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The application of some polymeric type-I photoinitiators based on α -hydroxymethylbenzoin and α -hydroxymethylbenzoin methyl ether

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Abstract

Some polymeric photoinitiators based on α -hydroxymethylbenzoin and its methyl ether are used to initiate the polymerization of methyl methacrylate in solution and the crosslinking of an epoxyacrylate formulation in thin films. In general the polymeric photoinitiators perform better than corresponding low molecular weight model compounds. Moreover, it is found that polymeric photoinitiators based on α -hydroxymethylbenzoin methyl ether perform better than those based on α -hydroxymethylbenzoin. Explanations for these observations are advanced. © 1998 Elsevier Science S.A. All rights reserved.

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

1. Introduction

In a previous communication [1] we reported on the synthesis and characterization of a number of copolymers of the acrylic and methacrylic esters of α -hydroxymethylbenzoin and its methyl ether with methyl acrylate and methyl methacrylate, respectively. Their potential as photoinitiators for radical polymerizations, i.e. the release of reactive benzoyl radicals from the polymer backbone on irradiation, was shown using radical trapping agents such as 2,2,6,6-tetramethylpiperidin-1-oxyl and 2,2-di(*p*-tolyl)ethylene.

In the present communication their performance as photoinitiators for the radical polymerization of methyl methacrylate in solution and the radical crosslinking (UV-curing) of an epoxyacrylate formulation in thin films is reported.

2. Experimental

2.1. Materials

The polymerizable photoinitiators, the polymeric photoinitiators, and the corresponding low molecular weight model compounds, collected in Scheme 1, have all been described in our previous communication [1].

N-methyldiethanolamine (NMDEA), trimethylolpropane triacrylate (TMPTA), methyl methacrylate (MMA), and tetraethyleneglycol diacrylate (TEGDA) were all obtained from Aldrich.

UVE 74, the epoxyacrylate of Setacure[®] AP-570 was obtained from Akzo Nobel Resins.

2.2. Irradiation procedures

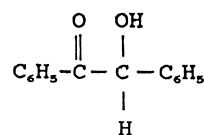
2.2.1. Photoinduced crosslinking of TMPTA in solution

Solutions of TMPTA (10 g l^{-1}) in 2-propanol containing the various photoinitiators ($10^{-2} \text{ mol l}^{-1}$) were irradiated in cuvettes (polystyrene, 4 ml; from Witeg) with a high pressure Hg-lamp (90 W; Ealing Optics No. 26-2865) at a distance of 10 cm. The crosslinking (insolubilization) of TMPTA was monitored by laser nephelometry as described by Decker and Fizez [2]. Induction periods (T_{ind}) were determined as irradiation time (in seconds) until the onset of crosslinking. Relative rates of crosslinking were determined from the slope of the curves ($\tan \alpha$) using a calibration curve obtained by plotting the amount of polymer formed (by gravimetry) versus time (in seconds), benzoin isopropyl ether (BIPE) being used as the standard [3].

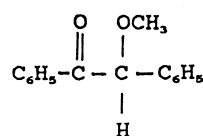
2.2.2. Photoinduced polymerization of MMA in solution

10^{-2} M solutions of low molecular weight and polymeric photoinitiators (i.e. photoreactive groups), respectively in a

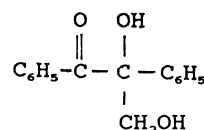
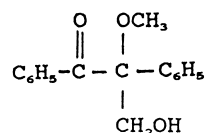
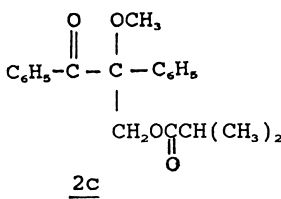
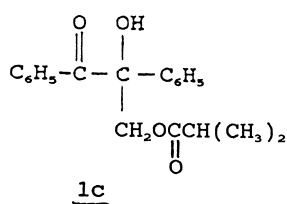
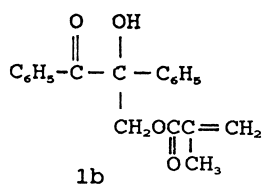
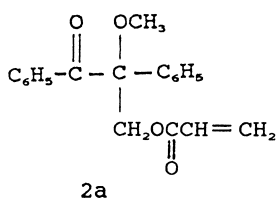
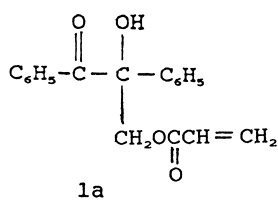
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benzoin (B)



benzoin methyl ether (BME)

 α -hydroxymethyl-B α -hydroxymethyl-BME

Scheme 1.

5 : 1 (v/v) benzene/MMA mixture were irradiated in stoppered Pyrex tubes (Rayonet Photoreactor RPR-208 fitted with 350 nm lamps) for 2 h. The irradiated solutions were then poured out into a five-fold volume of methanol with vigorous stirring. The precipitated poly (MMA) samples were isolated by filtration and dried overnight in a vacuum oven at 30°C.

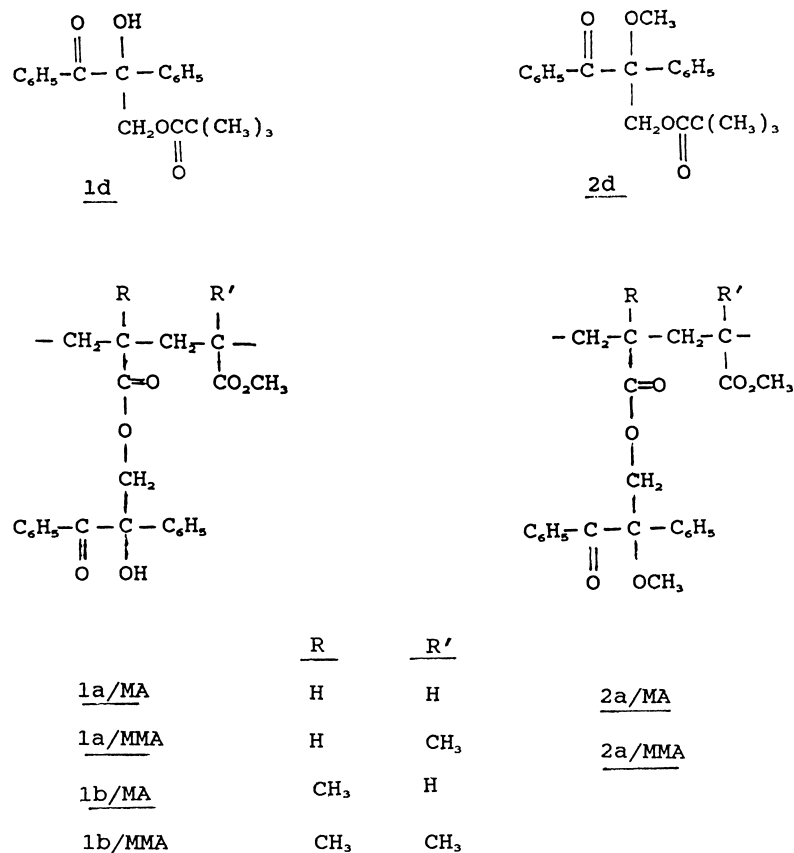
2.2.3. Photocuring of acrylate formulations in thin films

10^{-1} M solutions of low molecular weight and polymeric photoinitiators (i.e. photoreactive groups), respectively, either in TEGDA or in a UVE 74/TEGDA (26.6/

73.4 wt.%) mixture were used. In some cases NMDEA (6 : 1 molar ratio NMDEA/photoreactive group) was added as *t*-amine 'synergist'.

The solutions were coated onto strips of satinized paper or GNT paper (from Wiggins Teape). Films of uniform thickness were produced using Erichsen K-bars (6 and 50 μm films).

The coated paper was passed beneath the light source, either a high pressure Philips HOK-6 Hg-lamp (80 W cm^{-1}) or a medium pressure Hg-lamp (ColorDry, 80 W cm^{-1}). Films were considered as being cured when a finger-rub test ceased to leave a visible track.



Scheme 1. (Continued)

3. Results

3.1. Results from crosslinking of TMPTA

Benzoin (B) and a number of monomeric benzoin derivatives all induced the crosslinking of TMPTA in solution on irradiation (cf. Table 1). Benzoin methyl ether (BME) apparently shows a shorter induction period and higher rate of polymerization than B. α -Hydroxymethyl-BME and α -hydroxymethyl-B show a similar relationship. Esters 1c and 1d clearly show a higher rate of polymerization than α -hydroxymethyl-B. Testing the polymeric photoinitiators,

Table 1
Crosslinking of TMPTA in solution^a

Photoinitiator	$T_{\text{ind}}(\text{S})$	$\tan \alpha$	$10^{-3} R_p$ (mol l ⁻¹ s ⁻¹)
B	42.4	6.9	3.08
BME	28.4	9.2	4.10
BIPE	35.5	7.8	3.48
α -Hydroxymethyl-B	43.3	7.4	3.30
α -Hydroxymethyl-BME	25.4	8.0	3.57
<u>1c</u>	33.9	10.4	4.64
<u>1d</u>	40.5	10.7	4.77

^aBIPE, the calibrated standard applied [3].

unfortunately, was not possible due to their insolubility in 2-propanol.

3.2. Results from polymerization of MMA

All the monomeric and polymeric photoinitiators induced the polymerization of MMA on irradiation (cf. Table 2). In

Table 2
Polymerization of MMA in solution^a

Photoinitiator	Polymer yield g mmol ⁻¹ photoinitiator
Blank	0
BME	7.3
α -Hydroxymethyl-B	6.9
α -Hydroxymethyl-BME	7.0
<u>1a</u>	9.8
<u>1b</u>	7.3
<u>1c</u>	8.0
<u>1d</u>	7.7
<u>2c</u>	6.1
<u>1a/MA</u> (1 : 3; 120)	9.6
<u>1b/MA</u> (1 : 3; 70)	7.5
<u>1b/MMA</u> (1 : 3; 70)	9.0
<u>2a/MA</u> (2 : 1; 120)	17.2
<u>2a/MMA</u> (1 : 3; 120)	15.0

^a[Photoinitiator] = 10⁻²; irradiation time 2 h; light source; RPR 208.

Table 3
Curing of acrylate formulation in thin films^a

Photoinitiator ^b	Irradiation time (s)
Blank	No curing
BME	18.0
α -Hydroxymethyl-B	18.0
α -Hydroxymethyl-BME	14.4
<u>1a</u>	21.6
<u>1b</u>	27.6
<u>1c</u>	22.8
<u>1d</u>	25.2
<u>2a</u>	10.8
<u>2c</u>	13.2
<u>1a</u> /MA (1 : 3; 120)	9.6
<u>1b</u> /MA (1 : 3; 70)	n.d.
<u>1b</u> /MMA (1 : 3; 70)	12.0
<u>2a</u> /MA (2 : 1; 120)	4.8
<u>2a</u> /MMA (1 : 3; 120)	n.d.

^aUVE 74/TEGDA; absence of *t*-amine; film thickness 50 μ m; light source: Philips HOK-6.

^b10⁻¹ M photoreactive groups.

general the results tabulated demonstrate that the polymeric photoinitiators show a greater initiating efficiency in the polymerization of MMA than both the corresponding monomeric parent compounds and low molecular weight model compounds. This observation is in agreement with the results reported by Ahn et al. [4] and others [5–8], respectively with photosensitive polymers carrying BME side-chains.

3.3. Results from curing of acrylate formulations

All the photoinitiators induced the crosslinking of the acrylate formulations on irradiation (cf. Table 3). A marked difference is seen between the initiating efficiencies of the polymeric photoinitiators and their low molecular weight model compounds. For each type of polymeric photoinitiator the irradiation time required to affect complete surface cure was less than half that for the corresponding model compounds, confirming the results of the solutions' polymerization experiments. The (meth) acrylate monomeric parent compounds also show a greater initiating efficiency than the corresponding model compounds.

In some selected cases the influence of the photoinitiator concentrations was also investigated (cf. Table 4). The results clearly show an increase in curing rate with increasing photoinitiator concentration up to an optimum concentration. Increasing the concentration beyond this value apparently leads to no further increase in the curing rate, only surface cure being considered.

4. Discussion

In general it is found that both in the polymerization of MMA in solution and in the curing of acrylate formulations

Table 4
Curing of TEGDA in thin films^a

Influence of photoinitiator concentration			
Photoinitiator concentration (M)	Irradiation time (s)		
	<u>1a</u> /MA (-CTA)	<u>1a</u> /MA (+CTA)	<u>1c</u>
0.10	9.0	9.0	17.9
0.15	n.d.	5.6	12.3
0.20	n.d.	5.6	6.7
0.25	n.d.	5.6	6.7
0.30	n.d.	5.6	6.7

^aTEGDA + *t*-amine; film thickness 6 μ m; light source: medium pressure Hg-lamp (ColorDry).

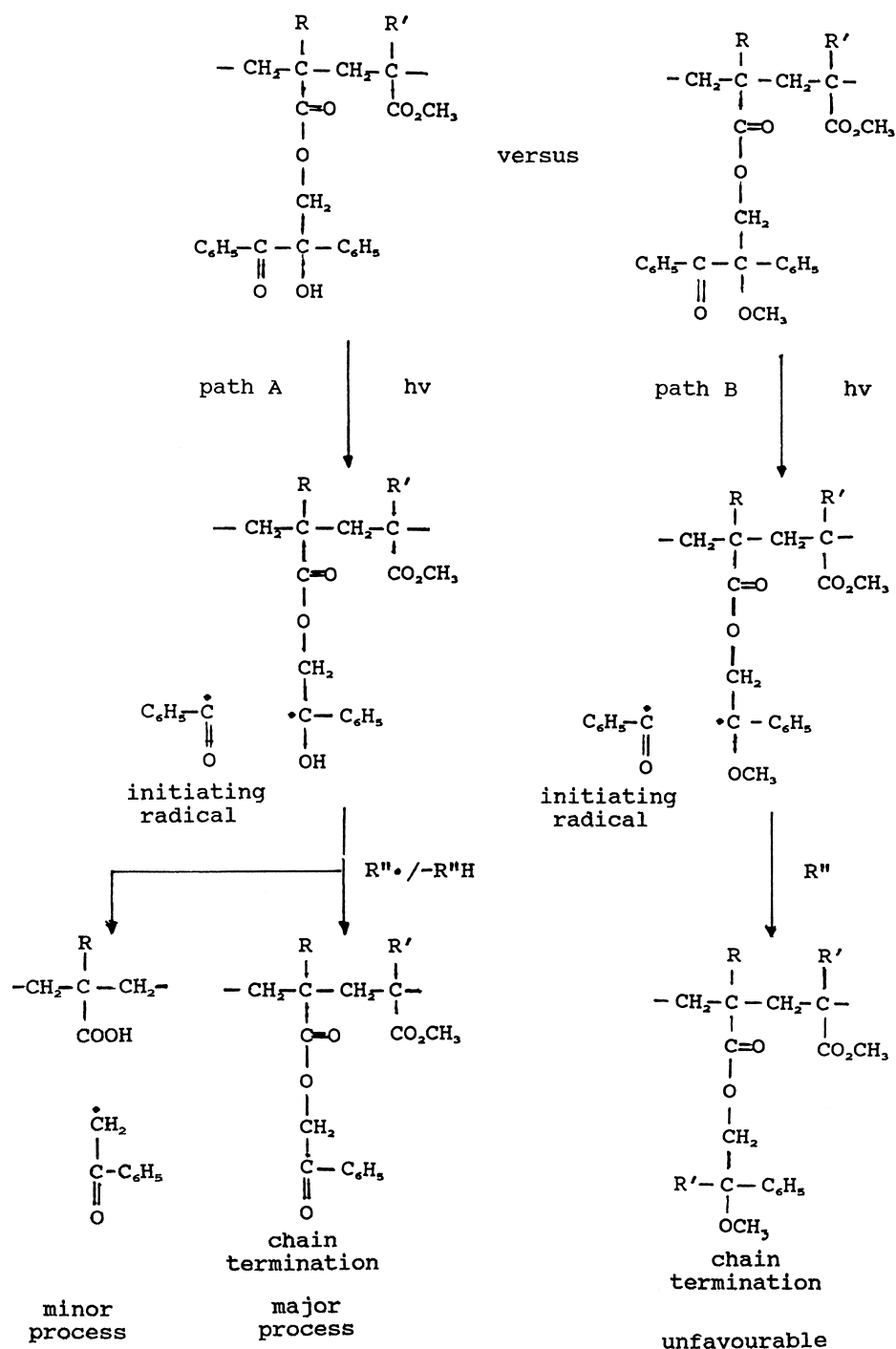
in thin film the polymeric photoinitiators perform better than their corresponding low molecular weight model compounds. Moreover, it is found that the polymeric photoinitiators based on α -hydroxymethyl-BME perform better than the corresponding copolymers based on α -hydroxymethyl-B, e.g. 2a/MA > 1a/MA, 2a/MA > 1b/MA, and 2a/MMA > 1b/MMA (cf. Tables 2 and 3).

The first observation can possibly be explained by an increased absorption by the polymeric photoinitiators, i.e. hyperchromism as was discussed previously [1]. On account of their hyperchromic absorption one might expect the polymeric photoinitiators to make a better use of the light emitted by the light source and as a consequence display higher initiating efficiency.

To explain the second observation, however, we have to look into the course of the photochemical events in more detail (cf. Scheme 2). In both cases absorption would lead through a singlet excited manifold to the lowest short-lived triplet excited state following efficient intersystem crossing [8,9]. Subsequently, in both paths A and B an extremely rapid α -cleavage ($k_{\alpha} > 10^9 \text{ S}^{-1}$) takes place to release the highly reactive benzoyl radical from the polymer backbone. We expect k_{α} (path B), to be higher than k_{α} (path A), since benzoin methyl ether (BME) shows a considerably shorter T_{ind} than benzoin, and similarly, α -hydroxymethyl-BME shows a shorter T_{ind} than α -hydroxymethyl-B in the crosslinking of TMPTA, in which T_{ind} is considered to represent the rate of radical formation (cf. Table 1).

In addition, the behaviour of the radicals remaining attached onto the polymer backbone may also be expected to be partly responsible for the differences in initiating efficiency actually observed.

From previous work using ESR, CIDNP, and radical-trapping techniques [9,10], the α -acyloxymethylketyl radicals formed in path A are known to undergo further reactions, such as releasing the benzoylmethyl radical ('elimination of acid'), which in the case of relatively weak carboxylic acids is a minor process [9], and hydrogen-transfer ('cross-disproportionation') to any radicals present to give the polymer-bound benzoylmethyl carboxylate, which is the major process. Both 'in-cage' benzoyl radicals



Scheme 2.

and propagation radicals may be among the radicals involved in these disproportionation reactions, obviously resulting in a decreased initiating potential, and chain termination, respectively.

From previous work on BME [11,12] it is known that α -alkoxybenzyl radicals act predominantly, if not entirely, as terminating radicals through radical recombination reactions, except in the case of strong acids being attached in the β -position of the benzyl radical as in α -alkoxy- α -sulpho-

nyloxymethyl-benzyl radicals [13], which still generate benzoylmethyl radicals through the elimination of sulphonic acid. α -Alkoxy- α -acyloxymethylbenzyl radicals formed in path B, however, carboxylic acids being relatively weak acids, will behave more like that α -alkoxybenzyl radicals, i.e. as terminating radicals. The terminating radical recombination reactions of these α -alkoxy- α -acyloxymethylbenzyl radicals which are still attached onto the polymer backbone (path B), are likely to be suppressed by their

restricted mobility on the one hand and possibly by steric hindrance (coiling of the polymer backbone on the other).

It may therefore be concluded that the most efficient polymeric photoinitiators with pendent type-I moieties, which undergo α -cleavage into two radicals of different reactivity, will in general be those with the less reactive radical remaining attached onto the polymer backbone.

Acknowledgements

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