Macromolecules **2002,** *35,* 7963−7967

Effect of Amine Structure on Photoreduction of Hydrogen Abstraction Initiators

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Received November 19, 2001; Revised Manuscript Received June 11, 2002

ABSTRACT: The photocuring rates of acrylate monomers initiated by abstraction type photoinitiators (benzophenone, isopropylthioxanthone, and *N*-methylmaleimide) and a series of structurally different tertiary amine combinations are reported. Photo-DSC results confirm that transferable hydrogens on tertiary amines are essential for efficient acrylate polymerization. Laser flash photolysis experiments were carried out to define the electron/proton transfer reactions which occur between excited triplet states of the photoinitiators and tertiary amines. In the case of *N*-methylmaleimide, an intermediate radical anion was detected for amines with no readily transferable proton. This confirms that the photoreduction of the triplet state of N-substituted maleimides by tertiary amines occurs by an electron/proton transfer when the tertiary amine electron donor has a transferable proton.

Introduction

The photoreduction of triplet benzophenone (^{3}BP) by tertiary amines has been extensively investigated[1−3] and found to result in the formation of the radical anion of benzophenone ($BP^{\bullet-}$) followed by a proton transfer from the radical cation of the amine to form the semipinacol radical $BPH^{\bullet}$ and a radical derived from the amine (α-aminoalkyl radical). Accordingly, benzophenone has been shown to initiate free radical polymerization of acrylic systems when excited directly in the presence of amines such as triethylamine (TEA) and methyldiethanolamine (MDEA) which have readily transferable hydrogens.[4−7] The amine-derived radical initiates polymerization while the ketyl radical $BPH^{\bullet}$ is inefficient in initiating free-radical polymerization,[8] serving as a terminating species only. Isopropylthioxanthone (ITX) has also been shown to participate in an electron/proton transfer process with tertiary amines, forming an amine-derived radical and a diaryl ketyl radical similar to that for benzophenone.[9] And, as with BP/amines, ITX/amine systems also serve as effective photoinitiating system for free-radical polymerization.[6,10,11] Very recently, we proposed that the triplet states of N-substituted maleimides also participate in an electron/proton transfer process with tertiary amines and initiate free-radical polymerization.[4,5] It was suggested that a rapid electron transfer process occurred from the amine to the excited triplet state maleimide to give a radical anion (maleimide)/radical cation (amine) pair followed by subsequent transfer of a proton from the amine (Scheme 1). Unfortunately, because of the apparent rapid proton transfer, it was impossible to detect the maleimide radical anion with the laser flash photolysis apparatus used.

Recently, it has been reported that 1,4-diazabicyclo[2.2.2]octane (DABCO), diisopropyl-3-pentylamine (DIPA), and triisopropylamine (TIPA) quench ^{3}BP by an electron transfer process forming the anion radical of BP with no subsequent proton transfer due to the absence of a stabilizing two-center−three-electron interaction.[3,12] The BP radical anion was readily observed by laser flash photolysis. Thus, the use of such amines which have no readily transferable protons provides us with an excellent method for identification of radical ion intermediates in photochemical reduction processes such as those proposed in Scheme 1 for *N*-alkylmaleimides and amines. In this paper, we will use a combination of amines with and without readily transferable protons to substantiate the mechanism for generation of the reactive radical species produced by reduction of excited-state *N*-alkylmaleimides by trialkylamines depicted in Scheme 1. Before using laser flash photolysis to detect the radical anion of an *N*-alkylmaleimide, we will present results for the photoinitiated polymerization of a typical difunctional acrylate (1,6-hexanedioldiacryalte (HDDA)) using BP, ITX, and *N*-methylmaleimide (MMI) in combination with the series of amines. Two of the amines, TEA and MDEA, have readily transferable hydrogens while DABCO, TIPA, and DIPA do not. Thus, it is expected that the systems incorporating DABCO, TIPA, and DIPA will exhibit low rates of polymerization in cases where a proton transfer is necessary to produce initiating radical species. The various BP/amine and ITX/amine combinations will first be used to initiate the polymerization of HDDA. Only the initiator combinations which use the amines with transferable hydrogens (MDEA and TEA) are expected to yield rapid exotherm rates due to the generation of reactive initiating radicals. If, indeed, MMI/amine combinations proceed through a radical anion/radical cation pair as proposed in Scheme 1 (which is modeled after the electron/proton transfer reactions of BP and ITX with amine), then a similar pattern for photopolymerization to that observed for the BP/amine and ITX/amine systems should be observed for the MMI/amine mixture. After presenting the exotherm results and clearly showing the similarity in the MMI/amine be-

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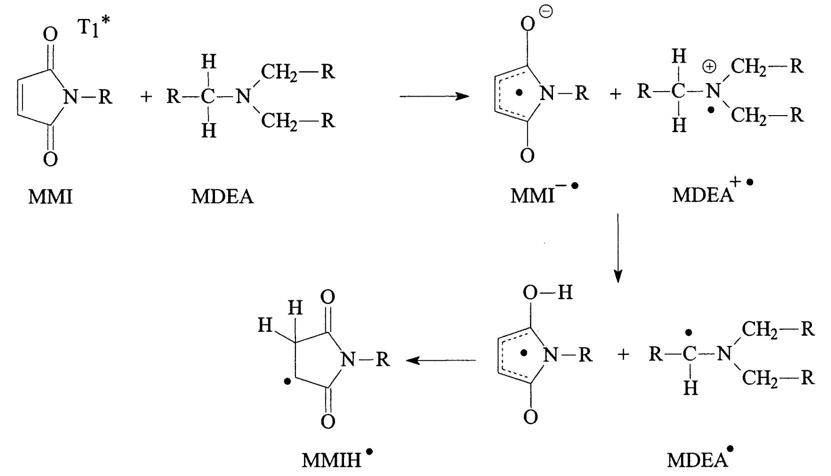
10.1021/ma0120308 CCC: $22.00

Scheme 1



Where

MMI = N-methylmaleimide

MDEA = Methyldiethanolamine

$MMI^{-\bullet}$ = Anion radical of N-methylmaleimide

$MDEA^{+\bullet}$ = Cation radical of methyldiethanolamine

$MDEA^{\bullet}$ = Methyldiethanolamine radical

$MMIH^{\bullet}$ = Succinimidyl radical

havior to the behavior of the BP/amine and ITX/amine systems, laser flash photolysis will be used to identify the radical anion of MMI and thus substantiate the mechanism proposed in Scheme 1.

Experimental Section

Materials. *N*-Methylmaleimide (MMI) was obtained from Aldrich Chemical Co. and purified by recrystallization and/or sublimation. 1,6-Hexanedioldiacrylate (HDDA) was obtained from UCB Radcure and used as received. Diisopropyl-3-pentylamine (DIPA) was obtained from Fluka Chemical Co. Isopropylthioxanthone (ITX) was obtained from Albemarle Corp. Acetonitrile was purchased from Burdick and Jackson. All other reagents, solvents, and materials were obtained from Aldrich Chemical Co. and used as received unless otherwise specified.

Laser Flash Photolysis Spectroscopy (LFP). LFP was performed using a Continuum Surelite Nd:YAG laser excitation source and a UV–vis absorption/emission monitoring system from Applied Photophysics. 266 nm excitation wavelength was used with laser energy of approximately 70 mJ. UV–vis absorbance at specific wavelengths was measured for each sample before the laser pulse (10 ns duration) and as a function of time after the laser pulse. Exponential fits of the resulting absorbance decay curves allowed calculation of the lifetimes of the transient excited-state species. The transient absorbance and lifetimes were measured as a function of monitoring wavelength, allowing reconstitution of the time-resolved UV–vis absorption spectrum of the transient excited-state species. Measurement of the transient lifetime at the transient absorption peak maximum as a function of quencher concentration allows calculation of the Stern–Volmer quenching rate constant (k_q) [13] through eq 1,

$$\tau_0/\tau = 1 + k_q\tau_0[Q] = k/k_0 = 1 + k_q[Q]/k_0 \qquad (1)$$

where τ_0 is the lifetime in the absence of quencher, τ is the lifetime at a given quencher concentration [Q], $k = 1/\tau$ is the rate for transient decay at a given [Q], $k_0 = 1/\tau_0$ is the rate for transient decay in the absence of quencher, and k_q is the Stern-Volmer quenching rate constant in L mol^{-1} s^{-1}.

Photo-Differential Scanning Calorimetry (Photo-DSC). Photo-DSC was performed on a Perkin-Elmer DSC-7 modified with quartz windows in the sample head cover and a shuttered 450 W medium-pressure mercury lamp. On-sample light intensities were maximal at about 65 mW/cm^2, with lower intensities obtained by increasing the distance between the lamp and DSC head. 2 μL samples were added to specially crimped aluminum DSC pans, leading to a theoretical sample thickness of about 190 μm, and then purged with nitrogen for 1 min prior to and during irradiation. Exotherms are presented in terms of polymerization rates (% s^{-1}) using a density of 1.01 mg/mL for HDDA and a heat of polymerization for HDDA of 689 mJ/mg.[14]

Results and Discussion

As indicated in the Introduction, to systematically study the effect of transferable hydrogens on the photopolymerization process of BP and ITX, which are known to undergo electron transfer process in the presence of amines, the photopolymerization exotherms must be recorded. The plots of polymerization rates vs irradiation time for 1,6-hexanedioldiacrylate (HDDA) incorporating BP in the presence of the five tertiary amines as the initiating system were recorded under identical conditions (Figure 1). As expected, the BP/MDEA and BP/TEA combinations in HDDA exhibit the largest polymerization rates. The BP/TEA system is less efficient than the BP/MDEA due, at least in part, to evaporation of TEA. (A separate experiment with a very low nitrogen purge time proves that BP/TEA exotherms are only slightly smaller than those for BP/MDEA.) In cases where no transferable hydrogens are present (DABCO, DIPA, and TIPA), the rates are very low, indicating inefficient polymerization. The slow rate of polymerization of HDDA using DABCO, DIPA, and TIPA results, no doubt, from a limited extent of proton transfer from the intermediate cation radical of the amine to the anion radical of BP resulting in the formation of a low concentration of the radical derived from the amine. Rates for HDDA polymerization incorporating ITX were also recorded in the presence of each amine (Figure 2). As in the case with BP, ITX/MDEA and ITX/TEA initiate acrylate polymerization very efficiently whereas rates using ITX with DABCO, DIPA, and TIPA are comparatively slow. These results in

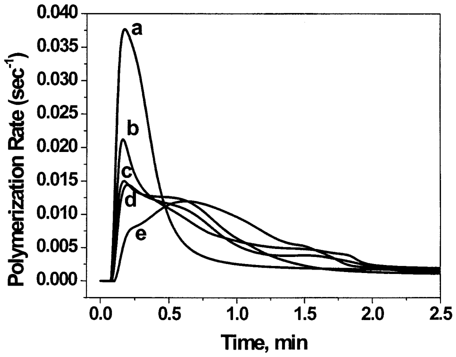


Figure 1. Polymerization rates for HDDA initiated by BP in the presence of tertiary amine synergist. Samples contain 0.275 M BP and the following amines (0.09 M): (a) MDEA, (b) TEA, (c) TIPA, (d) DIPA, and (e) DABCO. 2 μL samples were polymerized at 25 °C under a nitrogen atmosphere, with an on-sample light intensity of 53 mW/cm^2 from the full arc spectrum of a medium-pressure mercury light source.

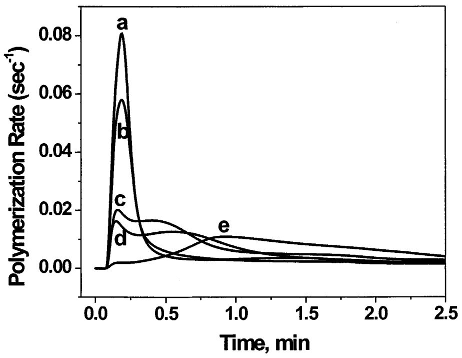


Figure 2. Polymerization rates for HDDA initiated by ITX in the presence of tertiary amine synergist. Samples contain 3.75 × 10^{-3} M ITX and the following amines (0.09 M): (a) MDEA, (b) TEA, (c) TIPA, (d) DIPA, and (e) DABCO. 2 μL samples were polymerized at 25 °C under a nitrogen atmosphere, with an on-sample light intensity of 64 mW/cm^2 from the full arc spectrum of a medium-pressure mercury light source.

Chart 1

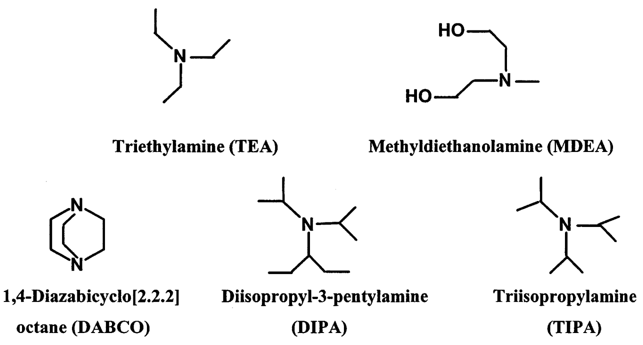


Figure 1 and 2 clearly show that the α-aminoalkyl radicals derived from the electron/proton transfer from TEA and MDEA efficiently initiate the polymerization of HDDA. Apparently, the anion radicals of BP and ITX and the amine-based cation radical, which are derived from electron transfer from DABCO, DIPA, and TIPA, are not capable of initiating free-radical polymerization efficiently.

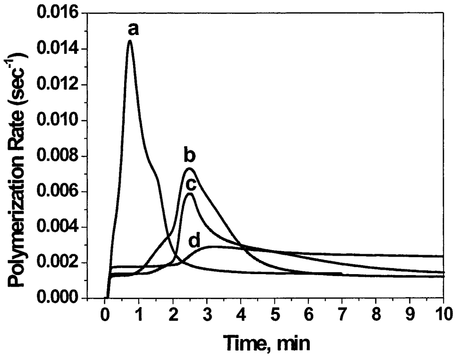


Figure 3. Polymerization rates for HDDA initiated by MMI in the presence of tertiary amine synergist. Samples contain 0.09 M MMI and the following amines (0.09 M): (a) MDEA, (b) TIPA, (c) DIPA, and (d) DABCO. 2 μL samples were polymerized at 25 °C under a nitrogen atmosphere, with an on-sample light intensity of 65 mW/cm^2 from the full arc spectrum of a medium-pressure mercury light source.

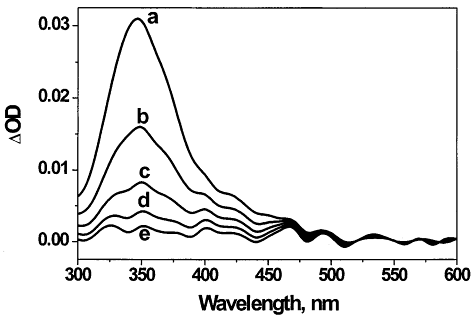


Figure 4. Transient UV–vis absorption spectra of 0.003 M MMI in nitrogen-sparged acetonitrile excited at 266 nm and recorded (a) 100, (b) 200, (c) 300, (d) 400, and (e) 500 ns after the laser pulse.

Figure 3 shows the polymerization rates vs irradiation time plots for MMI with the various amines. Although the exotherms are moderate due to the low triplet quantum yield for direct excitation of MMI ($\Phi_{ISC} \sim 0.2$),[15] the MDEA/MMI combination clearly initiates HDDA polymerization more efficiently than initiation by MMI with DABCO, DIPA, or TIPA. (The combination of the high volatility of TEA and a low polymerization rate made it impossible to obtain reliable exotherms for HDDA polymerization using the MMI/TEA initiator system.) A contributing factor to this low rate may be TEA evaporation. The results in Figure 3 strongly suggest that electron transfer from DABCO, DIPA, and TIPA to the triplet MMI results in the formation of the anion radical of MMI and the cation radical of the amine which are apparently inefficient in initiating polymerization. To verify the electron transfer processes and identify the intermediate maleimide radical anion, laser flash photolysis studies were carried out for the above MMI/amine combinations.

The transient absorption spectra of MMI in nitrogen-sparged acetonitrile (excited with a Nd:YAG laser at 266 nm) are shown in Figure 4. The peak maximum around 340 nm is assigned to the triplet state.[4] A decrease in lifetime of the MMI transient was observed in the presence of low concentrations of the tertiary amines, indicating efficient quenching of triplet maleimide by the tertiary amine. Earlier, we have shown that the MMI triplet lifetime is quenched by MDEA[4] with a rate constant of 4.3 × 10^9 L mol^{-1} s^{-1}. From the Stern–Volmer plot of triplet lifetime quenching displayed in Figure 5, a quenching rate constant of 8 × 10^9 L mol^{-1} s^{-1} was calculated for the MMI triplet quenching by DABCO. The quenching rate constants (k_q) for triplet MMI quenching by each of the tertiary amines with/without transferable hydrogens are tabulated in

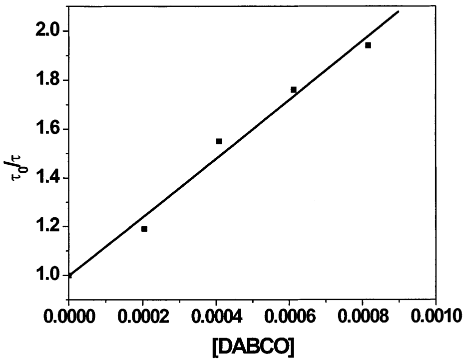


Figure 5. Stern−Volmer plot for quenching of 3 × 10^{-3} M MMI triplet transient (excited at 266 nm and monitored at 340 nm) by DABCO in nitrogen-sparged acetonitrile.

Table 1. Rate Constants for Triplet Quenching of Benzophenone and *N*-Methylmaleimide by Amines with and without Transferable Hydrogens[a]

amine	k_q[BP] × 10^{-9} (L mol^{-1} s^{-1})	k_q[MMI] × 10^{-9} (L mol^{-1} s^{-1})
MDEA	1.1[1]	4.3
DABCO	7.8[6]	8.0
TIPA	7.8[6]	1.1
DIPA	7.2[6]	7.8

[a] Samples in nitrogen-sparged acetonitrile are excited at 266 nm and the transients monitored at 520 and 340 nm for benzophenone and *N*-methylmaleimide, respectively.

Table 1. The presence of transferable hydrogens on the amines does not influence the quenching rate constant as the k_qs for all of the combinations are greater than 10^9 L mol^{-1} s^{-1} and not much less than that for diffusion-controlled quenching. It is noted that triplet BP is similarly quenched ($k_q > 10^9$ L mol^{-1} s^{-1}) by each of the amines irrespective of the presence of transferable hydrogens (Table 1). Since amines without transferable hydrogens (DABCO, DIPA, and TIPA) quench the maleimide triplet as efficiently as MDEA which has transferable hydrogens, it can be concluded that the electron transfer process is responsible for the quenching of the MMI triplet, producing a radical cation/radical anion pair. This conclusion agrees with that in ref 3 for BP quenching. As shown in Scheme 1, after formation of the anion radical of MMI, a proton transfer process is expected to follow if the amine has a transferable proton, as for example in the case of MDEA. If no transferable proton is present on the amine radical cation, then the radical anion of the maleimide should be detectable. The transient absorption spectra of MMI recorded in the presence of DABCO indeed confirm the formation of a relatively long-lived radical anion of MMI (Figure 6) by comparison with literature references for the absorption spectra of the radical anion of N-substituted maleimides obtained by pulse radiolysis.[16,17] The radical anion absorbs at almost the same wavelength (~330 nm) as the maleimide triplet but is clearly identified by its long lifetime. The peak absorption maximum of the radical anion at 330 nm is accompanied by a broad and weak absorption around 420 nm.[16] Note that even after 1 μs the anion radical is still clearly present. The transient decay at 330 nm can be fit to a double-exponential decay with lifetimes 75 ns and ~1 μs corresponding to the quenched triplet and radical anion, respectively. At these concentrations, in the absence of DABCO, MMI decays at 340 nm with a lifetime of ~150 ns. TIPA and DIPA, which also lack transferable hydrogens, also produce the anion radical of MMI as identified by laser flash photolysis. These results for MMI are in agreement with quenching of benzophenone triplet by DABCO, DIPA, and TIPA to form the BP anion radical absorbing at 710 nm.[3] Contrary to the results for DABCO, DIPA, and TIPA, addition of MDEA to MMI results in the complete loss of the triplet MMI absorption at 340 nm with no detectable long-lived absorbance with peak maximum near 330 nm attributable to a radical anion, i.e., there is no measurable transient species that persists at 1 μs in the MMI/MDEA system. These observations are consistent with a rapid proton transfer from the MDEA cation radical to the anion radical of MMI.

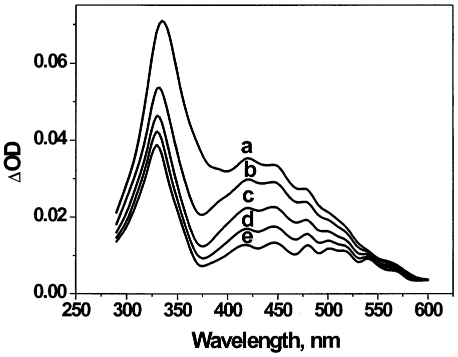


Figure 6. Transient UV−vis absorption spectra of 3.33 × 10^{-3} M MMI with 4.4 × 10^{-4} M DABCO in nitrogen-sparged acetonitrile excited at 266 nm and recorded (a) 100 ns, (b) 250 ns, (c) 500 ns, (d) 750 ns, and (e) 1 μs after the laser pulse.

Conclusions

Photo-DSC studies confirm that transferable hydrogens on tertiary amines are essential for initiating polymerization involving the triplet states of benzophenone, isopropylthioxanthone, and *N*-methylmaleimide. These results provide corroborating evidence that quenching of the triplet state of maleimide by amines with transferable protons occurs by an electron transfer process that is succeeded by a proton transfer. The anion radical of MMI was observed by laser flash in the presence of tertiary amines with no transferable hydrogens. When tertiary amines with transferable hydrogens are present, the anion radical of MMI is not observed due to a rapid proton transfer from the cation radical of the amine to the anion radical of MMI to produce the succinimidyl radical.

Acknowledgment. We gratefully acknowledge the financial support of Fusion UV Curing Systems and Albemarle Corporation for this investigation.

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MA0120308