, 74.98; H, 6.29. Found: C, 75.00; H, 6.42.

α-Hydroxymethylbenzoin acrylate **1a** was synthesized from α-hydroxymethylbenzoin and acryloyl chloride in chloroform in the presence of triethylamine followed by conventional work-up, m.p. 80.0–81.0°C after recrystallization from ethanol.

^{1}H NMR ($CDCl_3$): $\delta = 7.9$–7.7 (m, 2H, 2×*o*-benzoyl); 7.6–7.1 (m, 8H, arom.); 6.5–5.9 (m, 3H, –$CH{=}CH_2$); 5.2–4.5 (dd, $J = 12$ Hz, 2H, –CH_2O).

$C_{18}H_{16}O_4$ (296.35): Calcd.: C, 72.96; H 5.44. Found: C, 72.66; H, 5.44.

α-Hydroxymethylbenzoin methacrylate **1b** was synthesized from α-hydroymethylbenzoin and methacryloyl chloride in chloroform in the presence of triethylamine followed by conventional work-up, m.p. 87.0–87.5°C after recrystallization from toluene.

^{1}H NMR ($CDCl_3$): $\delta = 7.9$–7.7 (m, 2H, 2×*o*-benzoyl); 7.6–7.2 (m, 8H, arom.); 6.0–5.9 (m, 1H, *trans* –$CH{=}C(CH_3)$–); 5.6–5.4 (m, 1H, *cis* –$CH{=}C(CH_3)$–); 5.2–4.5 (dd, $J = 12$Hz, –CH_2O–); 1.8 (s, 3H, –CH_3).

$C_{19}H_{18}O_4$ (310.35): Calcd.: C, 73.53; H, 5.84. Found: C, 73.47; H, 5.94.

α-Hydroxymethylbenzoin methyl ether acrylate **2a** was synthesized from α-hydroxymethylbenzoin methyl ether and acryloyl chloride in chloroform in the presence of triethylamine followed by conventional work-up, m.p. 56.0–57.0°C after recrystallization from ethanol (reported 56°C [8]).

^{1}H NMR ($CDCl_3$): $\delta = 7.8$–7.6 (m, 2H, 2×*o*-benzoyl); 7.3–6.8 (m, 8H, arom.); 6.0–5.3 (m, 3H, –$CH{=}CH_2$); 4.9, 4.3 (dd, $J = 12$ Hz, 2H, –CH_2O–); 3.0 (s, 3H, –OCH_3).

$C_{19}H_{18}O_4$ (310.35): Calcd.: C, 73.53; H, 5.84. Found: C, 73.50; H, 5.80.

α-Hydroxymethylbenzoin isobutyrate **1c** was synthesized from α-hydroxymethylbenzoin and isobutyryl chloride in ether in the presence of triethylamine followed by conventional work-up, m.p. 85.0–86.0°C after recrystallization from toluene.^{1}H NMR ($CDCl_3$): $\delta = 7.9$–7.7 (m, 2H, 2×*o*-benzoyl); 7.6–7.1 (m, 8H, arom.); 4.9, 4.3 (dd, $J = 12$ Hz, 2H, –CH_2O–); 2.7–2.1 (m, 1H, –$CH<$); 1.2–0.9 (d, $J = 7$ Hz, 6H, 2×CH_3).

$C_{19}H_{20}O_4$ (312.37): Calcd.: C, 73.06; H, 6.45. Found: C, 72.86; H, 6.73.

α-Hydroxymethylbenzoin pivalate **1d** was synthesized from α-hydroxymethylbenzoin and pivaloyl chloride in tetrahydrofuran in the presence of triethylamine and 10 mol% of 4-dimethylaminopyridine followed by conventional work-up, m.p. 97.0–97.5°C after recrystallization from ethanol.

^{1}H NMR ($CDCl_3$): $\delta = 7.9$–7.7 (m, 2H, 2×*o*-benzoyl); 7.6–7.2 (m, 8H, arom.); 5.1, 4.5 (dd, $J = 12$ Hz, –CH_2O–); 1.1 (s, 3H, –$C(CH_3)_3$).

$C_{20}H_{22}O_4$ (326.40): Calcd.: C, 73.60; H, 6.79. Found: C, 73.56; H, 6.82.

α-Hydroxymethylbenzoin methyl ether isobutyrate **2c** was synthesized from α-hydroxymethylbenzoin methyl ether and isobutyryl chloride in tetrahydrofuran in the presence of triethylamine and 10 mol% of 4-dimethylaminopyridine followed by conventional work-up, m.p. 49.0–50.0°C after recrystallization from ethanol.[1] ^{1}H NMR ($CDCl_3$): $\delta = 8.0$–7.6 (m, 2H, 2×*o*-benzoyl); 7.5–7.2 (m, 8H, arom.); 5.1, 4.5 (dd, $J = 12$ Hz, 2H, –CH_2O–); 3.3 (s, 3H, –OCH_3); 2.6–2.1 (m, 1H, –$CH<$); 1.1–0.9 (q, $J = 7$ Hz, 6H, 2×–CH_3).

$C_{20}H_{22}O_4$ (326.40): Calcd.: C, 73.60; H, 6.79. Found: C, 73.39; H, 6.89.

α-Hydroxymethylbenzoin methyl ether pivalate **2d** was synthesized from α-hydroxymethylbenzoin methyl ether and pivaloyl chloride in tetrahydrofuran in the presence of triethylamine and 10 mol% of 4-dimethylaminopyridine followed by conventional work-up, m.p. 86.0–87.0°C after recrystallization from ethanol.

^{1}H NMR ($CDCl_3$): $\delta = 8.0$–7.8 (m, 2H, 2×*o*-benzoyl); 7.6–7.0 (m, 8H, arom.); 5.1, 4.5 (dd, $J = 12$ Hz, 2H, –CH_2O); 3.3 (s, 3H, –OCH_3); 1.0 (s, 9H, –$C(CH_3)_3$).

$C_{21}H_{24}O_4$ (340.42): Calcd.: C, 74.09; H, 7.10. Found: C, 74.26; H, 7.37.

Benzoylmethyl isobutyrate **3c** was synthesized from α-bromoacetophenone, isobutyric acid and triethylamine in dimethyl-formamide [10], m.p. 28.3–30.1°C after recrystallization from isopropanol (reported b.p. 101°C at 0.1 mm [11]).^{1}H NMR ($CDCl_3$): $\delta = 7.9$ (d, $J = 8$ Hz, 2H, 2×*o*-benzoyl); 7.6–7.4 (m, 3H, arom.); 5.3 (s, 2H, –CH_2O–); 2.79–2.73 (sept, $J = 7$ Hz, 1H, –$CH<$); 1.25 (d, $J = 7$ Hz, 6H, –$CH(CH_3)_2$).

Benzoylmethyl pivalate **3d** was similarly synthesized from α-bromoacetophenone, pivalic acid and triethylamine, 59.2–59.8°C after recrystallization from isopropanol (reported 61–62°C [11]).^{1}H NMR ($CDCl_3$): $\delta = 7.9$ (d, $J = 8$ Hz, 2H,

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[1] Known compound, but no m.p. given [9].

2×*o*-benzoyl); 7.6–7.4 (m, 3H, arom.); 5.3 (s, 2H, $-CH_2O-$); 1.3 (s, 9H, $-C(CH_3)_3$).

3,3-Di(*p*-tolyl)propiophenone **7** was synthesized from benzylideneacetophenone and toluene as described [12], m.p. 98.4–99.4°C after recrystallization from ethanol (reported 77–78°C [12], and 96–97°C [13], respectively).

^{1}H NMR ($CDCl_3$): $\delta = 7.92$ (m, 2H, 2×*o*-benzoyl); 7.57–7.38 (m, 3H, $(m+p)$-benzoyl); 7.14, 7.06 (dd, $J = 8$ Hz, 8H, $(o+m)$-tol.); 4.75 (t, $J = 7$ Hz, 1H, $-CH<$); 3.69 (d, $J = 7$ Hz, 2H, $-CH_2-$); 2.27 (s, 6H, 2×$-CH_3$).

2,2-Di(*p*-tolyl)vinyl phenyl ketone **8** was synthesized from 3,3-di(*p*-tolyl)propiophenone **7** through a (mono)-bromination/dehydrobromination sequence, m.p. 107.2–108.0°C after recrystallization from ethanol.

^{1}H NMR ($CDCl_3$): $\delta = 8.0$ (m, 2H, 2×*o*-benzoyl); 7.50–7.15 (m, 7H, one tol. + $(m+p)$-benzoyl); 7.08, 7.07 ('s,s', 5H, one tol. + $-CH=$); 2.38, 2.32 (2×s, 6H, 2×$-CH_3$).

2.4. Copolymerization reactions

The copolymers were synthesized by reacting the 'photoinitiator' acrylic (**1a** and **2a**) and methacrylic (**1b**) esters with methyl acrylate (MA) and methyl methacrylate (MMA), respectively. The copolymerizations were carried out in methyl isobutyl ketone (MIBK) and were thermally initiated by azobisisobutyronitrile (AIBN). The reactants to initiator ratios were kept constant: PI-(meth)acrylate: MA(MMA):AIBN = 1:3:0.2, except in the syntheses of copolymers **2a/MA** (1:2) and (2:1), respectively.

The solutions were degassed on a vacuum line using the pump–freeze–thaw technique. The sample tubes were then sealed and heated to 80°C in an oil bath. After a given reaction time the samples were poured into petroleum ether (60/80°C) and the copolymers were isolated by filtration and dried in a vacuum oven at 35°C for 48 h.

A similar '**1a/MA**' copolymerization was carried out (60 min) in the presence of a chain transfer agent (1-dodecanethiol, 14 mol% based on **1a**) to control the molecular weight.

^{1}H NMR ($CDCl_3$): $\delta = 7.95$–7.80 (m, *o*-benzoyl H); 7.63–7.48 (m, *o*-benzyl H); 7.47–7.17 (m, other arom. H); 3.72–3.38 (s, $-OCH_3$) 2.41–2.20 (m, $-CH-$); 1.80–1.54 (s, $-CH_2-$). The ratio of methanoate to aromatic integrals gave a photoinitiator content of 59%.

GPC of this copolymer (**1a/MA**, '+CTA') gave $\bar{M}_W = 3796$ and $\bar{M}_N = 2593$ ($\bar{M}_W/\bar{M}_N = 1.46$).

A control experiment in the absence of 1-dodecanethiol gave a copolymer (**1a/MA**, '−CTA') with a similar ^{1}H NMR spectrum. The ratio of methanoate to aromatic integrals gave a photoinitiator content of 54%. GPC gave $\bar{M}_W = 26588$ and $\bar{M}_N = 7960$ ($\bar{M}_W/\bar{M}_N = 3.34$).

2.5. Characterization of the copolymers

Both UV and ^{1}H NMR spectral analyses in $CHCl_3$ and $CDCl_3$, respectively, were used to determine the photoinitiator content of the various copolymers.

In the UV spectral analyses the benzoin carbonyl n-π^* absorption located in the 320 nm region was used, applying the molar absorptivity of the relevant monomeric model compound and the Lambert–Beer Law.

In the ^{1}H NMR spectral analyses a comparison of the integrals of the methanoate signals associated with MA and MMA, respectively, and the aromatic signals associated with the benzoin moiety, were used.

2.6. Photodecomposition of some monomeric model compounds and copolymers in the presence of radical trapping agents

Solutions (10^{-2} M) of the monomeric model compounds **1c** and **1d** in benzene in the presence of TMPO and DTE, respectively, were irradiated under nitrogen in a Rayonet photoreactor (model RPR-208) equipped with 350 nm lamps as described before [4–6,14]. Molar ratios of TMPO:**1c**(**1d**) of 2:1 and of DTE:**1c**(**1d**) of 2:1 were employed. The quan-

Table 1

Copolymer	Reaction time (min)	$\bar{M}_N$	Photoinitiator content (wt.%)		
			UV	^{1}H	Ratio
1*a*/*MA* (1:3)	20	17039	64	51	1.25
	45		57	46	1.25
	90		57	44	1.30
	120	10876	60	48	1.25
	140		60	49	1.22
	150		48	40	1.20
	180	9169	53	44	1.20
	210		60	49	1.22
1*a*/*MMA* (1:3)	20		40		
	70	9629	50		
	120	8583	51		
1*b*/*MA* (1:3)	20	22248	76		
	70	17717	65	64	1.02
	120		54	51	1.06
1*b*/*MMA* (1:3)	20	8785	79	60	1.32
	70	8421	58	49	1.18
	120	8149	57	51	1.12
	150		58	49	1.18
	180	7095	54	52	1.04
	200	6746	55	44	1.25
	240		55	49	1.12
2*a*/*MA* (1:3)	20		61	54	1.13
	70	7170	60	59	1.02
	120		58	55	1.05
	150		54	55	0.98
	180	6422	50	57	0.88
	210		59	58	1.02
	240	6001	63	58	1.09
2*a*/*MA* (1:2)	120	6008	63	59	1.07
2*a*/*MA* (2:1)	120	6284	74	68	1.09
2*a*/*MMA* (1:3)	20		32		
	120	6769	41	37	1.11

titative analyses of the irradiation mixtures were carried out by HPLC as described before [4–6,14].

Solutions (10^{-2} M photoinitiator units) of some copolymers in benzene in the presence of TMPO and DTE, respectively, were similarly irradiated. Molar ratios of TMPO:photoinitiator units of 2:1 and of DTE:photoinitiator units of 4:1 were employed. The qualitative analyses of the irradiation mixtures were carried out by TLC.

3. Results and Discussion

From the number average molecular weight $\bar{M}_N$ results collected in Table 1 it can be seen that for each type of copolymer $\bar{M}_N$ has its highest value at the shortest reaction time and decreases with increasing reaction time throughout the series, which is consistent with a mechanism governed by primary radical termination for both chemical and physical reasons. Clearly, as the polymerization proceeds, monomer levels will be depleted and since the viscosity increases with reaction time, the mobility of the propagating chain radicals, and as a consequence, the probability of bimolecular termination (k_t), will be increasingly restricted. The primary initiator radicals, however, being of far smaller size, are considerably less restricted in their mobility and are therefore expected to be able to interact more freely with the propagating chain radicals (k_t'), e.g., for the polymerization reactions of styrene and MMA initiated with AIBN at 60°C, the ratio of k_t'/k_t has been reported to be approximately 100 [15].

It can further be seen that the MA copolymers have a much higher $\bar{M}_N$ than the corresponding MMA copolymers prepared with similar reaction times, which is attributed to a higher reactivity of MA on the one hand and a greater degree of chain transfer in the case of MMA on the other.

Table 2
The photodecomposition of **1c** in the presence of TMPO[a]

Product	Amount of product in mmol	Corresponding amount (mmol) of		
		Benzoyl	Benzoylmethyl	TMPO
1c	0	0	0	
3	30.1		30.1	
TMPO	25.2			25.2
4	29.1	29.1		29.1

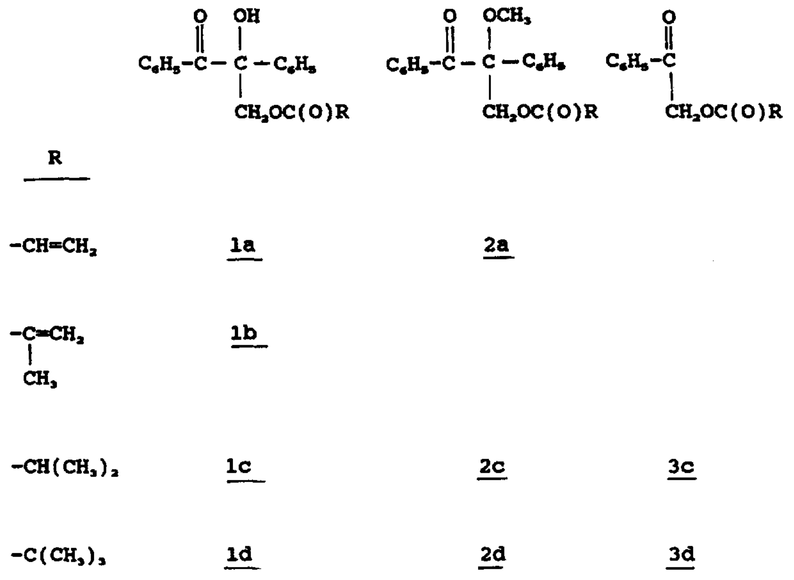
[a]The starting solution contained 30 mmol of **1c** and 60 mmol of TMPO. Irradiation time is 6 h.

Table 3
The photodecomposition of **1d** in the presence of TMPO[a]

Product	Amount of product in mmol	Corresponding amount (mmol) of		
		Benzoyl	Benzoylmethyl	TMPO
1d	0	0	0	
3d	30.3		30.3	
TMPO	30.0			30.0
4	29.7	29.7		29.7

[a]The starting solution contained 30 mmol of **1d** and 60 mmol of TMPO. Irradiation time is 6 h.

The determination of the photoinitiator group content of the various copolymers shows a clear difference between the two methods used, the UV-method consistently showing a 10–20% higher value. The UV-method is based on the assumption that the molar absorptivity of the photoreactive group equals that of its appropriate monomeric model compound (**1c**, **1d** and **2c**, respectively) and is dependent only on its total concentration. The results suggest that for the n-π^* transition the molar absorptivity per benzoin-derived unit increases on going from monomer to polymer, a phenomenon known as hyperchromism. Similar hyperchromic effects have been reported by Majumdar et al. [16] for copol-



Scheme 1.

ymers of MA with styrene, and by Angiolini et al. [17], with α-hydroxymethylbenzoin methyl ether acrylate, and by Stutzel et al. [18] for copolymers of MMA with styrene. Hyperchromism has been attributed to dipole–dipole interactions between neighbouring chromophoric groups. In addition the occurrence of hydrogen-bonding between the chromophoric carbonyl and hydroxyl groups may be a contributing factor. The absence of such hydrogen-bonding in the copolymers based on **2a** which has a methoxy group instead of a hydroxyl group as in **1a** and **1b**, could explain the much lower hyperchromicity observed for these copolymers.

The NMR-method is based simply on the integrals of specific signals and it is fully justified to consider these results the more reliable in calculating the photoinitiator group content.

The photodecomposition of the monomeric model compounds **1c** and **1d** in the presence of TMPO and DTE, respectively, indicate the occurrence of α-cleavage into benzoyl and α-hydroxy-α-acyloxymethylbenzyl radicals, confirming previous observations [14].

In the presence of TMPO the major reactions taking place are the coupling of the benzoyl radicals with TMPO to give 2,2,6,6-tetramethyl-1-piperidino benzoate **4**, and the redox reaction between the respective α,α-disubstituted benzyl radicals and TMPO to give the benzoylmethyl carboxylates **3c** and **3d** (cf. Tables 2 and 3).

In the presence of DTE the major reactions are the addition of the benzoyl radicals to DTE to give 3,3-di(p-tolyl)-propiophenone **7** and 2,2-di(p-tolyl)vinyl phenyl ketone **8**, and the disproportionation of the α,α-disubstituted benzyl radicals with other radicals to give the benzoylmethyl carboxylates **3c** and **3d**. Some unidentified (not isolated) products (**9** and **10**) are, by inference [5,14,19], assigned to 4,4-di(p-tolyl)butyrophenone and 3,3-di(p-tolyl)-2-propenyl phenyl ketone, respectively (cf. Tables 4 and 5).

A qualitative TLC analysis of the reaction mixtures resulting from the photodecomposition of some selected copolymers indicated the formation of **4** in the presence of TMPO and of **7** and **8** in the presence of DTE implying their potential as photoinitiators (cf. Schemes 1, 2 and 3).

Table 4
The photodecomposition of **1c** in the presence of DTE[a]

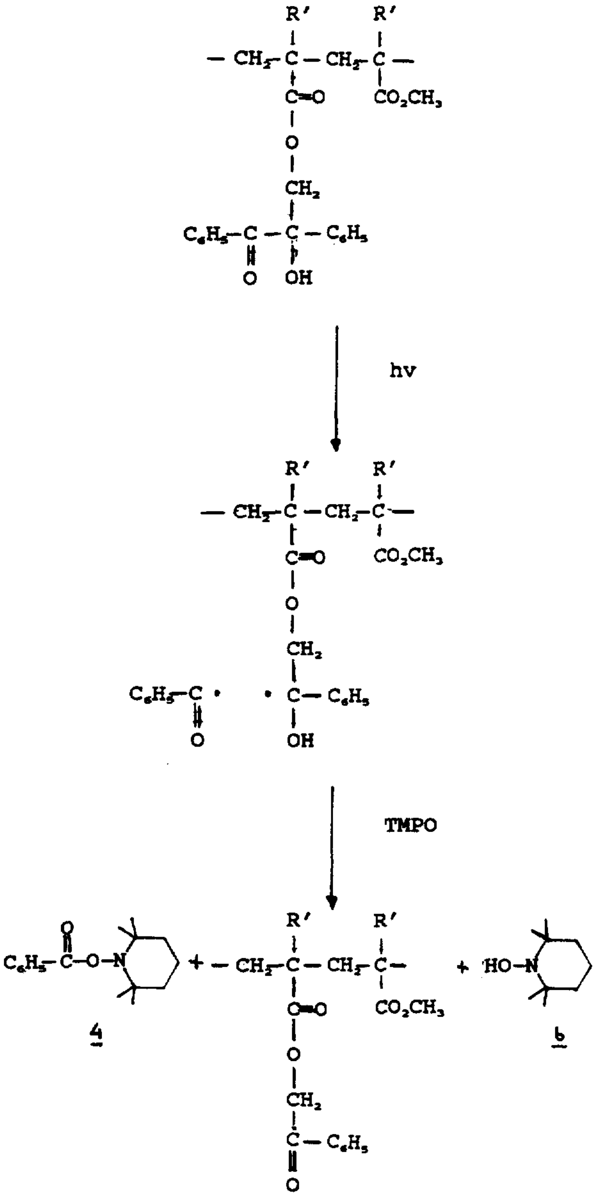
Product	Amount of product in mmol	Corresponding amount (mmol) of		
		Benzoyl	Benzoylmethyl	DTE
1c	12.0	12.0	12.0	
3c	6.0		6.0	
DTE	30.9			30.9
7	6.9	6.9		6.9
8	4.8	4.8		4.8
9/10	7.2		7.2	7.2

[a] The starting solution contained 30 mmol of **1c** and 60 mmol of DTE. Irradiation time is 6 h.

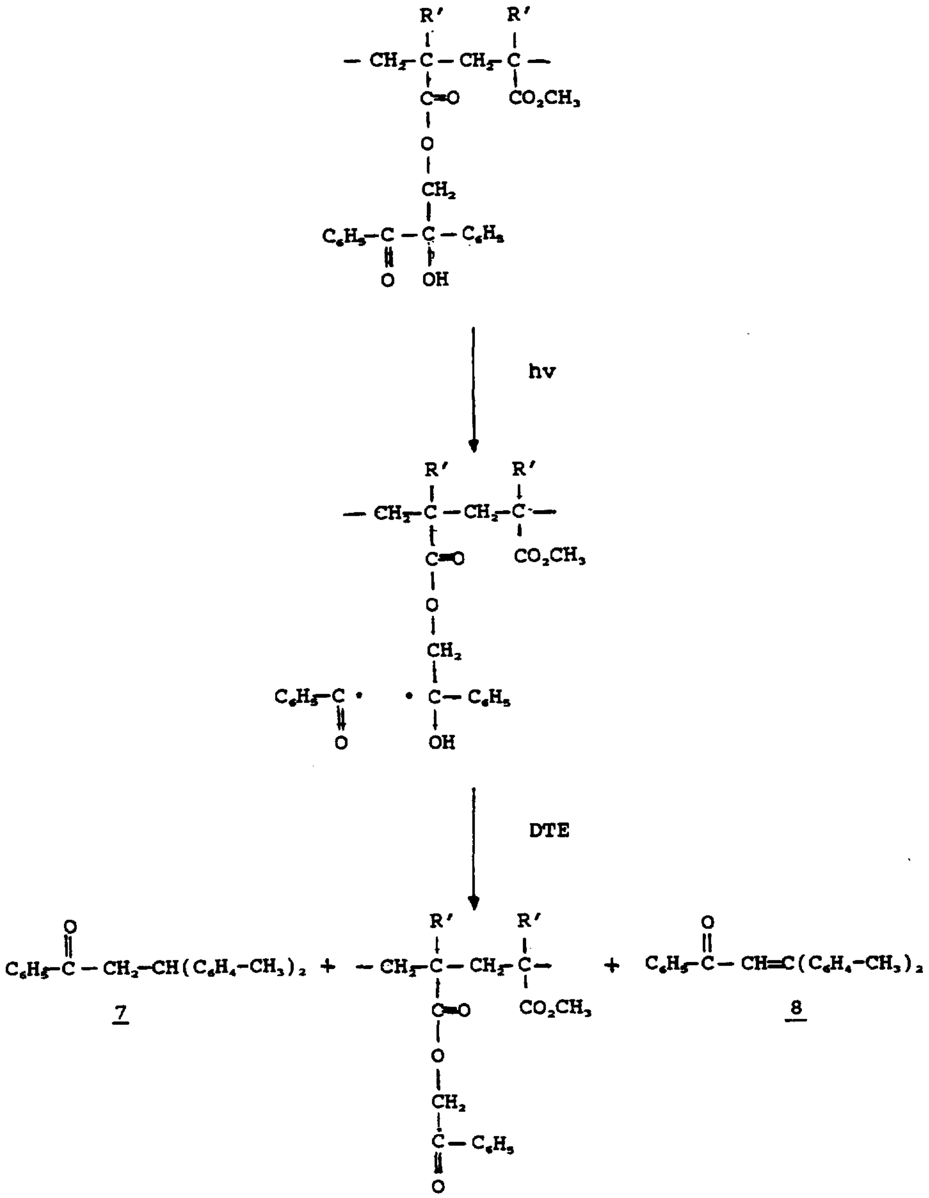
Table 5
The photodecomposition of **1d** in the presence of DTE[a]

Product	Amount of product in mmol	Corresponding amount (mmol) of		
		Benzoyl	Benzoylmethyl	DTE
1d	12.0	12.0	12.0	
3d	4.5		4.5	
DTE	31.5			31.5
7	6.3	6.3		6.3
8	4.8	4.8		4.8
9/10	6.3		6.3	6.3

[a] The starting solution contained 30 mmol of **1d** and 60 mmol of DTE. Irradiation time is 6 h.



Scheme 2.



Scheme 3.

Their application as photoinitiators for the polymerization of MMA in solution and for the UV-curing of some acrylate formulations will be the subject of a forthcoming paper [20].

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