Maleimides as Visible Photoinitiators

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Abstract

An N-substituted maleimide has been used in conjunction with ketocoumarins and a tertiary amine to initiate the polymerization of hexanedioldiacrylate in the visible region (365 nm and 436 nm) of the electromagnetic spectrum. The rate of polymerization of a ketocoumarin/tertiary amine combination is significantly increased with the addition of a substituted maleimide.

Introduction

The most commonly used photoinitiators are Norrish Type I (cleavage). Common types of cleavage photoinitiators are aromatic carbonyl compounds such as derivatives of benzoin, benzilketal and acetophenone. Abstraction photoinitiators (Type II) are typically diaromatic ketones, such as derivatives of thioxanthones and benzophenones. Thioxanthone derivatives are typically used in pigmented systems.

Most Type I (cleavage) and Type II (abstraction) photoinitiators absorb light in the ultraviolet region of the electromagnetic spectrum. This is not suitable for some applications such as pigmented systems since the pigments absorb and scatter ultraviolet light, which results in less light being available to the photoinitiator thus reducing the efficiency. Applications benefiting from visible light curing range from UV curable printing inks to printed circuit boards. Visible light free-radical photoinitiators include Type I and Type II systems.   Type II photoinitiators can be tailored to a specific wavelength, as an example dyes have been implemented that include camphorquinone, thioxanthone and ketocoumarin derivatives.[1] Some Type I systems with absorption maxima beyond 300 nm have also been developed such as phosphineoxides and are in common use.[2]

There has been considerable activity regarding the use of *N*-substituted maleimides as photoinitiators/comonomers for free-radical polymerization.[3] The maleimide produces an initiating species and is also a comonomer in the polymerization, thus being consumed in the process. The photoreduction of

maleimide has been reported to generate radicals to initiate polymerization.[4-7] Direct excitation of *N*-alkyl and *N*-aromatic maleimides when incorporated as initiator/comonomer in an acrylic system, though it initiates polymerization, yields a less efficient polymerization compared to a conventional cleavage type photoiniaitor, such as 2,2-dimethoxy-2-phenylacetophenone (DMPA). Previous results have shown that when conventional bimolecular photoinitiators, such as benzophenone and thioxanthone derivatives in the presence of a tertiary amine, are used in conjunction with maleimides, the rate of polymerization is markedly increased approaching the efficiency of a cleavage type photoinitiator.[3,8-10] The mechanism of initiation is proposed to involve a dual mechanism. The first mechanism involves an energy transfer from a triplet sensitizer to the maleimide. The excited state maleimide then undergoes a rapid electron/proton transfer with a tertiary amine to produce a succinimidyl and aminyl radical, both capable of initiating acrylate polymerization (Figure 1).
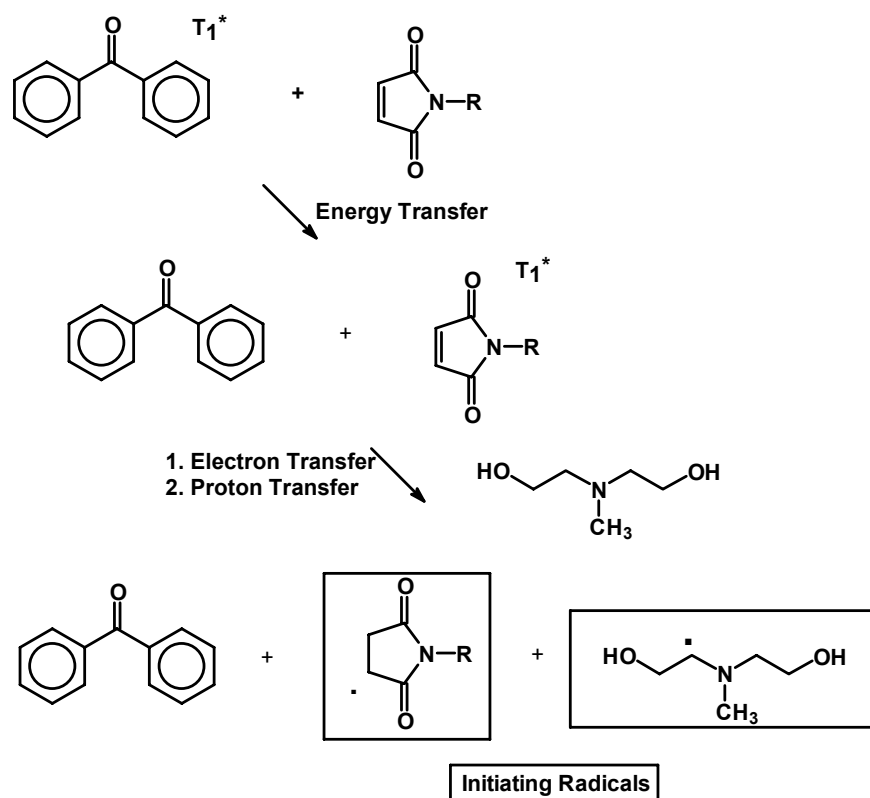
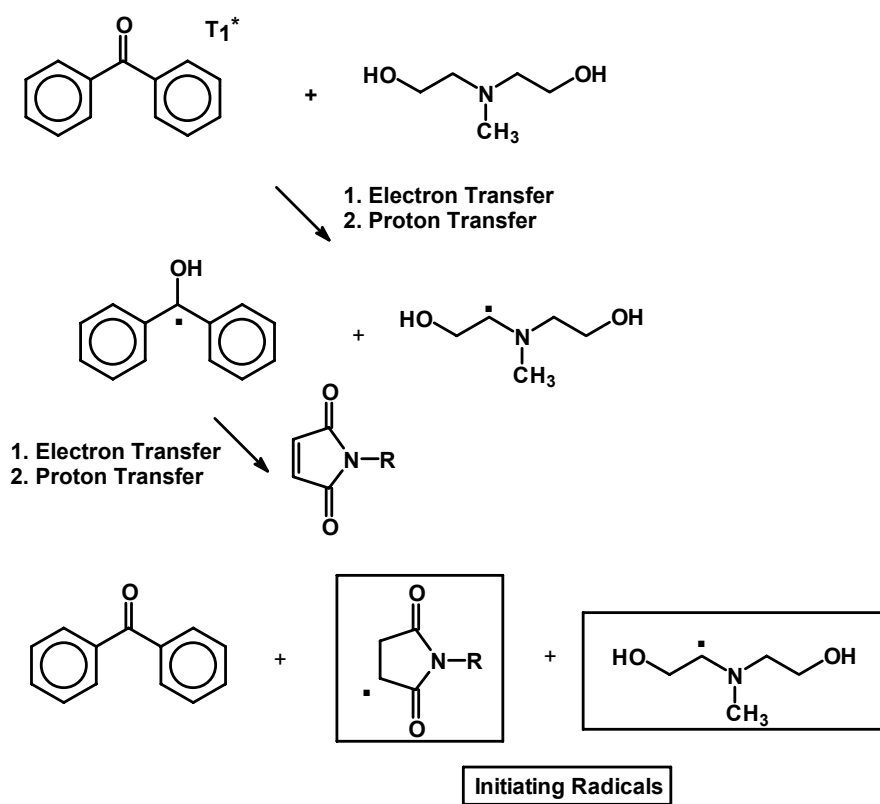**Figure 1. Energy Transfer Mechanism.**

Figure 2. Ketyl radical reduction by maleimide.

The second mechanism has the sensitizer (excited state) participating in an electron/proton transfer reaction with an amine to produce the ketyl and aminyl radicals. The ketyl radical is then reduced by ground state maleimide by an electron/proton transfer to produce the succinimidyl radical and ground state sensitizer.   The two radicals that are produced (succinimidyl and aminyl) are both capable of initiating acrylate polymerization (Figure 2). Both mechanisms can yield two radicals that are capable of initiating acrylates polymerization. Huyser and Neckers have provided evidence that the reaction of alcohol radicals with aryl ketones can be caused by using other radical initiators and solutions of aryl ketones in alcohols (Figure 3).[11]
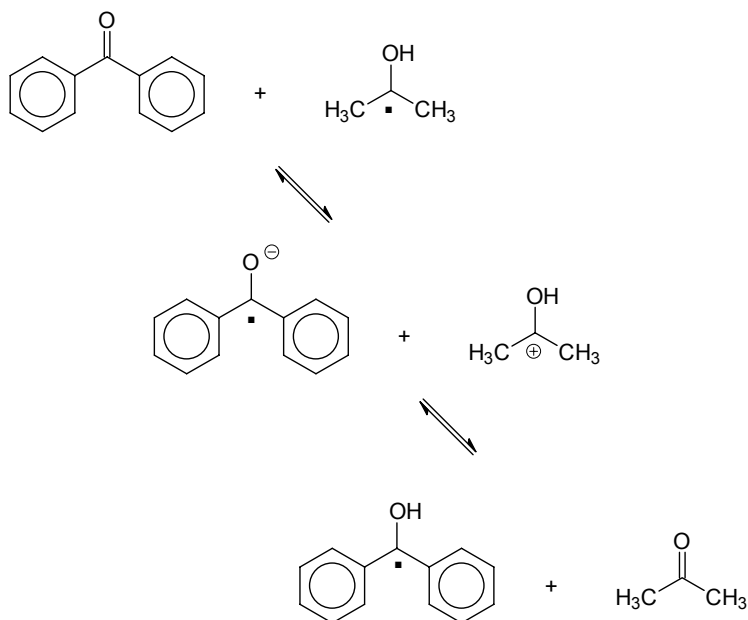

Figure 3. Reduction of ketyl radical by aromatic ketone.

Since dyes are used to extend existing absorption maxima of current visible photoinitiators, we have included some of these in an initiative to extend the use of maleimides into the visible.   Herein, we use ketocoumarins in conjunction with a substituted maleimide/tertiary amine combination in comparison to an efficient cleavage photoinitiator, DMPA on a per quantum basis.

Experimental

N-methylmaleimide (MMI) and N-methyl-N,N-diethanolamine (MDEA) used in these experiments were purchased from Aldrich and used without further purification. 5,7-dimethoxy-3-(1-naphthoyl)coumarin and 3,3'-carbonylbis-(7-methoxycoumarin) was obtained from Kodak, and 3,3'-carbonylbis(7-diethylaminocoumarin) was purchased from Acros (Figure 4). Hexanedioldiacrylate was obtained from UCB Chemicals, Inc.
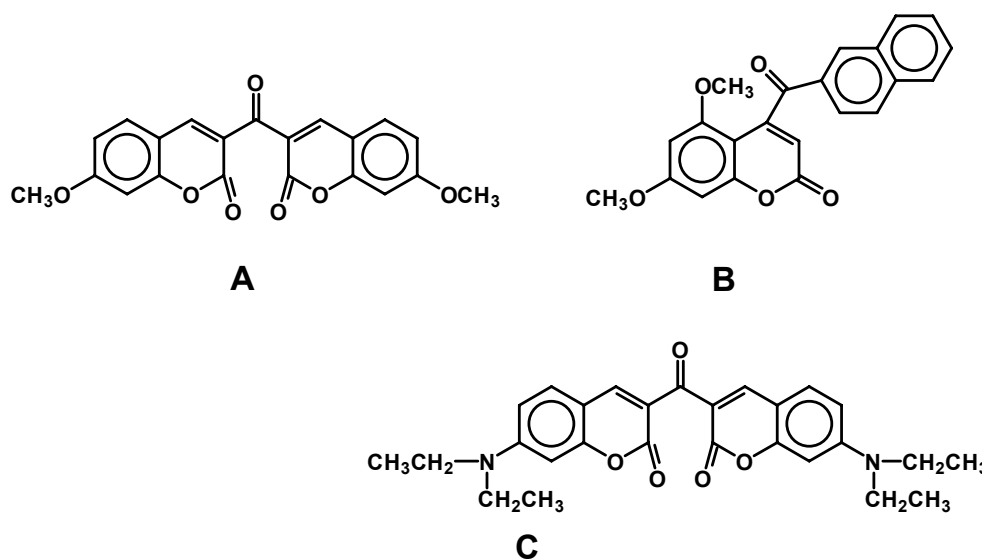
Figure 4. Ketocoumarins used (A) 3,3'-carbonylbis-(7-methoxycoumarin)or CBC (B) 5,7-dimethoxy-3-(1-naphthoyl)coumarin or DMC (C) 3,3'-carbonylbis(7-diethylaminocoumarin) or CBD.

Photo–Differential Scanning Calorimetry (Photo-DSC) was performed using a Perkin-Elmer DSC 7, with modifications to accommodate quartz windows in the DSC head and a UV light source. The sample cell was purged with nitrogen prior to and during the irradiation. The lamp source was a Hanovia medium-pressure mercury lamp from Ace Glass with an on-sample light intensity of 30mW/cm^2 (full arc) and specific spectral bands were isolated by the use of band-pass filters 365 nm and 436 nm. 2 µL samples were injected into specially crimped aluminum pans with corresponding film thicknesses of 180-250 µm.

Results and Discussion

Previous results have shown an enhancement in relative rates of polymerization of acrylic systems containing N-alkyl and aromatic maleimides in the presence of benzophenone, isopropylthioxanthone and 4-benzoylbiphenyl.[9-11]

Figure 5 shows the polymerization of 1,6-hexanedioldiacrylate (HDDA) when incorporating MMI into a 5,7-dimethoxy-3-(1-naphthoyl)coumarin (DMC) and *N*-methyl-*N,N*-diethanolamine (MDEA) initiator package, compared to DMPA at the isolated line of a medium pressure mercury lamp at 365 nm. To accurately compare the quantum efficiency of the DMC package, the absorbance was matched to that of DMPA at 1.0% by weight. At 365 nm, MMI does not absorb appreciably at 0.1% by weight to competitively absorb with DMC. Curve 'c' depicts the exotherm produced when DMC is reduced by MDEA, the exotherm has a peak maximium ~70 mW. The mechanism involves an electron/proton transfer to produce the ketyl radical of DMC and the aminyl radical of MDEA. When 0.1% of MMI is added to the DMC/MDEA mixture, a marked increased in the overall rate of the polymerization is attained (curve 'a'), with a polymerization exotherm of ~180 mW, which is comparable to that observed with 1.0% weight of DMPA (curve 'b') with a peak maximum of ~160 mW. The amount of DMC used to match the absorbance of 1.0% by weight of DMPA is 0.008% by weight of DMC. Since DMC has a triplet energy below MMI (estimated ~ 56 kcal mol^{-1})[12], the mechanism could possibly involve the reduction of the DMC by MDEA, by an electron/proton transfer, yielding

the ketyl radical of DMC to be reduced by ground state MMI, yielding the succinimidyl radical and ground state DMC (Figure 8).
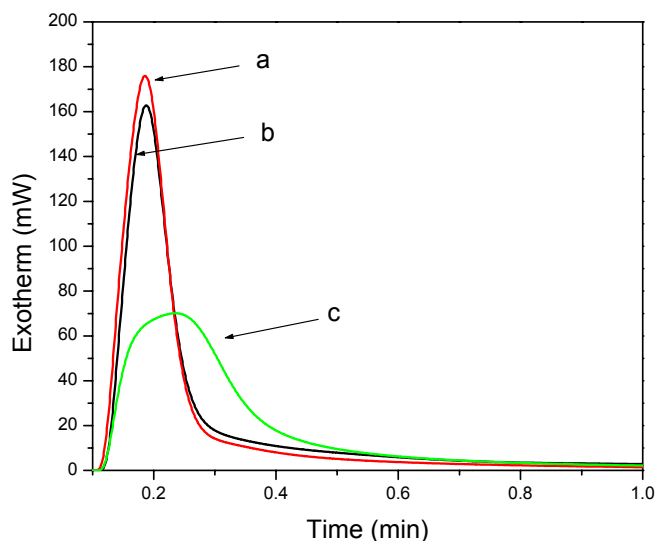

Figure 5. Representative photo-DSC exotherms for HDDA initiated by sensitized N-methylmaleimide(MMI) in the presence of an amine synergist (MDEA). Sensitizer 5,7-dimethoxy-3-(1-naphthoyl)coumarin (DMC) concentration equal to absorbance of 1.0% by weight of DMPA. Irradiance was 0.75 mW cm^{-2} at 365 nm in N$_2$. (a) 5,7-dimethoxy-3-(1-naphthoyl)coumarin, 0.1% MMI and 1.0% MDEA (b) 1.0% by weight of DMPA (c) 5,7-dimethoxy-3-(1-naphthoyl)coumarin and 1.0% MDEA.

The second set of photo-DSC experiments as shown in Figure 6, was performed using MMI/MDEA and 3,3'-carbonylbis-(7-methoxycoumarin) or CBC. The absorbance of CBC was matched to 1.0% by weight of DMPA at 365 nm. Curve 'a' represents the polymerization exotherm observed with 1.0% by weight of DMPA. Curve 'c' shows the exotherm for CBC with MDEA. This reaction is also a reduction of the coumarin by MDEA through an electron/proton transfer to produce the ketyl radical of CBC and the aminyl radical of MDEA. Only the aminyl radical is capable of initiating polymerization, while the ketyl radical cannot efficiently initiate acrylate polymerization. Upon addition of 0.1% of MMI (curve 'b'), there is an overall increase in the rate of polymerization.
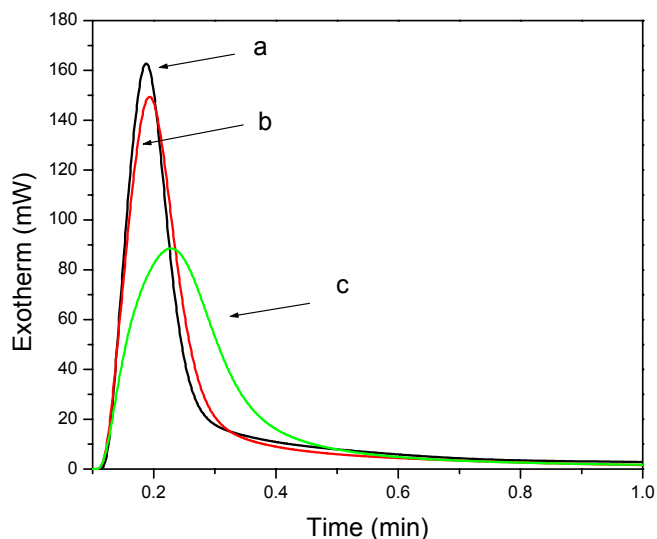
Figure 6. Representative photo-DSC exotherms for HDDA initiated by sensitized N-methylmaleimide (MMI) in the presence of an amine synergist (MDEA). Sensitizer (3,3'-carbonylbis-7-diethylaminocoumarin)or CBC, concentration was equal to absorbance of 1.0% by weight of DMPA. Irradiance was 0.75 mW cm-^{2} at 365 nm, in N_2. (a) 3,3'-carbonylbis-(7-methoxycoumarin), 0.1% MMI and 1.0% MDEA (b) 1.0% by weight of DMPA (c) 3,3'-carbonylbis(7-diethylaminocoumarin) and 1.0% MDEA.

The third set of photo-DSC experiments was performed using *N*-methylmaleimide (MMI), an amine coinitiator *N*-methyl-*N,N*-diethanolamine (MDEA) with 3,3'-carbonylbis(7-diethylaminocoumarin) or CBD with absorbance equivalent to 1.0% by weight of DMPA at 365 nm (Figure 7). DMPA could not be compared at 436 nm, since it does not absorb at that wavelength. However, for comparative purposes, curve 'a' depicts the polymerization exotherm observed with 1.0% by weight of DMPA at 365 nm. Curve 'c' shows the exotherm produced when using CBD with MDEA at 436 nm. This mechanism is also a reduction of the coumarin by MDEA through an electron/proton transfer to produce the ketyl radical of CBD and the aminyl radical of MDEA, where only the aminyl radical is capable of initiating polymerization. Upon addition of 0.1% of MMI (curve 'b') and irradiation at 436 nm, there is an overall increase in the rate of polymerization. The aforementioned mechanism is detailed in Figure 8.
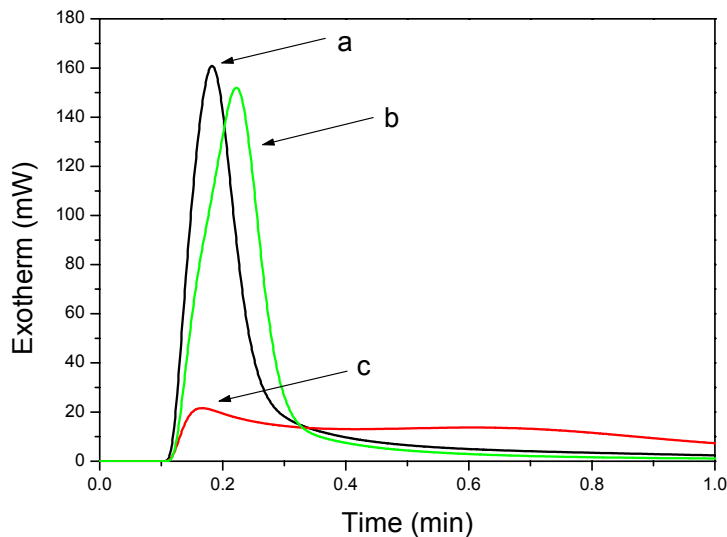
Figure 7. Representative photo-DSC exotherms for HDDA initiated by sensitized N-methylmaleimide (MMI) in the presence of an amine synergist (MDEA). Sensitizer (3,3'-carbonylbis-7-diethylaminocoumarin) or CDB, concentration equal to absorbance of 1.0% by weight of DMPA at 365 nm. Irradiance was 0.86 mW cm^{-2} at 365 nm and 1.90 mW cm^{-2} at 436 nm, N$_2$. (a) 1.0% by weight of DMPA at 365 nm, (b) 3,3'-carbonylbis(7-diethylaminocoumarin), 0.1% MMI and 1.0% MDEA at 436 nm(c) 3,3'-carbonylbis(7-diethylaminocoumarin) and 1.0% MDEA at 436 nm.
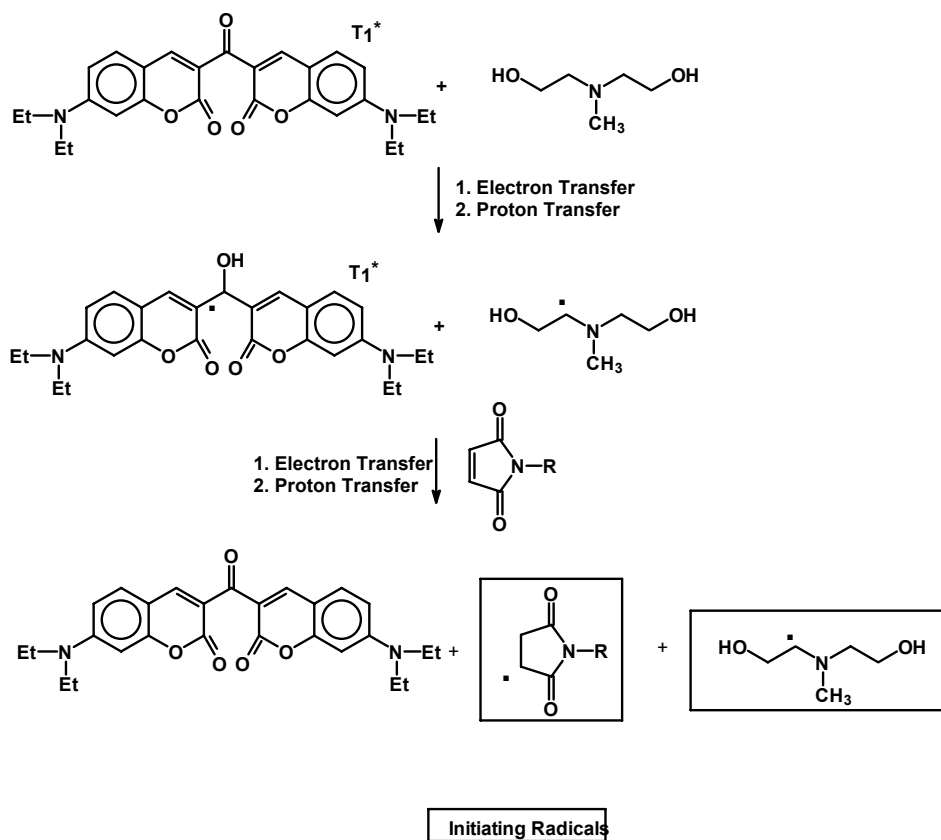

Figure 8. Ketyl radical reduction by maleimide.

Conclusions

In the previous discussion, we have shown that it is possible to initiate acrylate polymerization with *N*-methylmaleimide in the presence of ketocoumarins and MDEA. In the absence of of *N*-methylmaleimide, the ketocoumarin/amine system efficiently initiates acrylate polymerization, although not as efficiently as with DMPA, when compared at equal absorbance at 365 nm. Upon addition of a small amount of *N*-methylmaleimide, the overall rate of polymerization approaches that of DMPA, as we have shown with other sensitizers. When using a ketocoumarin with an absorbance at 436 nm, we find that the addition of *N*-methylmaleimide to the ketocoumarin/amine systems, also increases the overall rate of polymerization. This lends ability to extend the use of maleimides as photoinitiators into the visible region of the electromagnetic spectrum.

Acknowledgements

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