Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 45 (2004) 1119–1123
polymer
www.elsevier.com/locate/polymer

Initiation of 1,6-hexanedioldiacrylate polymerization by three component photoinitiators incorporating 2,3-dimethylmaleic anhydride

T. Brian Cavitt[a], Charles E. Hoyle[a,*], Viswanathan Kalyanaraman[a], Sonny Jönsson[b]

[a]School of Polymers and High Performance Materials, University of Southern Mississippi, Box 10076, Hattiesburg, MS 394060076, USA
[b]Fusion UV Systems, Gaithersburg, MD, USA

Received 17 July 2003; received in revised form 1 December 2003; accepted 9 December 2003

Abstract

Three component photoinitiators mixtures comprised of benzophenone (BP), 4-benzoylbiphenyl (BBP), or isopropylthioxanthone (ITX) with a tertiary amine and an electron deficient anhydride *ene* result in rapid photoinitiation rates of acrylate polymerization. Concentrations of less than 0.1 weight percent 2,3-dimethylmaleic anhydride (DMMA) added to 1,6-hexanedioldiacrylate (HDDA) containing any of the aforementioned diarylketones and *N*-methyl-*N*,*N*-diethanolamine (MDEA) results in an increase in the polymerization rate maximum by a factor of as much as three times that attained for samples with only MDEA and BP, BBP, or ITX. Laser flash photolysis results confirm that BP, BBP, and ITX are readily quenched by MDEA and DMMA. An initiation mechanism is proposed.

Keywords: Three component photoinitiators; Laser flash photolysis; Acrylate polymerization

1. Introduction

Since the initial beginnings of the radiation curing industry, a large number of photoinitiating systems have been proposed and evaluated [1–4]. To date all photoinitiators for free-radical polymerization proceed by either a cleavage process or a hydrogen transfer process. The hydrogen transfer can occur by either of two mechanisms. The first involves a simple hydrogen abstraction by a triplet excited state species, while the second involves an electron transfer followed by a proton transfer. The electron transfer/proton transfer process is effectively a hydrogen atom transfer, although no single hydrogen atom is transferred as in the case of simple hydrogen abstraction. In all of the successful electron/proton transfer type photoinitiating systems used commercially, the excited state triplet species is a diarylketone, such as benzophenone or a substituted thioxanthone, and the hydrogen source is a tertiary amine. Unfortunately, only the radical on the amine is capable of initiating polymerization since the diarylketyl radical is very stable and only reacts with polymer radicals or other small molecule radicals in a termination process. Hence, compared to cleavage type photointiators, which produce two radicals that initiate polymerization, the hydrogen transfer photoinitating systems are relatively inefficient.

Since diarylketones are inexpensive, it would be desireable to incorporate them into a multicomponent system which would produce two radicals capable of initiating polymerization upon excitation of the diarylketone. Three component dye/tertiary amine/onium salt initiating systems have been reported [4]. We have reported that addition of an N-substituted maleimide *ene* to a system comprised of a diarylketone [(BP, ITX, or benzoylbiphenyl (BBP)] and a tertiary amine results in a markedly increased overall rate of polymerization compared to the diarylketone/amine system alone [5–11]. In these three component systems, the diarylketyl radical, which is produced by the hydrogen transfer from the amine to the excited triplet diarylketone, is oxidized by the electron deficient N-substituted maleimide to give the ground state diarylketone and the corresponding succinimidyl radical. The three component system thus produces two radicals, an alpha amino radical and the succinimidyl radical, both of which initiate free-radical polymerization. This of course is much better than the two component diarylketone/amine photoinitiators which generate an initiating radical and a terminating radical. These

---

[*] Corresponding author. Tel.: +1-601-266-4868; fax: +1-601-266-5504.
E-mail address: charles.hoyle@usm.edu (C.E. Hoyle).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.12.021

three component systems rival the photoinitiation efficiency of commercial cleavage photoinitiators.

Based on the success of the diarylketone/maleimide/amine three component photoinitiator systems, other similar *ene* compounds that should function in a similar manner to maleimides were evaluated. Herein, maleic anhydride (MA), 2-methylmaleic anhydride (CCA—citraconic anhydride) and 2,3-dimethylmaleic anhydride (DMMA) were examined for their ability to serve as coinitiators for 1,6-hexanedioldiacrylate (HDDA) polymerization in the presence of a diarylketone and the tertiary amine methyldiethanolamine (MDEA). The results indicate that indeed this electron poor *ene* can also function in the same capacity as N-substituted maleimides.

2. Experimental

2.1. Materials

BP, BBP, MDEA, MA, CCA, and DMMA were obtained from the Aldrich Chemical Company. UCB provided 1,6-hexanedioldiacrylate (HDDA). ITX was donated by the Albemarle Corporation.

2.2. Photo-differential scanning calorimetry

Exotherms were measured on a Perkin–Elmer Differential Scanning Calorimeter 7 modified with quartz plates to allow the light from a Canrad–Hanovia medium pressure mercury lamp source obtained from Ace Glass to impinge upon the reference pan and the sample pan containing the photopolymerizable samples. Light intensities were measured at the sample pans with a black body absorber. A mechanical shutter was placed between the light source and the sample chamber to provide control of exposure time. Open sample pans without tops were crimped and injected with 2 μl samples, giving a film thickness on the order of 200 μm (about 8 mils). All samples were purged with nitrogen for 2.5 min prior to light exposure. Exotherms were converted from milli Watt to fraction of monomer converted per second (given as s^{-1}): this is the polymerization rate R_p. It is noted that R_p values in the case of HDDA polymerization greater than about 0.105 s^{-1} are essentially 'off scale' and thus represent *minimum values* for the polymerization rates.

2.3. UV–vis spectroscopy

The extinction coefficients of the triplet cosynergists were determined using a Varian Cary 500 Scan UV–vis–NIR spectrophotometer.

2.4. Laser flash photolysis

Laser flash photolysis lifetime quenching data were obtained by using a system based upon a Continuum Nd-YAG laser as the excitation source at 355 nm and a pulsed xenon probe and data acquisition/analysis system from applied photophysics. The ultimate time resolution of the laser flash instrument is approximately 15–20 ns. Samples were prepared in acetonitrile to have optical absorbances of ~1.0 at 355 nm.

2.5. Phosphorescence

The phosophorescence spectrum of ITX was measured on a Spex Fluorolog fluorescence spectrometer. The triplet energy was determined from the position of the high energy vibrational band.

3. Results and discussion

Photo-differential scanning calorimetry (Photo-DSC) is a convenient method for measuring the rate of polymerization as a function of exposure time to a light source, a medium pressure mercury lamp in the present case. The results are displayed in plots of time on the *x*-axis and polymerization rate (R_p in terms of fraction converted per second, displayed in units of s^{-1}) on the *y*-axis. The *peak* of the rate vs time plots in terms of s^{-1} is defined as *the maximum polymerization rate*. In the ensuing sections, the photo-DSC derived acrylate polymerization rates using three component diarylketone/electron poor *ene*/tertiary amine photoinitiators were compared to the rates obtained using two component diarylketone/tertiary amine photoinitiators. The diarylketones were BP, BBP, and ITX, the electron poor *ene* was DMMA, and the tertiary amine was MDEA.

3.1. N-Methyl-N,N-diethanolamine as a hydrogen source

Initially, three anhydrides, MA, CCA and DMMA were considered for use in the three component photoinitiator systems. Unfortunately, when even very low concentrations of MA were added to a mixture of HDDA, BP, and MDEA the mixture immediately became cloudy. When MA was mixed with HDDA and BP in the absence of MDEA, the solution was transparent for several days. Apparently either an insoluble product between MA and MDEA is produced, or a stable charge transfer complex which precipitates in HDDA is formed. The use of MA as a component in a three component photoinitiator for HDDA was not pursued further. Next, a simple methyl derivative of maleic anhydride, CCA, was considered. Samples containing low concentrations (e.g. 0.05 wt%) of CCA and 1 wt% MDEA in HDDA also became cloudy after mixing. This preempted their use in the three component systems. Fortunately, mixtures of up to 0.05 wt% DMMA, a dimethyl derivative of MA, and 1 wt% MDEA in HDDA were fully transparent and remained so for several days. Therefore,

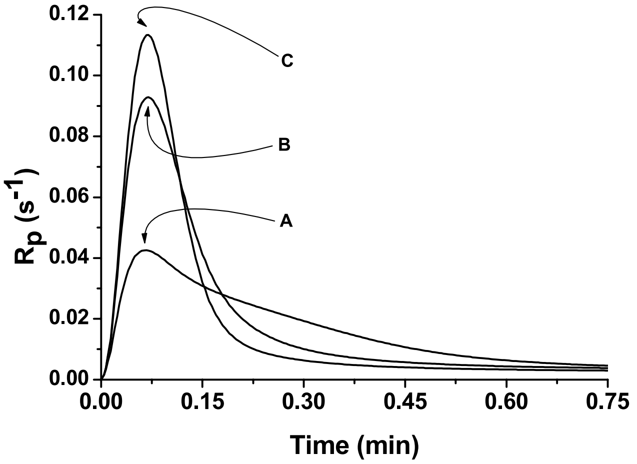

Fig. 1. (A) 1% BP by weight, 1% MDEA by weight, HDDA; (B) 0.01% DMMA by weight, 1% BP by weight, 1% MDEA by weight, HDDA; (C) 0.05% DMMA by weight, 1% BP by weight, 1% MDEA by weight, HDDA. Output of unfiltered medium pressure mercury lamp was 68.8–69.5 mW/cm^2; nitrogen purge of 2.5 min; 2 μl sample.

three component photoinitiators involving DMMA were evaluated.

DMMA was added to a sample of BP and MDEA in HDDA. The photo-DSC exotherm rates in Fig. 1 clearly show that addition of only 0.05 wt% DMMA to a sample of BP (1.0 wt%) and MDEA (1.0 wt%) results in a significant increase in the maximum polymerization rate of HDDA compared to a sample with only BP and MDEA. In order to determine if a lower concentration of DMMA can be used, another photo-DSC exotherm was recorded for a sample with only 0.01 wt% DMMA. It is apparent from Fig. 1 that a sample with even 0.01 wt% DMMA is effective in generating a faster polymerization that with only BA and MDEA present.

The propensity of DMMA to initiate acrylate polymerization in the presence of MDEA and either ITX or BBP was investigated next. Rate results in Fig. 2 clearly show that the addition of 0.05 wt% DMMA increases the overall rate of polymerization of HDDA significantly compared to an ITX/MDEA photoinitiator. Likewise, the mixture containing optimized concentrations of DMMA and BBP in the presence of MDEA results in a greater rate of HDDA polymerization than that of the BBP/MDEA initiator system (Fig. 3).

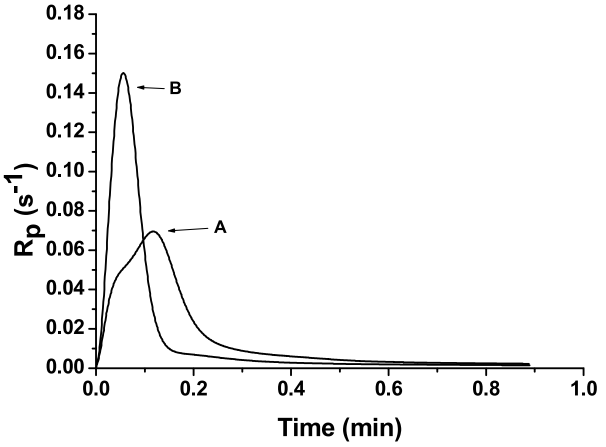

Fig. 2. (A) 0.028%ITX by weight, 1%MDEA by weight, HDDA; (B) 0.05%DMMA by weight, 0.028%ITX by weight, 1%MDEA by weight, HDDA. 73.89 mW/cm^2 output of unfiltered medium pressure mercury lamp; nitrogen purge of 2.5 min; 2 μl sample.

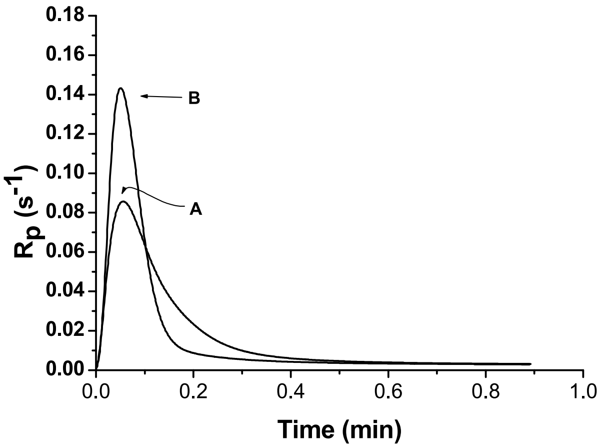

Fig. 3. (A) 0.69%BBP by weight, 1%MDEA by weight, HDDA; (B) 0.05%DMMA by weight, 0.69%BBP by weight, 1%MDEA by weight, HDDA. 73.89 mW/cm^2 output of unfiltered medium pressure mercury lamp; nitrogen purge of 2.5 min; 2 μl sample.

3.2. Laser flash photolysis

In order to delineate how efficiently BP, ITX, and BBP interacts with both MDEA and DMMA, a laser flash photolysis investigation of the quenching of the transient triplet state of each diarylketone was conducted. Quenching was analyzed according to the Stern–Volmer equation (Eq. (1)), which relates the triplet lifetime of a chromophore to the concentration of a quencher molecule

$$\tau_o/\tau = 1 + \tau_o k_q[Q] \quad (1)$$

where τ_o is the triplet lifetime of the chromophore in the absence of a quencher, τ is the triplet lifetime of the chromophore in the presence of a certain concentration of the quencher, $[Q]$, and k_q is the quenching rate constant. The Stern–Volmer plot for quenching of the BP triplet state by DMMA in acetonitrile is given in Fig. 4. The quenching rate constants for the triplet transient of BP, ITX, and BBP by DMMA in acetonitrile determined from the slopes of Stern–Volmer plots similar to that in Fig. 4 are listed in Table 1. From the results in Table 1, it is obvious that for each diarylketone triplet quenching constants by MDEA and DMMA are of the same order of magnitude. For BP and ITX the quenching rate constants are very high, indicating that quenching of BP and ITX by both species is very efficient. Before posing a mechanism for initiation of polymerization one final laser flash photolysis result was obtained. Analysis of the quenching of the benzophenone derived semipinacol radical ($k_q = 2.57 \times 10^6\ M^{-1}\ s^{-1}$)

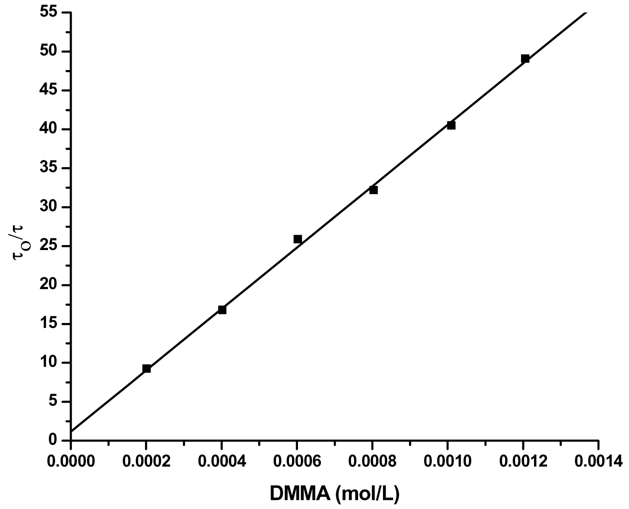

Fig. 4. Stern–Volmer plot for lifetime quenching of BP (0.0005 M) by DMMA in acetonitrile.

indicates that it is quenched by DMMA (although very inefficiently), probably by a relatively slow electron/proton transfer to produce BP and the 2,3-dimethylmaleic radical. (It is noted that the presence of the semipinacol radical in the laser flash analysis was determined temporally by the difference in triplet lifetimes of 67 ns for BP and 21 μs for the semipinacol radical under the conditions employed.)

4. Proposed initiation mechanism

In the three component system consisting of a diarylketone, MDEA, and DMMA, two quenching processes are possible as indicated by the results in Table 1. Based upon the quenching constants in Table 1 and the actual concentrations of MDEA and DMMA used in the three component photo-DSC experiments, estimates of the relative quenching rates of BP, ITX and BBP triplet states by DMMA and MDEA were calculated. Assuming that the ratios would be the same in HDDA and acetonitrile, results are tabulated in Table 2 for the ratio of the quenching rate of the process under consideration to that of the respective quenching rate of the diarylketone by MDEA. A careful perusal of the results in Table 2 shows that MDEA quenches excited state diarylketones by up to eleven times faster than quenching by DMMA. Based upon these results, and by analogy with the published mechanism for the three component photoinitiators involving maleimides, a scheme for generating radical initiators in the three component system under investigation in this paper is proposed in Fig. 5, where ITX is used to illustrate the mechanism. According to this mechanism, after ITX is quenched by MDEA via an electron/proton transfer, the ketyl radical subsequently formed is oxidized by an electron transfer to DMMA followed by proton transfer. In this two step process, ITX is reformed in the ground state, and a 2,3-dimethylmaleic radical capable of initiating polymerization is generated. As in the case of N-substituted maleimides, two radicals, an alpha amino radical and the 2,3-dimethylmaleic radical, both of which initiate polymerization, are formed. Thus, the diarylketyl terminating radical is replaced by an initiating radical resulting in a substantial increase in initiation rate.

Table 1
Quenching rate constants for several diarylketones in acetonitrile

Transient	Quencher	k_q (× 10^9 l/mol/s)
BP	MDEA	1.1
BP	DMMA	6.35
ITX	MDEA	1.8
ITX	DMMA	3.47
BBP	MDEA	0.16
BBP	DMMA	0.391

Table 2
Relative rates of quenching where MDEA is assumed to completely quench the diaryl ketone, and the quenching efficiency of DMMA is shown compared to that of MDEA

Cosynergist	Quencher	Relative quenching rates
BP	MDEA	1
BP	DMMA	0.27
ITX	MDEA	1
ITX	DMMA	0.091
BBP	MDEA	1
BBP	DMMA	0.12

Finally, we comment on a minor process shown in the mechanistic scheme depicted in Fig. 5: quenching of the ITX (or BP) triplet state excited by DMMA. Recall from Table 1 that both ITX and BP are quenched effectively by DMMA. The triplet energy of DMMA has been reported [12] by Steinmetz to be 61–63 kcal/mol. The magnitude of the rate constants for quenching BP and ITX by DMMA (> 10^9 l/mol/s) are certainly consistent with BP and ITX, which have triplet entries as listed in Table 3, acting as efficient triplet sensitizers for DMMA. While we have not confirmed conclusively that the quenching mechanism involves energy transfer, and keeping in mind that it is possible that other quenching possibilities are possible, it certainly seems reasonable that it does. Interestingly, the lower quenching rate for BBP by DMMA is consistent with the reported triplet energy of DMMA being around 61–63 kcal/mol, which is very close to the triplet energy of BBP

Table 3
Triplet energies of several diarylketones

Diarylketone	Triplet energy (kcal/mol)
BP	69[a]
ITX	64[b]
BBP	61[a]

[a] See Ref. [13].

[b] Determined in our lab via phosphorescence at 77 K in a 1:1 ethanol/methylene chloride glass.

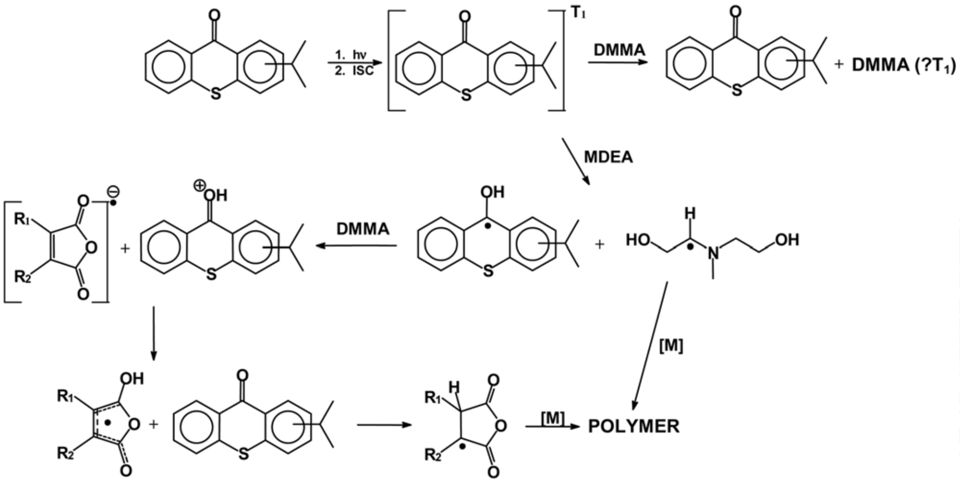

Fig. 5. Proposed initiation mechanism for DMMA/diarylketone/MDEA systems: ITX is shown as the representative diarylketone.

(Table 3). Notwithstanding this evidence, since at this time we do not have absolute proof of the triplet state of DMMA being formed by an energy transfer, we denote formation of the DMMA triplet state with a question mark. If indeed the triplet state of DMMA is formed, it might be expected energetically that it would interact with MDEA and participate in an electron/proton transfer to give a 2,3-dimethylmaleic radical and a alpha amino radical. However, if this process occurs, it only makes a minor contribution to initiating polymerization since from Table 2 one can project that ~92% of the ITX excited triplet states are quenched by MDEA via an electron/proton transfer process.

5. Conclusions

The addition of an electron poor anhydride *ene* to an acrylate monomer in the presence of three selected diarylketones and a tertiary amine was found to enhance the rate of acrylate polymerization significantly. Laser flash photolysis data confirmed that all of the diarylketones, BP, ITX, and BBP, are quenched by both the tertiary amine and DMMA: the rate constants were greater for ITX and BP than BBP. For the concentrations employed in this investigation, a mechanism involving an electron/proton transfer process from a carbon centered diarylketyl radical to the anhydride was proposed to account for the generation of a new radical initiating species.

Acknowledgements

The support of Albemarle Company and Fusion UV Systems is gratefully acknowledged.

References

[1] Oldring PKT, editor. Chemistry and technology of UV and EB formulation for coatings, inks, and paints, vol. I–V. London: SITA Technology; 1994.
[2] Roffey CG. Photopolymerization of surface coatings. New York: Wiley; 1982.
[3] Fouassier JP, Rabek JF, editors. Radiation curing in polymer science and technology, vol. I–V. London: Elsevier; 1993.
[4] Fouassier JP, editor. Photoinitiator, photopolymerization and photocuring: fundamentals and applications. New York: Hanser; 1995.
[5] Hoyle CE, Clark SC, Jönsson S, Shimose M. Polymer 1997;38:5695.
[6] Clark SC, Jönsson S, Hoyle CE. PMSE Polym Preprints 1996;(2):348.
[7] Clark SC, Hoyle CE, Jönsson S, Morel F, Decker C. RadTech '98 North Am Conf Proc 1988;177:1998.
[8] Kohli; P, Scranton AB, Blanchard GJ. Macromolecules 1998;31:5681.
[9] Viswanathan K, Clark SC, Miller C, Hoyle CE, Jönsson S, Shao LL. Polym Prepr 1998;39(2):644.
[10] Hoyle CE, Viswanathan K, Clark SC, Miller C, Nguyen C, Jönsson S, Shao LL. Macromolecules 1999;32:2793.
[11] Bowers J, Nagarajan R, Cui H, Miller C, Shao L, Hoyle CE, Jönsson S. RadTech '98 North Am Conf Proc 1998;182.
[12] Steinmetz R. Fortschr Chem Forsch 1967;445.
[13] Murov SL, Carmichael I, Hug GL. Handbook of photochemistry. New York: Marcel Dekker; 1993.