

Volume 38, Number 18 September 6, 2005

© Copyright 2005 by the American Chemical Society

Communications to the Editor

Synthesis, Initiation, and Polymerization of Photoinitiating Monomers

Tai Yeon Lee,[†] C. Allan Guymon,[‡] E. Sonny Jonsson,[§] Sukhendu Hait,[†] and Charles E. Hoyle^{*,†}

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi; Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa; and Fusion UV Curing Systems, Gaithersburg, Maryland

Received April 21, 2005 Revised Manuscript Received June 22, 2005

Developing novel and improved photoinitiation systems is one of the most exciting challenges in photopolymerization research. Herein, we describe the synthesis, photoinitiation, and copolymerization of a series of new monomers that efficiently photoinitiate free-radical polymerization. Photoinitiators are essential in freeradical photopolymerization, but unfortunately, only a small fraction of the photoinitiator is actually consumed during reaction. After polymerization the residual photoinitiator will continue to react with light and form photobyproducts which lead to vellowing and polymer degradation during use, thereby reducing long-term stability.¹ Many of the problems associated with traditional photoinitiators would, of course, be eliminated if appropriate initiators could be developed that act as both initiator and monomer. Producing a system without residual photoinitiator would improve the long-term stability of photopolymerized films and enhance their viability in many applications.

A number of monomer systems have been examined as possible photoinduced initiating monomers. Maleimides, for example, can self-initiate free radical photopo-

[§] University of Iowa.

* To whom correspondence is to be addressed: e-mail Charles.Hoyle@usm.edu; Ph 601-266-4873; Fax 601-266-5504.



Figure 1. Chemical structure of (1) vinyl acrylate, (2) monovinyl fumarate, (3) divinyl fumarate, and (4) divinyl maleate.

lymerization in the presence of hydrogen donors;² however, the high cost of maleimides and their low initiation efficiency limit their use as initiating monomers. Recently, vinyl acrylate (1) has been reported to self-initiate free-radical photopolymerization and produce a highly cross-linked network.³⁻⁵ Vinyl acrylate can self-initiate free-radical polymerization due to the existence of both acrylate and vinyl groups in the same molecule, which allows for significantly red-shifted UV absorption and a particularly low electron density on the acrylate double bond.⁸ In addition to being a viable photoinitiator, vinyl acrylate also exhibits very interesting homo- and copolymerization behavior.^{4,6} Despite its attractive attributes, vinyl acrylate is highly volatile at room temperature and has a relatively low extinction coefficient at typical photoinitiation wavelengths, thereby limiting its use as a polymerizable photoinitiator.

While vinyl acrylate (see Figure 1 for structure), in and of itself, is not viable as a practical initiating monomer, it represents an intriguing platform upon which other, perhaps even more efficient, initiating monomers can be based. It is reasonable to expect that analogues of vinyl acrylate with a more extensive conjugated structure and higher molecular weight would exhibit greater UV absorbance than vinyl acrylate at wavelengths between 300 and 400 nm and have a lower room temperature vapor pressure than vinyl acrylate. On the basis of this premise, three monomers with structures closely related to vinyl acrylate, i.e., monoethyl ester vinyl fumarate (2), divinyl fumarate (3), and divinyl maleate (4) (see Figure 1 for structures), have

[†] University of Southern Mississippi.

[‡] Fusion UV-Curing Systems.

Table 1. Molar Extinction Coefficients of Initiating Monomers (L/(mol cm))

	1	2	3	4
254 nm	1262	3529	6813	7913
313 nm		83	379	448

been synthesized and examined as photoinitiators and comonomers. (see Supporting Information for detailed synthesis and characterization). We previously reported that **1** exhibits a red-shifted UV absorption spectra with an absorption tail approaching 300 nm while monofunctional analogues of 1 show UV absorption peaks below 230 nm.⁴ The acrylate group appears to be the core chromophore while the vinyl group contributes to a bathochromic (red-shifted) UV absorption. As anticipated on the basis of the chemical structure, 2, 3, and 4 also exhibited red-shifted UV absorption compared to the monofunctional analogues, diethyl fumarate and diethyl maleate. In particular, the species with two vinyl substituents (3 and 4) are characterized by strong UV absorption at wavelengths longer than 300 nm, a critical property for efficient photoinitiators. Quantitative information regarding the promising aspects of the UV absorption of these monomers can be provided by the molar extinction coefficients (ϵ) of 1-4 at 254 and 313 nm (two wavelengths emitted by mercury lamp sources) as shown in Table 1. Compounds 2-4 exhibit high ϵ values at 254 nm, comparable to ϵ values of conventional photoinitiators, which range from approximately 5×10^3 to 1.6×10^4 L/(mol cm) at 254 nm.¹ As shown in Table 1, ϵ values of compounds 3 and 4 are certainly in this range, while compound 2 absorbs significantly less light at this wavelength. All of the synthesized monomers, **2**–**4**, have much larger ϵ values at 254 nm than **1**, for which ϵ is approximately 1×10^3 L/(mol cm). Interestingly, 3 and 4 have molar extinction coefficients approximately 2 times greater than that of 2 at 254 nm due to the presence of two vinyl substituents. Moreover, their absorption extends to wavelengths greater than 350 nm. As shown in Table 1, ϵ values at 313 nm for monomers **3** and **4** are approximately 5 times higher that the ϵ value for compound **2** at 313 nm.

The true test of the viability of these materials is their ability to initiate polymerization. To examine their relative initiation efficiency, 1,6-hexanediol diacrylate (HDDA) was polymerized in the presence of 2-4 while conversion rates were monitored using real-time FTIR, as shown in Figure 2A. All polymerization experiments were performed in oxygen-free conditions between two salt plates. HDDA does not polymerize in the absence of a photoinitiator while samples with 2-4 polymerize rapidly. These samples polymerize quickly, attaining 50% conversion within 30 s, demonstrating their effectiveness as photoinitiators. The conventional initiator, dimethoxyphenyl acetophenone (DMPA), has a higher initiation efficiency than the initiating monomers at equal molar concentration. Additionally, the DMPA system reaches much higher conversion than the photoinitiating monomers. While the conversion is higher with the conventional photoinitiator, much higher HDDA conversion can be achieved at higher light intensity and different photoinitiating monomer concentrations. It is also important to note that the vast majority of DMPA remains unreacted after polymerization is complete. On the other hand, the initiating monomers can copolymerize as well as photoinitiate and therefore be completely consumed and be incorporated into the cross-linked network during polymerization. To demonstrate the self-



Figure 2. (A) Real-time IR conversion vs time plots of HDDA polymerizations in the presence of 3.9×10^{-2} mol/L of (a) DMPA, (b) **3**, (c) **4**, (d) **2**, (e) **1**, and (f) no photoinitiator in HDDA. Light intensity (full spectrum UV light) is 20 mW/cm², and sample is 15 μ m in thickness. (B) UV absorption spectra before and after polymerization of HDDA with 2.9×10^{-1} mol/L of **3** (DiVF). Sample is cured at 75 mW/cm² for 3 min with a medium-pressure mercury lamp.

initiating monomer consumption, Figure 2B shows the UV absorption of **3** during polymerization of HDDA, for which **3** was the only added photoinitiator. The shoulder peak observed from 240 to 330 nm before polymerization disappears after polymerization, indicating that the absorbing chromophore is disrupted as the initiating monomer is consumed by polymerization with the acrylate and becomes part of the cross-linked polymer film. The photolysis products have also been examined, indicating that two initiating radicals are produced by an α -cleavage reaction as observed for β , γ -unsaturated ketones.⁷ The details will be published elsewhere.

Having shown that these vinyl ester monomers serve as initiating monomers for acrylate polymerization, their use as a comonomer with other monomers is considered. Since fumarate ester monomers exhibit a strong alternating copolymerization tendency ($r_1 \ll 1$, $r_2 \ll 1, r_1 r_2 \simeq 0$ with electron-rich ene monomers due to a large electron density difference between the two double bonds,⁷ it might be expected that they would copolymerize readily with the electron-rich vinyl monomers and produce cross-linked networks without an external photoinitiator. To illustrate this point, 2 was copolymerized with triethylene glycol divinyl ether (DVE) without addition of an external photoinitiator. As is evident from the results in Figure 3, the polymerization of both the vinyl ether and vinyl ester groups proceeds at a substantial rate. Even without external photoinitiator, fumarate group conversion reaches ~60%, with $\sim 30\%$ conversions of both the vinyl ether and vinyl ester groups, after 60 s of exposure. Interestingly, the sum of vinyl ester and vinyl ether conversion is approximately the same as the fumarate conversion throughout the polymerization, indicating that the fumarate group of 2 polymerizes in an alternating fashion with both vinyl ester of 2 and vinyl ether double



Figure 3. Real-time IR conversion rates of 2:1 molar mixture of 2 and DVE. Light intensity (full spectrum UV light) is 10 mW/cm². Functional group molar ratios are 1:1:1.

bonds of the divinyl comonomer. In addition, the vinyl ester conversion rate is essentially identical to the vinyl ether conversion rate, unlike traditional systems where vinyl ethers react faster than vinyl esters with fuma-rates.⁸ Apparently, the electron density of the vinyl ester groups is approximately equal to that of the vinyl ether group, resulting in equivalent vinyl ester and vinyl ether conversion rates.

In conclusion, the initiating monomers synthesized in this study exhibit high UV absorptivity, efficiently initiate acrylate photopolymerization, and are consumed during the subsequent polymerization process. The rapid copolymerization of these monomers with an electron-rich vinyl ether illustrates the potential of vinyl ester-based initiating monomers for use in a wide variety of polymerization processes. Such initiating monomers provide an opportunity for applications where residual photoinitiating species are undesireable in the final cured films. **Acknowledgment.** The authors acknowledge NSF (Tie Grant EEC-0120965) and Fusion UV Curing Systems for funding this work.

Supporting Information Available: Synthesis details, monomer characterization, and photopolymerization techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

- Fouassier, J.-P. Photoinitiation Photopolymerization and Photocuring; Fundamentals and Applications; Hanser Publishers: Munich, 1995. Pappas, P. Radiation Curing, Science and Techonology; Plenum Press: New York, 1992. Fouassier, J. P.; Rabek, J. F. Radiation Curing in Polymer Science and Technology; Elsevier Applied Science: London, 1993; Vol. II.
- (2) Anderson, H.; Gedde, U. W.; Hult, A. Macromolecules 1996, 29, 1649. Matsumoto, A.; Kubota, T.; Otsu, T. Macromolecules 1990, 23, 4508. Hoyle, C. E.; Viswanathan, K.; Clark, S. C.; Miller, C.; Nguyen, C.; Jonsson, S.; Shao, L. Macromolecules 1999, 32, 2793.
- (3) Kudyakov, I. V.; Fos, W. S.; Purvis, M. B. Ind. Eng. Chem. Res. 2001, 40, 3092. Mattias, W.; Khudyakov, I. V.; Turro, N. J. J. Phys. Chem. A 2002, 106, 1938.
- (4) Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Kudyakov, I.; Viswanathan, K.; Nason, C.; Guymon, C. A.; Hoyle, C. E. *Polymer* **2003**, *44*, 2859.
- (5) Jonsson, E. S.; Lee, T. Y.; Viswanathan, K.; Hoyle, C. E.; Roper, T. M.; Guymon, C. A.; Nason, C.; Khudyakov, I. V. *Prog. Org. Coat.* 2005, *52*, 63.
- (6) Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Guymon, C. A.; Hoyle, C. E. *Macromolecules* **2004**, *37*, 3606.
- (7) Turro, N. J. Modern Molecular Photochemistry; University Science Books: Mill Valley, CA, 1991.
- (8) Odian, G. Principles of Polymerization; Wiley-Interscience: New York, 1982. Brandrup, J.; Immergut, E. H. Polymer Handbook; Wiley-Interscience: New York, 1975.

MA050852P