Communications to the Editor

Sensitized Polymerization of an Acrylate/Maleimide System

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For about three decades, it has been known that N-substituted maleimides can readily polymerize by a free-radical polymerization process upon exposure to light.[1−5] Recently, there has been considerable activity dealing with the use of N-substituted maleimides as photoinitiators for the free-radical polymerization (copolymerization) of a variety of functional species including acrylate, vinyl ether, and styryloxy monomers.[6−15] In each of these cases, the maleimide participates in producing the initiating radical species and also participates as a comonomer in the resultant polymerization process. Hence, maleimides are consumed efficiently (loss quantum yield > 1.0) by the radical polymerization process which they initiate and are lost at a much greater rate than if they were lost by a simple photochemical bleaching process where the maximum quantum yield for bleaching (i.e. loss of absorption by the initiating species) would be 1.0. N-substituted maleimides thus enjoy the unique advantage of being able to initiate radical polymerization of cross-linking systems while not remaining in the final film as an extractable or photoreactive contaminant. Photoreduction of excited maleimides has been proposed to account for generation of radicals to initiate polymerization.[2−5,13]

Unfortunately, direct excitation of an *N*-aliphatic maleimide or *N*-alkylmaleimide incorporated as an initiator/comonomer in a traditional photopolymerizable acrylate system, although it initiates polymerization, results in a polymerization process which is much slower than when a conventional cleavage type photoinitiator (such as 2,2-dimethoxy-2-phenyl acetophenone—DMPA) is used. Described herein is the use of a photosensitizer [benzophenone (BP) with a triplet energy of approximately 69 kcal/mol] to dramatically increase the polymerization rate of a difunctional acrylate incorporating *N*-methylmaleimide (MMI) and an amine co-initiator. Rates closer to those obtained with traditional cleavage type photointiators are achieved with the BP/MMI/amine system! The transient spectrum and lifetime of the triplet excited state of MMI are clearly defined, and the rate constant for quenching of the triplet state of the sensitizer by MMI is calculated. The rate constant for quenching of the triplet state of MMI by a tertiary amine is also determined by laser flash photolysis. Some of the work in this communication has been reported in unreviewed format in ref 16.

Figure 1 shows polymerization exotherms for 1,6-hexanedioldiacrylate (HDDA) incorporating a MMI/amine (methyldiethanol amine—MDEA) initiator package recorded on a photo-DSC (see ref 6 for details of instrumentation) in the absence and presence of benzophenone (BP) upon exposure to the isolated 366-nm line of a medium pressure mercury lamp source. It is obvious that the addition of a very small amount of MMI to a sample containing BP and MDEA has a dramatic effect upon the polymerization rate (curve a vs curve c). It is noted that direct excitation of MMI at a shorter wavelength (actual exotherm curve not shown) where the number of photons of light absorbed by MMI is comparable to that of the BP at 366 nm in Figure 1 would give a much smaller exotherm than that obtained by BP/MDEA in curve c. The exotherms in curves a and c are both markedly greater than for the HDDA/MMI/MDEA system at 366 nm where MMI has little absorption (curve e—essentially no exotherm) or for the HDDA/BP/MMI mixture (curve d—essentially no exotherm). For comparison, the exotherm for photopolymerization of HDDA with the conventional photoinitiator DMPA (with the concentration adjusted to have the same absorbance at 366 nm as by BP at 366 nm) is shown in curve b. The exotherm for the HDDA/DMPA has a peak maximum of ∼105 kcal/mol, not that much greater than the peak maximum of ∼63 kcal/mol for the HDDA/BP/MMI/MDEA combination. The inherent efficiency of the HDDA/BP/MMI/MDEA system (curve a) is even closer to that of the HDDA/DMPA system (curve b) than is portrayed by the results in Figure 1 since MMI is rapidly consumed (determined by independent FT-IR and UV analysis) by the acrylate polymerization that it initiates.

The results in Figure 1 suggest that sensitization of the maleimide triplet state by BP is occurring. To confirm this supposition and elucidate the mechanism for the observed polymerization rate enhancement when a small amount of MMI is added to an HDDA sample containing BP and MDEA, a laser flash photolysis investigation was conducted. First, the transient absorption spectrum of MMI (which will be shown to be a triplet) was recorded as a function of time in the absence of either an amine synergist or BP (triplet sensitizer). As shown in Figure 2, the transient spectrum of a 0.002 M solution of MMI in nitrogen-sparged acetonitrile upon excitation with a Nd:YAG laser at 266 nm has a peak maximum at about 340 nm that decreases with time. The shape and lifetime of the transient spectrum of MMI in Figure 2 is consistent with the results by Sonntag et al.[17] for the transient spectrum of maleimide. The decay of the MMI transient spectrum in Figure 2

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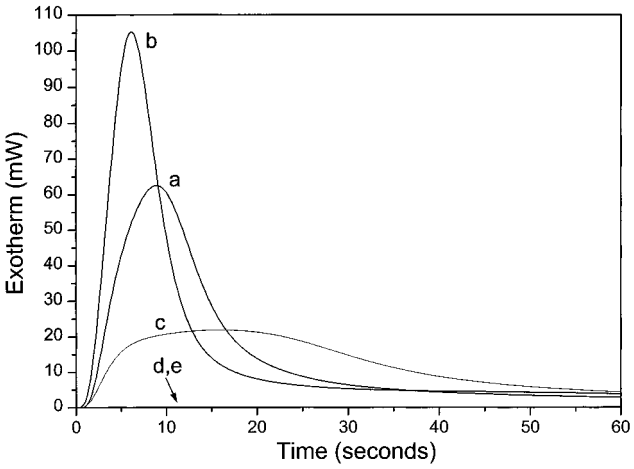

Figure 1. Exotherms for the photopolymerization of mixtures of HDDA with (a) 3 mol % BP + 1 mol % MDEA + 0.1 mol % MMI, (b) 1.57 mol % DMPA, (c) 3 mol % BP + 1 mol % MDEA, (d) 3 mol % BP + 0.1 mol % MMI, and (e) 1 mol % MDEA + 0.1 mol % MMI. Conditions: sample volume 2 μL, 366-nm line of medium-pressure mercury lamp with intensity 0.41 mW/cm^2, temperature 60 °C, and nitrogen purge time of 5 min.

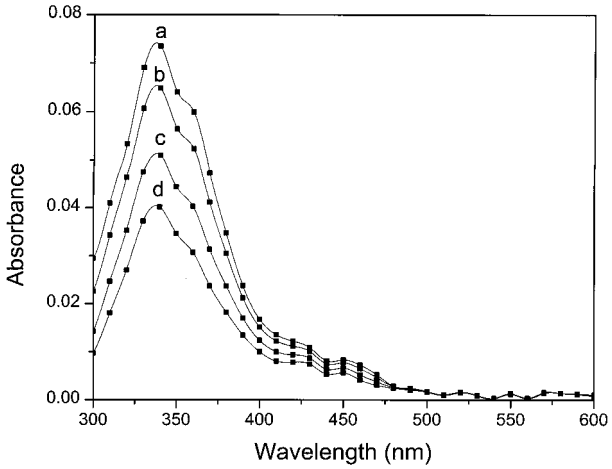

Figure 2. Transient spectra of 0.002 M MMI in nitrogen-sparged acetonitrile excited at 266 nm for (a) 75 ns, (b) 100 ns, (c) 150 ns, and (d) 200 ns after laser flash.

is exponential with a lifetime of 205 ns. There are three possibilities for the transient with peak maximum at 340 nm: a singlet state, a triplet state, or a radical. The transient is readily quenched by 1,3-cyclohexadiene at essentially a diffusion controlled rate ($\sim 10^{10}$ L mol^{-1} s^{-1}). Additionally, the transient spectrum of a solution comprised of MMI and β-carotene is characterized by a peak maximum between 500 and 600 nm due to the β-carotene triplet. These quenching results are consistent with assignment of the transient with peak maximum at 340 nm to a triplet state. By measurement of the transient lifetime at 340 nm as a function of MMI concentration, an extrapolated "zero concentration" lifetime of 414 ns for MMI and a self-quenching second-order rate constant of 1.3×10^9 L mol^{-1} s^{-1} are calculated from the intercept and slope, respectively, of a reciprocal lifetime vs MMI concentration plot. The extrapolated lifetime of 414 ns is fairly close to the value of 250 ns found by Sonntag[17] for unsubstituted maleimide, but somewhat larger than the value of the "zero concentration" lifetime of ~100 ns estimated by De-Schryver[18] for *N*-butylmaleimide in dichloromethane obtained by quenching of the dimer photoproduct. (Differences in the extrapolated lifetimes determined by-

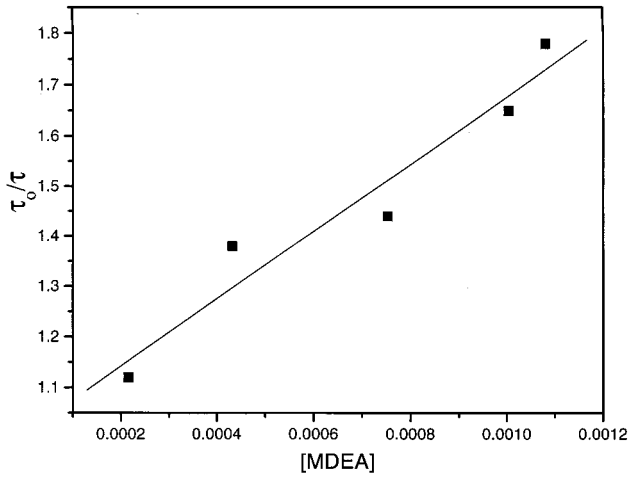

Figure 3. Stern−Volmer plot for quenching of 0.0029 M MMI triplet transient (excited at 266 nm—monitored at 340 nm) by MDEA in nitrogen-sparged acetonitrile.

product quenching and those measured by laser flash photolysis may be due to the methods used and assumptions made.) The self-quenching constant of 1.3×10^9 L mol^{-1} s^{-1} for MMI, an N-substituted maleimide, is very close to the 1.9×10^9 L mol^{-1} s^{-1} value for self-quenching of the unsubstituted maleimide triplet.[17] Self-quenching may be an important factor in certain cases where the initial maleimide concentration in a particular polymerizable system is high.

While the laser flash results in Figure 2 clearly show that N-substituted maleimides have a transient triplet with substantial absorbance between 300 and 350 nm, it is still necessary to determine the effect of MDEA and BP in order to explain the exotherm results in Figure 1. First, the addition of MDEA to a solution of MMI results in a rapid quenching of the MMI transient and a concomitant reduction in the triplet lifetime. If τ_o is defined as the MMI triplet lifetime in the absence and τ the MMI triplet lifetime in the presence of MDEA, a linear Stern−Volmer plot of τ_o/τ vs MDEA concentration (Figure 3) yields a quenching rate constant of 4.3×10^9 L mol^{-1} s^{-1}. The large magnitude of this quenching rate constant suggests that an electron transfer process is operative in the quenching process and accounts for the previously reported[14] rate enhancement in acrylate polymerization initiated by N-substituted maleimides in the presence of added aliphatic amines. The large rate constant for quenching of MMI triplet by MDEA is consistent with typical quenching constants for electron transfer and agrees with the reported mechanism proposed by Sonntag[17] to account for quenching of maleimide by vinyl ether and inorganic ion electron donors. As a frame of reference, the Stern−Volmer quenching of BP by MDEA in acetonitrile (plot not shown) gave a quenching constant of 1.1×10^9 L mol^{-1} s^{-1}, about 4 times lower than the value of 4.3×10^9 L mol^{-1} s^{-1} obtained for MMI. Next, the triplet state of BP is quenched by the addition of MMI. Figure 4 shows the Stern−Volmer plot for quenching of the BP triplet lifetime by MMI: a quenching rate constant of 6.4×10^9 L mol^{-1} s^{-1}, which is close to diffusion controlled, is consistent with a rapid energy transfer quenching process. (Indeed, literature reports suggest that N-substituted maleimide[18] and N-substituted dimethylmaleimide[19] triplet states can be populated by sensitization with BP.)

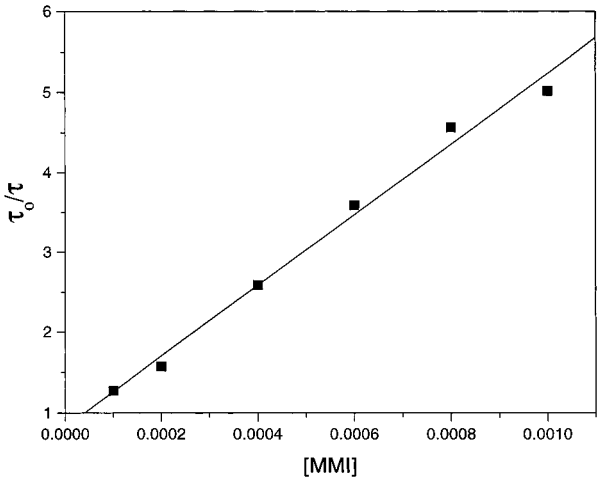

Figure 4. Stern−Volmer plot for lifetime quenching of 0.002 M benzophenone (0.002 M) triplet transient (excited at 266 nm—monitored at 530 nm) by MMI in nitrogen-sparged acetonitrile.

The laser flash results in Figures 3 and 4 are consistent with the rapid polymerization rate (Figure 1) for the HDDA/BP/MMI/MDEA system; i.e., the MMI triplet is populated by an efficient sensitization process ($k_q = 6.4 \times 10^9$ L mol^{-1} s^{-1}) from the triplet state of BP followed by an efficient ($k_q = 4.3 \times 10^9$ L mol^{-1} s^{-1}) electron transfer/proton transfer process. Since upon direct excitation the intersystem crossing quantum yield of BP is essentially 1.0 while that for N-substituted maleimides is approximately 0.23,[16] the triplet state population of *N*-alkylmaleimides is greatly enhanced by sensitization with BP. The production and subsequent reactivity of two reactive radicals which might be expected to result from the interaction of the MMI triplet with MDEA would be much more efficient in initiation of polymerization than for the direct BP/MDEA alone, where one of the radicals (the semipinacol) serves only as a chain terminator. Also, the smaller value ($k_q = 1.1 \times 10^9$ L mol^{-1} s^{-1}) for quenching of the BP triplet by MDEA, compared to the quenching of the BP triplet by MMI (6.4×10^9 L mol^{-1} s^{-1}), helps account for the ability of such a low concentration of MMI to quench the BP triplet, even in the presence of a higher concentration of MDEA. Herein, we have shown that sensitization of *N*-alkylmaleimides (in the presence of an aliphatic amine) by a triplet sensitizer results in enhanced production of radicals capable of initiating polymerization. We note that the results in this communication are consistent with the reported triplet sensitized cyclodimerizations of *N*-alkylmaleimides[18] and *N*-alkyldimethylmaleimides.[19]

In conclusion, we have shown that addition of benzophenone to a system containing a polymerizable acrylate monomer and an N-substituted maleimide results in a very rapid polymerization rate. Laser flash photolysis results show that benzophenone sensitizes the triplet state of *N*-methylmaleimide. Additionally, a very large rate constant for quenching the excited triplet state of *N*-methylmaleimide by an amine synergist suggests that an electron transfer process (presumably followed by proton transfer) is operative. The results presented herein provide a clear mechanistic account of the triplet sensitization of N-substituted maleimides and has implications for the future development of maleimides as photoinitiators for free-radical polymerization. Other results from our lab[16] show that a relatively slow hydrogen abstraction process (on the order of 10^7 L mol^{-1} s^{-1}) takes place for excited N-substituted maleimides with alcohols. Future publications describing sensitization of other types of N-substituted maleimides and related compounds will be forthcoming from our laboratory.

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