

Effect of Electron Donor Structure on the Kinetics of Visible Three-component Photoinitiator Systems

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ABSTRACT

Three-component initiators generally include a light absorbing molecule which is typically a dye, an electron donor which is often an amine, and the third component, which is usually an iodonium salt. To characterize the fundamental polymerization principles that determine the effectiveness three-component photoinitiator systems based upon methylene blue (MB) as the dye, a systematic series of electron donors was used. The Rhem-Weller equation was used to verify the thermodynamic feasibility for photo-induced electron transfer from the electron donors to the MB. For each initiator system, the corresponding rate of polymerization was measured upon illumination with filtered light (400 nm bandpass filter) from a xenon-mercury lamp. Comparison of the photopolymerization kinetics of each two-component initiator system (containing the dye and amine) to those of the corresponding three-component system (with the addition of diphenyliodonium chloride (DPI)) allowed fundamental information regarding the role of the DPI to be obtained. It was found that the DPI enhances the photopolymerization kinetics in two ways: 1) it converts an inactive MB neutral radical to an active phenyl radical thereby regenerating the original methylene blue, and 2) it reduces the back electron transfer reaction in the dye/amine radical/cation ion pair. We conclude that factors such as the efficiency of proton transfer, back electron transfer, and the formation of radicals that are active in termination but not polymerization all have important effects of the efficiency of two and three component visible light initiator systems.

INTRODUCTION

During the last decade, visible photoinitiator systems have emerged as attractive alternatives for a variety of light-induced polymerizations. The improvement of new laser technologies¹ and industrial use of visible lasers has stimulated the design of more efficient photoinitiator systems for many applications where visible light initiation is used. For example, visible lasers are preferable for visible light applications such as production of holograms, color printing and microencapsulation due to lower cost and better performance¹. In addition, visible light initiation is preferable for biological applications such as dental restorations² and orthopedics³ due to the damaging effects of UV radiation. Finally, inexpensive visible light sources are readily available and visible photoinitiator systems offer tremendous flexibility in the selection of the initiating wavelength.

The energy of a photon in the visible region of the spectrum is less than the bond dissociation energy of most carbon-carbon bonds on organic molecules,¹ therefore visible photoinitiators have been primarily bimolecular initiator systems in which active centers are produced via electron transfer followed by proton transfer from electron donor to a photo-excited dye. In these two-component initiator systems, back electron transfer reaction always competes with electron transfer reaction because the back electron transfer reaction is also thermodynamically feasible. In addition, an inactive radical is also produced simultaneously (which is not active for initiation, but is active for termination) from the electron transfer/proton transfer reaction step. For these reasons, most visible two-component photoinitiator systems cannot achieve the higher polymerization kinetics that traditional UV photoinitiator systems can.

Three-component initiator systems may be produced by adding an iodonium salt to the two-component systems described above.^{4,5} Three component photoinitiator systems are offer important advantages and versatilities. For example, the initiator systems have been consistently reported to yield higher polymerization at lower light intensities than the corresponding two-component initiator systems⁴. In addition, the systems may be used to initiate free radical, cationic or controlled sequentially curable hybrid cationic/free radical photopolymerizations⁸. Finally, efficient photo-curing of thick section may often be achieved using three-component systems because the dyes typically undergo photobleaching during the reaction.

In this study, we have characterized the polymerization kinetics obtained using three-component initiator systems containing methylene blue (MB) as the dye, a systematic series of amines as the second component, and diphenyliodonium chloride (DPI) as the third component. Since methylene blue is a cationic dye, it does not undergo direct interaction with the diphenyliodonium (which is also cationic) due to electrostatic repulsion. For each initiator system, the corresponding rate of polymerization was measured upon illumination with filtered light (400 nm bandpass filter) from a xenon-mercury lamp. The use of a series of electron donors containing significantly different chemical structure allows us to characterize the effect of the electron donor structure on the polymerization kinetics. The Rhem-Weller equation was used to verify the thermodynamic feasibility for photo-induced electron transfer from the electron donors to the MB. Comparison of the photo-polymerization kinetics of each two-component initiator system (containing the dye and amine) to those of the corresponding three-component system (with the addition of diphenyliodonium chloride (DPI)) allowed fundamental information regarding the role of the DPI to be obtained. This contribution will provide the underlying guideline that may be used to select electron donor and to design effective visible photoinitiator systems based upon cationic dyes.

EXPERIMENTAL METHODS

Materials. The organic dye methylene blue was purchased from Aldrich Chemical Company and was used as received. The monomer 2-hydroxyethylmethacrylate (HEMA) was obtained from Aldrich and hydroquinone inhibitor was removed by treating it with De-Hibit (from Polysciences) and filtered using an inhibitor removal column (from Polysciences) prior to use. Diphenyliodonium chloride (DPI) was purchased from Aldrich and was used as received. All other electron donors were obtained from Aldrich and were used as received. The chemical structures of methylene blue (MB) and diphenyliodonium chloride (DPI) are shown in Figure 1. The absorption spectrum of methylene blue (MB) and diphenyliodonium chloride (DPI) as a third component are illustrated in Figure 2.

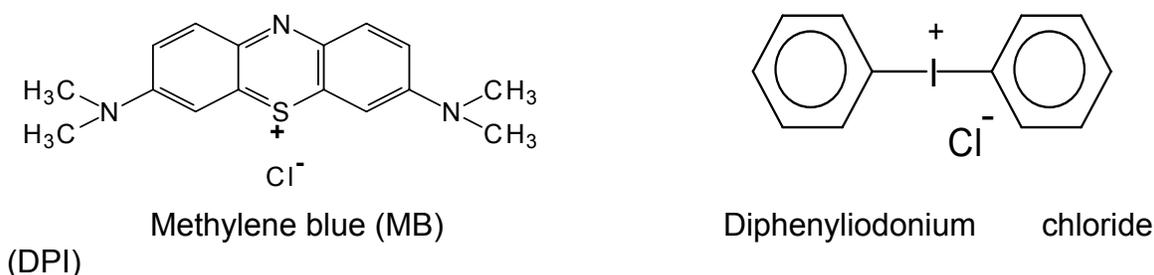


Figure 1. Light absorbing molecule and third component of photo-initiator systems

UV-Visible spectroscopy. The light absorbing molecule, Methylene blue (MB) dissolved completely upon addition to the monomer (HEMA). The UV-VIS absorption spectrum of the resulting solution was obtained using a Hewlett Packard 8452A diode array spectrophotometer. The UV-VIS absorption spectrum of DPI was obtained by the same method. Figure 2 illustrates the absorption spectrum of each component. The spectra show that only the methylene blue exhibits any absorption in the visible region of the spectrum. Diphenyliodonium chloride (DPI) absorbs only in the deep UV. The maximum absorption peak of MB in the HEMA solution is 662 nm.

Photo-differential Scanning Calorimetry (Photo-DSC). The rate of polymerization was measured by a Perkin-Elmer photo-differential scanning calorimeter 7 (Perkin-Elmer Photo-DSC 7) outfitted with a 200 W Oriel mercury-xenon (Hg:Xe) lamp. The output from the lamp was passed through a 400 nm bandpass filter and a water filter to remove both the ultraviolet and the infrared light. Methylene blue is the only component that absorbs the remaining visible light (indeed, no polymerization is observed in the absence of MB). The total light intensity of filtered light was $\sim 55 \text{ mW/cm}^2$, as measured by graphite disc absorption. The average sample size was approximately 12 mg. Nitrogen purging was used in Photo-DSC to eliminate oxygen inhibition of the polymerization. The heat flow data were collected by the DSC and the data can

be easily converted to the rate of polymerization using the heat of polymerization, which is 49.8 kJ/mol for HEMA⁹.

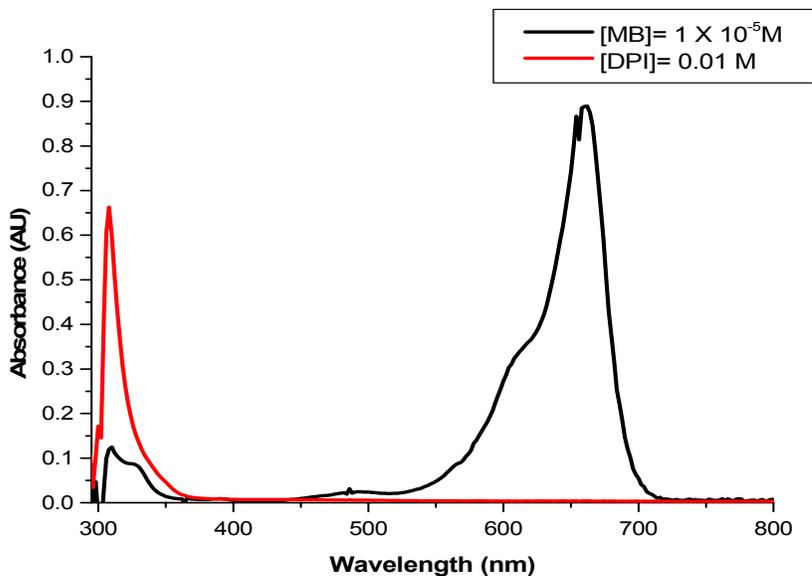


Figure 2. Absorption spectra of methylene blue (MB) and diphenyliodonium chloride (DPI). Each component was dissolved in HEMA.

RESULTS AND DISCUSSION

Thermodynamics of Photo-induced Electron Transfer Reaction. For the efficient design of photo-initiator systems, the thermodynamic feasibility for electron transfer from the electron donor to the dye must be verified. The results of the thermodynamic feasibility studies were used to select electron donors with varying chemical structures for the kinetic investigations. The Rhem-Weller^{10,11} equation was used to characterize the thermodynamic feasibility for photo-induced electron transfer from a variety of electron donors to the electron acceptor, methylene blue (MB). As shown below, the Rhem-Weller equation states that the free energy change associated with the photo-induced electron transfer corresponds to the energy change associated with the redox reaction, minus the excited state energy of the dye (effectively, the photon provides the energy necessary to make the electron transfer reaction happen).

$$\Delta G_{et} = F [E^{ox}(D/D^{\cdot+}) - E^{red}(A/A^{\cdot-})] - E^* + \Delta E_c \quad (1)$$

where

F is the Faraday constant

$E^{ox}(D/D^{\cdot+})$ is the oxidation potential of donor,

$E^{red}(A/A^{\cdot-})$ is the reduction potential of acceptor

E^* represents the excited state energy of the sensitizer (typically the triplet state)

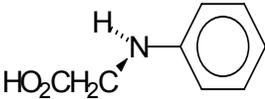
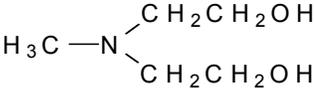
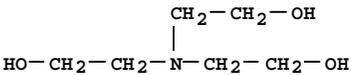
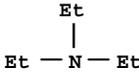
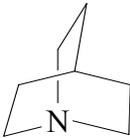
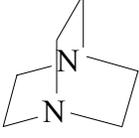
ΔE_c is the Coulombic stabilization energy (negligible for most systems)

This equation can be simplified by neglecting the Coulombic stabilization energy term, and is given by equation (2):

$$\Delta G_{\text{et}} = F [E^{\text{ox}}(\text{D}/\text{D}^{\cdot+}) - E^{\text{red}}(\text{A}/\text{A}^{\cdot-})] - E^* \quad (2)$$

Therefore, the free energy change can be estimated for a given dye and electron donor system if their redox potentials are known as well as the excited state energy of the dye.

Table 1. Thermodynamic Data for Electron Transfer from Amine to Methylene Blue

Electron Donor	Chemical Structure of Electron Donor	E_{ox} (V vs. SCE)	ΔG_{et} (kJ/mol)
NPG N-phenylglycine		0.77 ²	-33
MDEA N-methyldiethanolamine		0.72 ¹⁴	-38
TEOA Triethanolamine		0.90 ¹⁵	-20
TEA Triethylamine		0.97 ¹⁷	-14
ABCO quinuclidine		0.82 ²⁵	-28
DABCO 1,4-diazabicyclo[2.2.2]octane		0.57 ^{18,19,25}	-52

For these calculations, the reduction potential of MB is -0.32 V^{12} relative to a saturated calomel electrode (SCE) and the energy of the triplet excited state of the MB, 138 kJ/mol^{13} , relative to the ground state. Oxidation potentials of electron donors were taken from literature and converted to those relative to SCE in acetonitrile if SCE is not used as a reference electrode¹⁶.

For a photo-induced electron transfer reaction to be thermodynamically feasible, ΔG_{et} must be negative. For example, an electron transfer reaction between MB and electron donor can occur only if the oxidation potential of donor is below 1.11

V. Table 1 illustrates the oxidation potentials of electron donors and the Gibbs free energy changes for photo-induced electron transfer reactions with methylene blue.

Kinetics of photo-induced visible initiator systems. The thermodynamic feasibility of electron transfer from the donor to the acceptor described above is a strict requirement for all potential three component initiator systems. However, even if a three component initiator system is thermodynamically feasible, it may not be effective if there is not efficient kinetic pathway for production of the active centers. A wide variety of kinetic considerations may render an initiator system effective or ineffective. To investigate the structure of the electron donor on the polymerizations kinetics, photo-differential scanning calorimetry (photo-DSC) was used to investigate the polymerization kinetics. Figure 3 illustrates an example of a complete photopolymerization reaction profile obtained using photo-DSC. This figure illustrates the characteristic shape of the DSC reaction profile for free radical polymerizations of acrylates and methacrylates which exhibit autoacceleration. Both maximum rate of polymerization and time to reach maximum rate of polymerization can be obtained from the polymerization kinetic profile curve as shown in Figure 3, and these parameters were used to characterize the effectiveness of the photoinitiator systems.

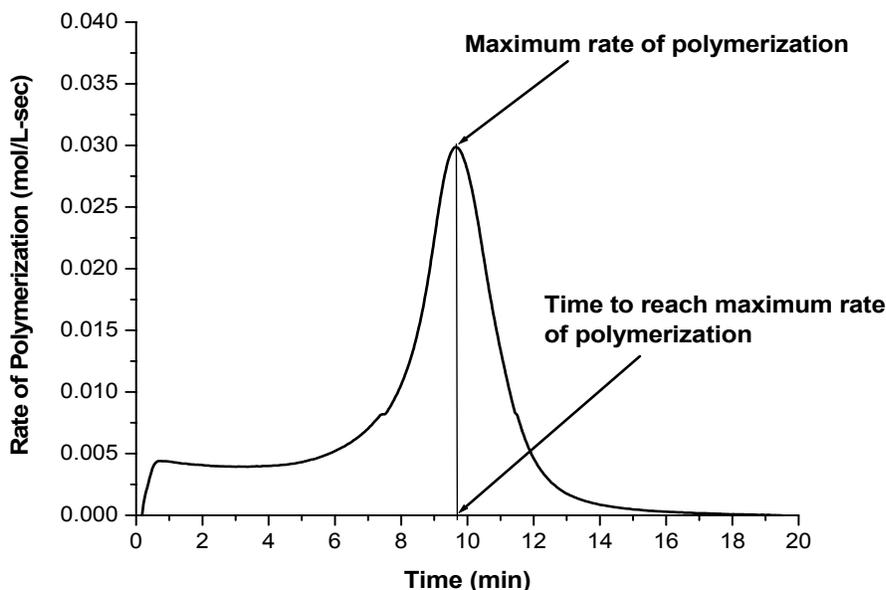


Figure 3. Representative photo-DSC reaction profile to illustrate the maximum rate of polymerization and time to reach maximum rate of polymerization.

Effect of unimolecular fragmentation on the polymerization kinetics. To characterize the effect of unimolecular fragmentation of the electron donor on the polymerization kinetics for reactions initiated using two-component initiator

systems, reaction rate profiles were obtained using methylene blue as the dye and four different amines as the electron donor. Three of the amines (MDEA, TEOA, and TEA) are “standard” electron donors which do not undergo unimolecular fragmentation, while the fourth, NPG, undergoes^{1,20} a unimolecular fragmentation reaction after it has donated an electron. This reaction is significant because it can effectively prevent back electron transfer. For each of the four initiator systems, the maximum rate of polymerization was obtained using photo-DSC, as shown in Figure 4. The most notable feature illustrated in the figure is the remarkable enhancement of the polymerization rate resulting from MB/NPG initiator system. The two-component initiator system containing MB and NPG exhibits the fastest reaction rate (maximum rate 0.017 ± 0.0017 mol/L-sec observed at 3.18 min). The MB/TEA initiator system shows the second highest maximum rate of polymerization (maximum rate 0.0069 ± 0.0003 mol/L-sec observed at 15 min). The third maximum rate of polymerization is observed in MB/MDEA initiator system (maximum rate 0.0056 ± 0.0002 mol/L-sec observed at 21 min) and MB/TEOA initiator system exhibits the lowest maximum rate of polymerization (maximum rate 0.0040 ± 0.0001 mol/L-sec observed at 22 min). MB and three typical amine two-component initiator systems demonstrate similar polymerization reaction profiles because these systems have similar typical kinetic mechanism and chemical structures of tertiary amines. The absorbance spectrum of the methylene blue is unaltered by the presence of the electron donors.

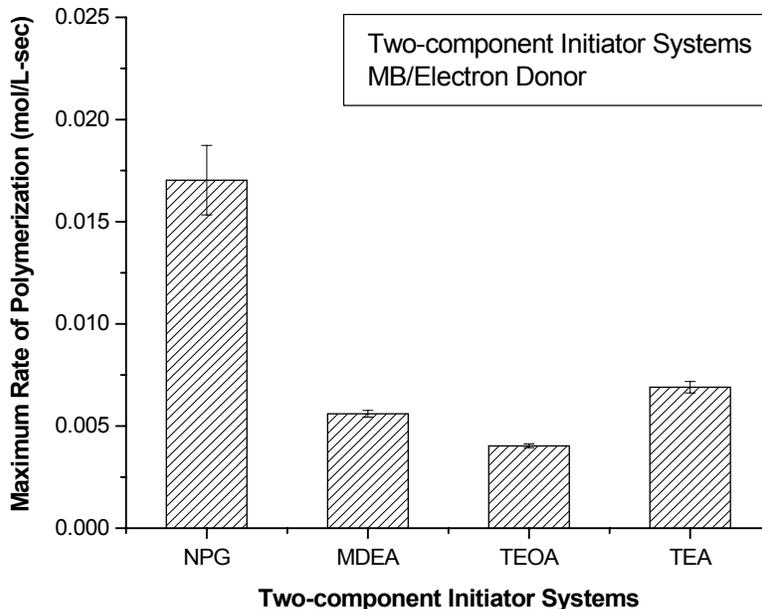


Figure 4. Maximum rate of polymerization for two-component initiator systems consisting of methylene blue and four different amines. For all systems, $[MB] = 5 \times 10^{-4}$ M and $[AMINE] = 0.25$ M in neat HEMA. Light intensity = ~ 55 mW/cm² (400 nm – 800 nm); Temperature = 50°C.

Figure 4 illustrates that the MB/NPG initiator system exhibits a maximum polymerization rate that is approximately three times faster than that observed any of the other two-component systems based upon methylene blue. This enhanced polymerization rate is attributed to the fact that the cation/radical of NPG formed by electron transfer decomposes rapidly to yield CO₂, a proton and a radical fragment^{1,20} as illustrated in Figure 5. This unimolecular fragmentation reaction, which is highly efficient and irreversible,¹ leads to the efficient yield of active radicals because this reaction helps to prevent back electron transfer. It is well accepted that, for an effective two-component initiator system, back electron transfer should be prevented. In addition, the unimolecular fragmentation reaction step does not need diffusion process or activation energy to yield active centers,¹ and the radical fragment directly initiates the photopolymerization. Gould *et al.*²¹, and Kucybala *et al.*² have demonstrated that the kinetics of decarboxylation in NPG-derivatives are extremely rapid. Therefore, the experimental results shown in Figure 4 demonstrate that MB/NPG initiator system leads to rapid polymerization rate due to the reduced back electron transfer.

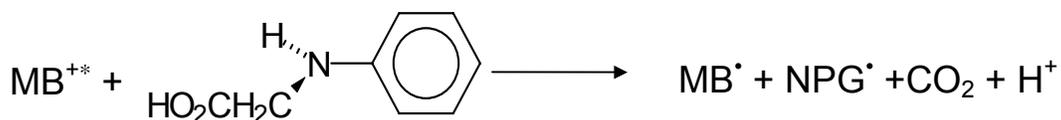


Figure 5. Photo-initiation by MB/NPG initiator system

Effect of a third (electron acceptor) component on the polymerization kinetics. A series of experiments were performed on the two-component initiator systems described above, to determine the effect of the addition of a third component, diphenyliodonium chloride (DPI) on the resulting polymerization kinetics. Therefore, photo-DSC polymerization profiles were obtained for each of the MB, amine combinations described in the previous sections, with the addition of 0.015 moles per liter of DPI. Note that since MB and DPI are both positively charged, they will not directly interact, and indeed the addition of the DPI had no effect on the absorbance spectrum of methylene blue. The results of these kinetic studies are shown in Figure 6, which contains a bar graph illustrating the maximum rate observed for each two component initiator system as well as the corresponding three component initiator system produced by the addition of DPI.

A number of interesting results are shown in Figure 6. First, the figure illustrates that in each case, the three component initiator system leads to a more rapid polymerization than the corresponding two component system. In addition, the figure illustrates that the two component systems containing the amines that do not undergo a unimolecular fragmentation reaction (MDEA, TEOA, and TEA) are enhanced more by the addition of the DPI than the one that does undergo this reaction (NPG). Specifically, the typical tertiary amine initiator systems such as MB/MDEA/DPI, MB/TEOA/DPI and MB/TEA/DPI generated approximately 9

times higher rate of polymerization than that of each two component initiator systems while MB/NPG/DPI initiator system produced approximately 3 times higher rate of polymerization than MB/NPG initiator system. Clues to the mechanism by which DPI enhances the effective of these initiator systems be found by examining the unique characteristics of the iodonium compounds. Most notably, iodonium salts are excellent electron acceptors. For example, the reduction potential (E_{red}) of the diphenyliodonium cation is only -0.2 V relative to a standard SCE (in contrast, the value for another class of electron acceptors, the triphenylsulphonium cation, is -1.2 V¹). Due to this very low reduction potential, a wide variety of compounds undergo thermodynamically feasible electron transfer with iodonium salts, including most compounds that possess an unpaired electron. Once the iodonium accepts an electron, it undergoes a rapid unimolecular fragmentation reaction, which prevents back electron transfer.⁴

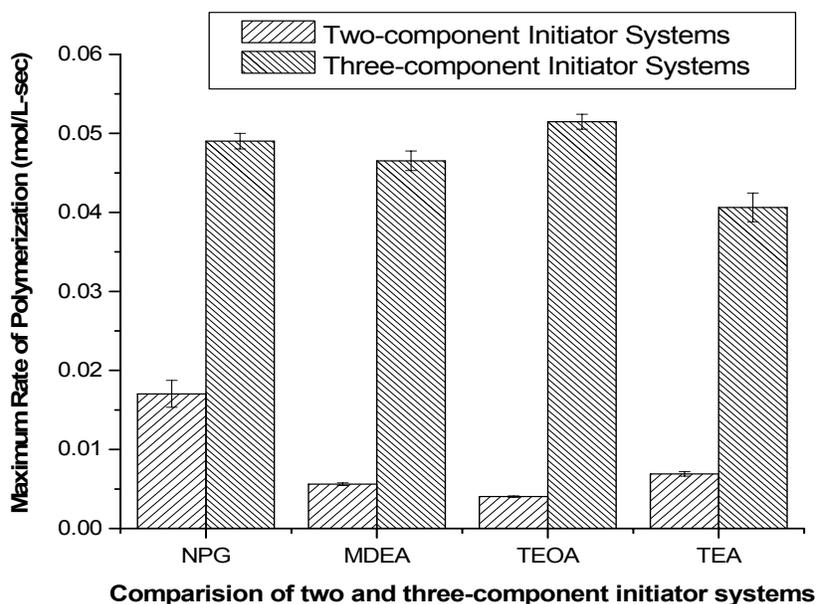


Figure 6. Maximum rate of polymerization for two and three-component initiator systems consisting of methylene blue and four different amines. For all systems, $[MB] = 5 \times 10^{-4}$ M, $[AMINE] = 0.25$ M, and $[DPI] = 0.015$ M, in neat HEMA. Light intensity = ~ 55 mW/cm² (400 nm – 800 nm); Temperature = 50°C.

Before explaining the mechanism by which the DPI enhances the polymerization rate, it is useful to examine the mechanism by which the two component initiator system produces active centers. In these systems, free radical active centers are produced by electron transfer from the amine to the photo-excited dye, followed by expulsion of a proton from the resulting amine cation. These two steps produce a neutral amine radical (which initiates polymerization) and a neutral MB radical (which is not active for initiation, but is active for termination^{4,5}). Based upon this information, the enhancement in

initiator effectiveness (illustrated in Figure 6), can be traced to ultimately arise from electron transfer from the neutral methylene blue radical to the DPI molecule, as shown in Figure 7 below. Therefore, according to this postulate, the primary photochemical reaction is the same in the two and three component initiator systems, and the effect of DPI arises from a secondary reaction step. It is notable that the original methylene blue dye will not interact with the DPI because they are both cationically charged. Therefore, this secondary reaction is the most likely explanation for the rate enhancement observed in the presence of the DPI. This is further supported by the observation that the rate of termination is reduced by the addition of DPI.⁵

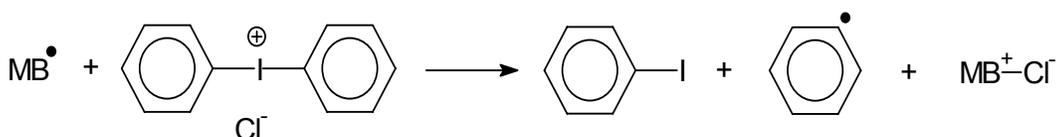


Figure 7. Electron transfer from the neutral methylene blue radical to the iodonium chloride.

The reaction shown in Figure 7 would enhance the photopolymerization rate due to dual roles of DPI : 1) in this reaction the DPI converts a neutral methylene blue radical (which is active for termination but not initiation) to a phenyl radical, which is active for initiation^{4,5,6,7} and the DPI regenerates the original MB dye, thereby allowing continue to participate in the primary photochemical reaction; 2) The secondary reaction step of three-component initiator mechanism also prevents back electron transfer from the amine to the dye since the neutral dye radicals formed by electron transfer with amine may directly react the an iodonium before they have the opportunity for back electron transfer. Of the four reaction systems shown in Figure 6, the MDEA, TEOA, and TEA systems benefit from all the effects upon addition of DPI while NGP system already has little back electron transfer. Thus, kinetic results shown in Figure 6 well illustrate that the evidence of dual roles of DPI on the polymerization kinetics. This may explain why the all four amines of three-component initiator systems lead to a similar polymerization rate in the presence of DPI.

Stereoelectronic effects of electron donors on the polymerization kinetics. In the two-component photoinitiator systems, an amine radical/cation is first produced by electron transfer from the amine to the photo-excited dye. The free radical active center is produced only upon proton transfer from this amine (to produce the active amine radical). The radical/cations formed by the first electron transfer step can be stabilized by conjugation between the unpaired electron and the nitrogen lone pair of electron donor²², and the amines assume 2-center-3 electron bonding after proton loss^{22,23}. As a result, proton transfer step or hydrogen abstraction step may be most easily carried out when the α -C-H bond broken can be eclipsed with the axis of the nitrogen lone pair orbital^{22,24}. However, electron donors containing rigid bicyclic structure such as 1,4-diazabicyclo[2.2.2]octane (DABCO)^{22,23,24,25} or quinuclidine²² (ABCO) have the α -

C-H bonds, which are held with a dihedral angle, θ of approximately 60° . Thus, these electron donors have C-H bonds, which are conformationally frozen into a 60° orientation with respect to the amine lone pairs²⁴ which prevents the 2-center-3 electron bonding after proton transfer²³. Therefore, the stereoelectronic effects of DABCO and ABCO make proton transfer or hydrogen abstraction virtually impossible for these amines even though electron transfer may occur²⁴ (recall that the thermodynamic feasibility of electron transfer with MB was confirmed in Table 1).

A series of experiments were performed to explore the impact of these stereoelectronic effects on two and three component initiator systems containing MB and DABCO or ABCO. The maximum rate of polymerization observed for MB/MDEA, MB/DABCO and MB/ABCO initiator systems are shown in Figure 8. The figure illustrates that the two-component initiator systems containing both MB/DABCO and MB/ABCO do not lead to any perceptible polymerization. These results illustrate the tremendous impact of the stereoelectronic effect and confirm the importance of proton transfer for the generation of an effective free radical active center. The literature contains a number of reports of electron transfer from DABCO and ABCO. For example, Raumer²³ *et al.*, observed free radical/cation ions of DABCO in the quenching of triplet benzophenone (BP). Pischel²⁴ *et al.*, also demonstrated high persistence of radical/cation ions of DABCO by the reversibility of the electrochemical oxidation. They suggested the persistence of the amine radical/cations is presumably related to a stereoelectronic effect rather than steric effects²⁴. Both proton transfer in the radical ion pair and deprotonation of the amine radical/cations are prevented from an unfavorable arrangement of the C-H bonds and the lone pair orbital in the radical/cations of DABCO²⁴. Based upon these results, DABCO and ABCO may undergo electron transfer with photo-excited dyes to produce radical/cations which exhibit higher stability than other electron donors.

We reason that the addition of DPI to the two-component systems MB/DABCO or MB/ABCO should lead to polymerization. In the electron transfer reaction, a neutral methylene blue radical is formed, and the oxidation of this radical by the DPI should lead to active centers, as illustrated previously in Figure 7. Therefore, photo-DSC reaction profiles were obtained for three component systems containing MB/DABCO/DPI or MB/ABCO/DPI, and the results are shown in Figure 9. Figure 9 illustrates that although the MB/DABCO and MB/ABCO two-component initiator systems do not lead to any appreciable polymerization, the corresponding three-component initiator systems (MB/DABCO/DPI and MB/ABCO/DPI) are effective as photoinitiators. These results provide convincing evidence of the secondary reaction step (as shown in Figure 7). Specially, these results verify that DABCO and ABCO do undergo electron transfer with methylene blue, and that the neutral methylene blue radical will react with DPI to produce a free radical active center.

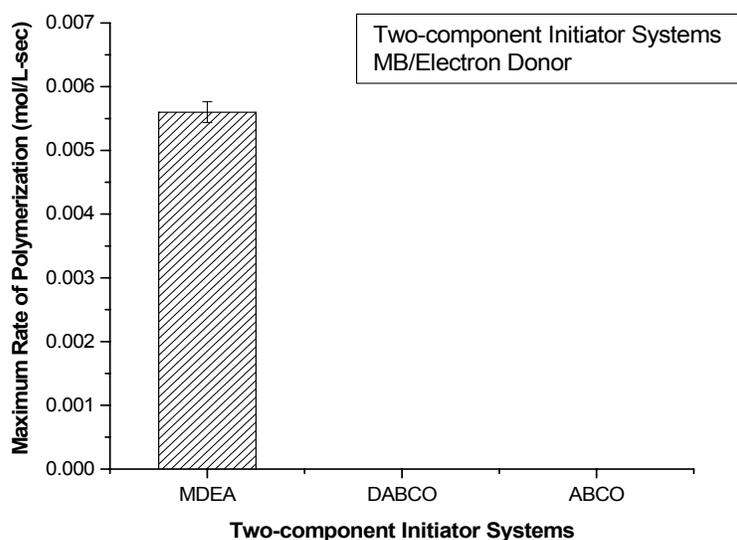


Figure 8. Maximum rate of polymerization for two-component initiator systems consisting of methylene blue and three different amines. $[MB] = 5 \times 10^{-4}$ M, $[AMINE] = 0.25$ M $[DPI] = 0.015$ M, all in neat HEMA. Light intensity = ~ 55 mW/cm², Temperature = 50 °C

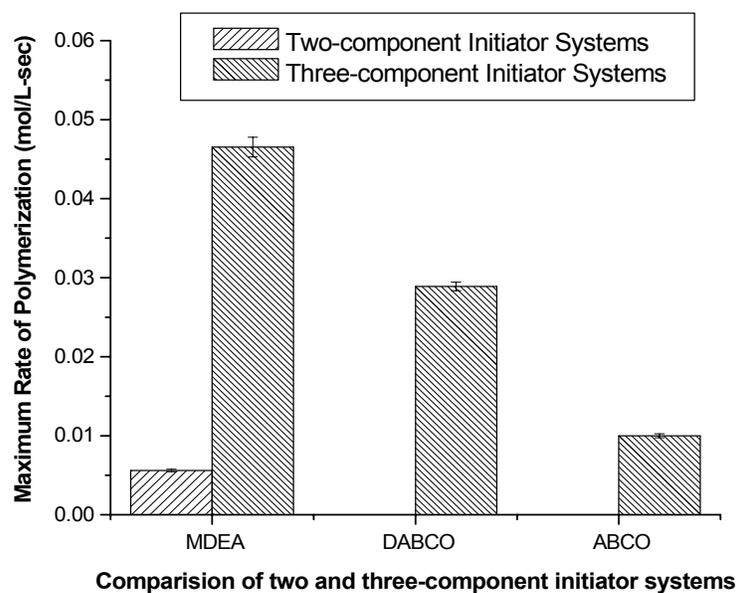


Figure 9. Maximum rate of polymerization for two and three-component initiator systems consisting of methylene blue and three different amines. $[MB] = 5 \times 10^{-4}$ M, $[AMINE] = 0.25$ M $[DPI] = 0.015$ M, all in neat HEMA. Light intensity = ~ 55 mW/cm², Temperature = 50 °C

CONCLUSIONS

In this study, a series of fundamental polymerization kinetics over two-component and three-component photo-initiator systems were presented. Thermodynamic feasibility for photo-induced electron transfer from a variety of electron donors to the electron acceptor, methylene blue (MB) was confirmed using the Rhem-Weller equation. A series of electron donors containing significantly different chemical structure were used to characterize the effect of the electron donor structure on the polymerization kinetics for two-component and three-component photo-initiator systems. Comparison of the photo-polymerization kinetics of each two-component initiator system (containing the dye and amine) to those of the corresponding three-component system (with the addition of diphenyliodonium chloride (DPI)) allowed fundamental information regarding the role of the DPI to be obtained. It was found that the DPI enhances the photopolymerization kinetics in two ways: 1) it converts an inactive MB neutral radical to an active phenyl radical thereby regenerating the original methylene blue, and 2) it reduces the back electron transfer reaction in the dye/amine radical/cation ion pair. In addition, we conclude that factors such as the efficiency of proton transfer, back electron transfer, and the formation of radicals that are active in termination but not polymerization all have important effects of the efficiency of two and three component visible light initiator systems.

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