

polymer communications

Photopolymerization using maleimides as photoinitiators

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The photoinitiated polymerization of 1,6-hexanedioldiacrylate (HDDA) has been investigated using a variety of N-substituted maleimides to initiate the polymerization process upon exposure to light from a mercury lamp. When readily abstractable hydrogens are available, the polymerization is rapid. A maleimide with a carbonate group attached gave the greatest exotherm for HDDA polymerization. Copyright © 1997 Elsevier Science Ltd.

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Introduction

During the past two decades, the use of light to initiate the rapid polymerization of a variety of multifunctional monomers to yield highly crosslinked films with excellent mechanical and physical properties has resulted in numerous applications ranging from printing inks to protective coverings on floors^{1–5}. Photocurable (or u.v. curable) free-radical polymerizable resin mixtures in use today are primarily based upon acrylate chemistry. In each of these 'photocurable' systems, it is necessary to add small molecule photoinitiators to absorb the light and produce radicals and/or cations capable of initiating chain growth polymerization. With the development of new and better photoinitiators that produce radicals with high quantum efficiencies, the field of u.v. curing has grown at a rapid pace.

One of the remaining frontiers in photocurable free-radical polymerization is to develop rapidly polymerizing systems which respond to u.v. light without the necessity of adding a photoinitiator. This prospect is particularly attractive since photoinitiators have several disadvantages. First, and foremost, they are only partially consumed in typical photopolymerization processes since relatively high concentrations are required to ensure adequate absorption of light. This, of course, leads to considerable 'leachable' small molecule contaminants in the final crosslinked network. A second problem with many photoinitiators is the generation of coloured or harmful side products in addition to the primary radical photoproducts for initiation of polymerization. Yamada *et al.* first reported⁶ that N-alkylmaleimides homopolymerize in the absence of added photoinitiator when exposed to u.v. light in solvents having abstractable hydrogens (i.e. tetrahydrofuran). Recently, we found^{7–9} that upon

subjection of multifunctional maleimide/vinyl ether systems to light, rapid free-radical polymerization also occurs producing crosslinked networks, even in the presence of oxygen. We have shown that excited N-alkylmaleimides, which have extinction coefficients of $\sim 700 \text{ l mol}^{-1} \text{ cm}^{-2}$, readily abstract available hydrogens from either the vinyl ether backbone or the N-alkylmaleimide itself. The resulting free-radicals initiate a rapid alternating copolymerization as verified by real time i.r. Although not as fast as acrylate polymerization in inert atmosphere initiated with an external photoinitiator, the polymerization rates of maleimide/vinyl ether systems are fast enough to make them potentially useful for a number of applications. The big advantage of the crosslinked films produced from these systems is their transparency at wavelengths greater than 300 nm. This occurs since n-alkylmaleimides consumed by the free-radical polymerization process are replaced by succinimide chromophores which have virtually no absorbance at wavelengths greater than 300 nm. This makes such films potentially useful for applications which require them to be exposed to sunlight for long periods of time.

Results and discussion

Since N-alkylmaleimides are rapidly consumed in free-radical polymerizations, it is advantageous to consider them as initiators of the free-radical polymerization of acrylates: this would expand their use considerably. Since maleimides produce no detrimental side products (only radical initiating species) upon photolysis, they are capable of rendering acrylic films which are relatively non-absorbing at wavelengths greater than 300 nm. The purpose of this communication is to relate results for polymerization of acrylates using various N-alkylmaleimides as initiators (see ref. 10 for preprint of some of the data in this communication). Herein, we focus on N-alkylmaleimides for which the initiation process is via

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hydrogen abstraction by the excited N-alkylmaleimide. The relationship between the N-alkylmaleimide structure and initiation efficiency is identified and optimized. 1,6-Hexanedioldiacrylate (HDDA) is chosen as the acrylate since it has relatively non-abstractable hydrogens, and polymerizes at a rapid rate which is readily monitored by a d.s.c. equipped with a medium pressure mercury lamp source. Three types of initiating systems are investigated: N-methylmaleimide (MMI) with small molecule cointiators, N-alkylmaleimides with N-alkyl groups having abstractable hydrogens, and N-substituted maleimides with heteroatoms and abstractable hydrogens on the N-substituted groups.

Figure 1 shows results for the exotherms produced by exposure of 90/10 HDDA/MMI samples to the output of a medium pressure mercury lamp with Pyrex filter. Of the three cases where a cointiator with readily abstractable hydrogens [methyldiethanolamine (MDEA), trimethylolpropane trismercaptopropionate (trithiol), or polyethyleneglycol with molecular weight of 1000 (designated PEG 1000)] were added, the exotherm rates were much greater than for the simple HDDA/MMI case with no cointiator. Since the hydrogens of HDDA itself are not relatively abstractable, it is apparent that the cointiators with abstractable hydrogens are interactive with the excited state of MMI. Incidentally, if HDDA without any additive is exposed to the mercury lamp, little exotherm is recorded. Conversely, if a HDDA sample with 1% conventional photoinitiator (such as 2,2-dimethoxy-2-phenylacetophenone) is exposed to the same light source, a very large exotherm occurs (well off the scale of the exotherm plot in Figure 1).

Since we know that excited N-alkylmaleimides will initiate polymerization via hydrogen abstraction and production of free-radical initiating species, we decided to compare results from a series of N-alkylmaleimides in which the structure of the N-alkyl group was systematically varied. Figure 2 shows exotherms for polymerization of HDDA samples with 10 wt% of the various N-alkylmaleimides added. As the complexity of the N-alkyl group, and also the relative availability of secondary and tertiary abstractable hydrogen atoms, increases from methyl to ethyl, hexyl and finally cyclohexyl, the exotherm rate also increases (judged by the peak maximum). The processes leading to radical initiation of the systems depicted in Figure 2 could be the result of intermolecular hydrogen abstraction processes, intramolecular hydrogen abstraction processes, or a combination of both. The exact process of hydrogen abstraction is the subject of an ongoing investigation and will be reported on in a full paper. For now, we simply note that the hydrogen abstraction efficiency increases as the alkyl group changes from methyl to ethyl, hexyl, and cyclohexyl. The literature suggests (refs 11, 12 and references therein) that abstraction of hydrogens atoms occurs from the ene group of the excited state N-alkylmaleimide triplet. Our preliminary results suggest that the hydrogen abstraction reaction of N-alkylmaleimides indeed proceeds from the excited state triplet.

In an attempt to enhance the propensity for hydrogen abstraction, an N-substituted maleimide monomer which incorporates a dialkyl carbonate unit attached to the maleimide chromophore was synthesized by reacting N-(2-hydroxyethyl)maleimide with ethylchloroformate product (designated as ECEMI). Figure 3 shows the

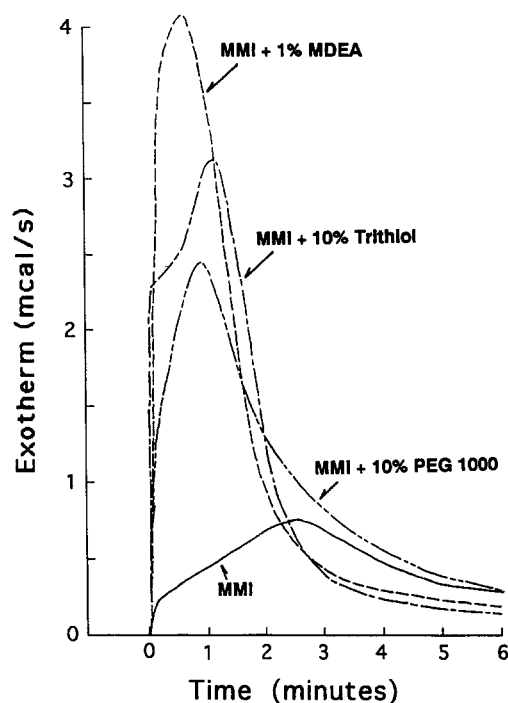


Figure 1 Exotherms of HDDA with 10 wt% MMI plus cointiators (as indicated on figure) upon exposure to Pyrex filtered medium pressure mercury lamp (approximately 14 mW cm^{-2}). Samples were approximately 3 mg each

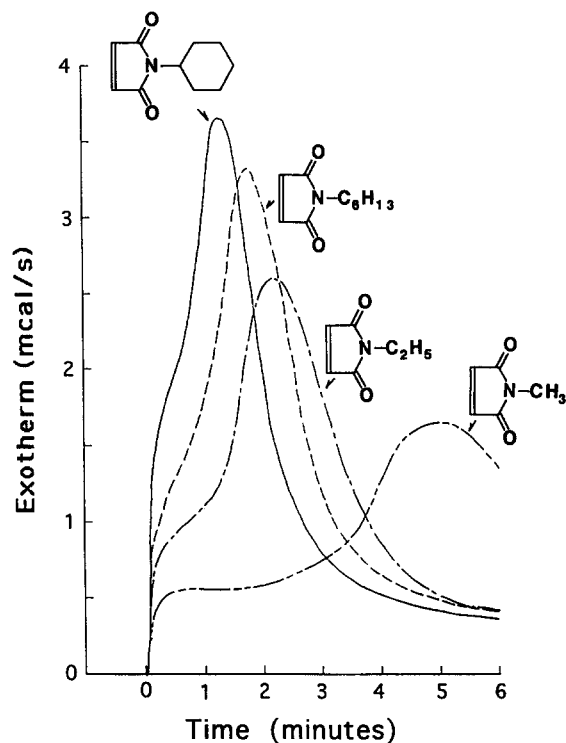
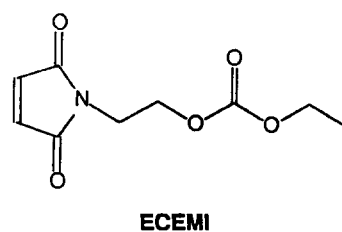


Figure 2 Exotherms of HDDA with 10 wt% various N-alkylmaleimides (as indicated on figure) upon exposure to medium pressure mercury lamp (approximately 19 mW cm^{-2}). Samples were approximately 3 mg each



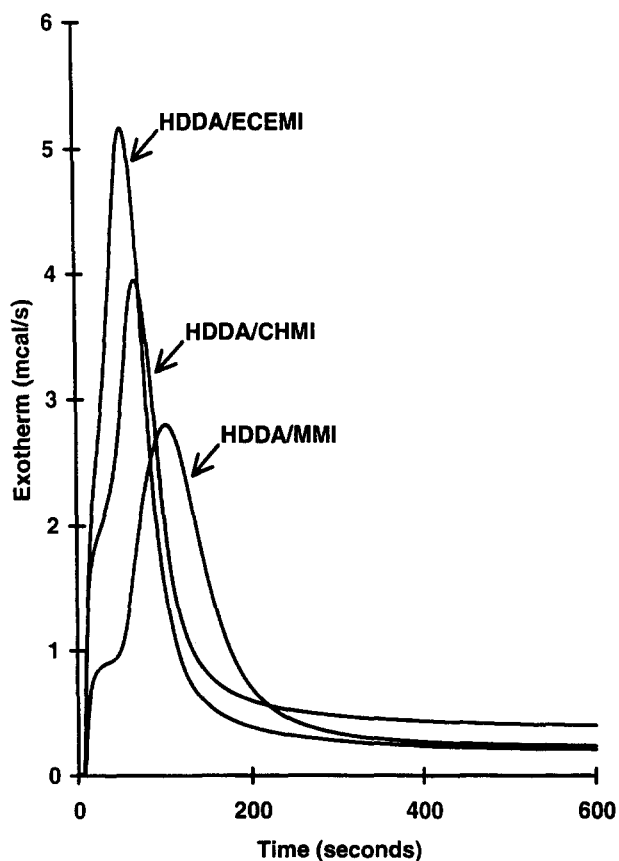


Figure 3 Exotherms of HDDA (90 mol%)/10 mol% N-substituted maleimides (as indicated on figure) upon exposure to medium pressure mercury lamp (approximately 28 mW cm^{-2}). Samples were approximately 3 mg each

exotherms for HDDA with 10 mol% MMI, N-cyclohexylmaleimide (CHMI), and ECEMI. It is quite obvious that the exotherm for the HDDA/ECEMI sample is substantially greater than for the HDDA/MMI, and even the HDDA/CHMI, system. This suggests that the hydrogens of ECEMI are readily abstractable. To demonstrate that ECEMI has hydrogens which are particularly labile, we measured (Figure 4) the exotherms for two systems: one HDDA (90%)/ECEMI (10%) and the other HDDA (80%)/ECEMI (10%)/DEC (10%) where DEC represents diethyl carbonate. The HDDA sample with 10% ECEMI has a substantially greater exotherm than the HDDA sample with 10% each of MMI and DEC. [Incidentally, the HDDA (80%)/MMI (10%)/DEC (10%) sample has a markedly greater exotherm than for an HDDA (90%)/MMI (10%) sample (exotherm not shown) without the DEC under the same exposure conditions]. Apparently, it is important to have the dialkyl carbonate attached to the maleimide in order to obtain the highest rate of polymerization. This is consistent with enhancement of hydrogen abstractability. Results of an ongoing investigation of maleimide photoinitiation in progress is designed to answer mechanistic questions (excited state spin multiplicity, intermolecular versus intramolecular hydrogen abstraction, etc.) related to photoinitiation of acrylates via excitation of maleimides. Details will be published in a full paper.

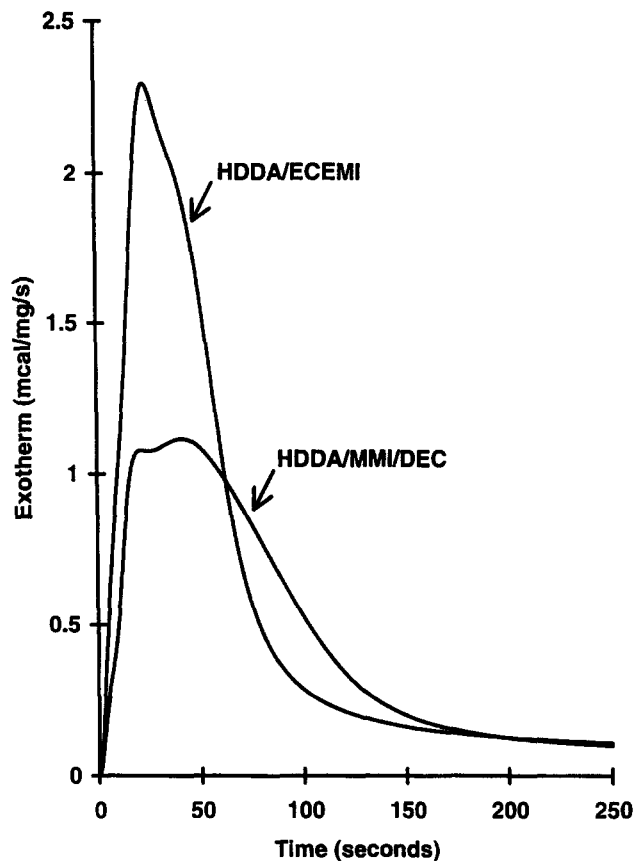


Figure 4 Exotherms of HDDA (80 mol%)/MMI (10 mol%)/DEC (10 mol%) and HDDA (90 mol%)/ECEMI (10 mol%) samples upon exposure to medium pressure mercury lamp (approximately $24\text{--}28 \text{ mW cm}^{-2}$). Plots normalized for sample weight

Acknowledgements

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References

1. *Radiation Curing in Polymer Science and Technology*, Vols I-IV, ed. J. P. Fouassier and J. F. Rabek. Elsevier Applied Science, New York, 1993.
2. *Radiation Curing: Science and Technology*, ed. S. P. Pappas. Plenum Press, New York, 1992.
3. *UV Curing: Science and Technology*, ed. S. P. Pappas. Technology Marketing Corp., Norwalk, CT, 1976.
4. *Radiation Curing of Polymeric Materials*, ACS Symposium Series 417, ed. C. E. Hoyle and J. F. Kinstle. American Chemical Society, Washington D.C., 1990.
5. *Radiation Curing: Principles and Practice*, Vols I-VI, ed. P. Oldring. EM Books, London, 1991.
6. Yamada, M., Takase, I. and Katour, N., *J. Polym. Sci., Part B*, 1968, **6**, 883.
7. Miller, C. W., Hoyle, C. E. and Howard, C., *Polymer Preprints*, 1996, **37**(2), 346.
8. Jonsson, S., Sundell, P. E., Shimose, M., Owens, J., Miller, C., Clark, S. and Hoyle, C. E., *PMSE Preprints*, 1996, **74**, 319.
9. Decker, C., Morel, F., Jonsson, S., Clark, S. C. and Hoyle, C. E., *PMSE Preprints*, 1996, **75**, 198.
10. Clark, S. C., Jonsson, S. and Hoyle, C. E., *Polymer Preprints*, 1996, **37**(2), 348.
11. Aida, H., Takase, I. and Noxi, T., *Makromol. Chem.*, 1989, **190**, 2821.
12. Zott, H. and Heusinger, H., *Europ. Polym. J.*, 1978, **14**, 89.