Effect of the Electron Donor Structure on the Shelf-Lifetime of Visible-Light Activated Three-Component Initiator Systems

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ABSTRACT: In this study, we investigated the effect of electron donor structures on the shelf life of three-component initiator systems which also included methylene blue (MB) as a photosensitizer and diphenyl iodonium salt (DPI) as an electron acceptor. For this research, N-phenylglycine (NPG), N-methyldiethanolamine (MDEA), N,N-diisopropyl-3-pentylamine (DIPA), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were used as electron donors, with different of proton transfer efficiencies and radical/cation persistence. To aid characterization of the shelf-life or dark storage stability of three-component initiator systems, the relative polymerization kinetic profile of each freshly prepared initiator system was first obtained using photo-DSC. The standardized photopolymerization reactions were repeated after various dark storage intervals. Thermal stability of each initiator system was compared by applying a ramped temperature program to monomer samples in the DSC in the dark. To analyze the kinetic changes as a function of storage time more quantitatively, we suggested an equation and characterized the shelf-lifetime constant (k) of three-component initiator systems. From the experiments and analysis, we conclude that the order of shelf-life is consistent with the of radical cation (DH$^{\cdot+}$) persistence; DABCO > DIPA > MDEA > NPG, and inversely related to the proton transfer efficiency of the electron donor; NPG > MDEA > DIPA > DABCO. The effects of electron donor structures on thermal stability were consistent with the results of kinetic shelf-life experiments. This investigation provides an effective means to characterize as well as predict shelf lifetimes of initiator systems. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1535–1542, 2009

Key words: initiators; photopolymerization

INTRODUCTION

Three-component initiator systems generally include a photosensitizer (PS), which is typically a dye; an electron donor (DH); and a third component, which is usually an electron acceptor (EA) such as an iodonium or sulfonium salt. In recent years, a number of researchers have been exploring visible-light activated, three-component initiator systems as alternatives to UV initiation because of tremendous potential performance and benefits.[1–8] For example, owing to the safety advantages for biological applications as well as in thick section photo-curing, visible-light activated three-component initiator systems have been expanding into application areas such as dental restorative materials, bio-detections, color printing, holographically photopolymerized composites and microencapsulation.[9–13]

Three-component initiator systems are very efficient for the production of free radical active centers and tremendously promising for a number of industrial and biomedical applications; however, a potential problem in many of these systems is thermal stability and long-term dark storage stability.[14,15] For practical consideration in all applications, initiator systems must provide adequate shelf-life stability while also producing efficient, rapid polymerization on demand.[14] However, some visible-light-induced photoinitiator systems undergo loss of sensitivity upon dark storage after only a few days.[14] For example, it was reported that the sensitivity of methylene blue/N-phenylglycine, two-component initiator system decreases to 43% after one day.[14,16] Alternatively, a lack of photoinitiator stability can result in premature polymerization. In addition, it is notable that the interaction of a nucleophilic electron donor with a dye may lead to loss of initiator efficiency.[15–18] The photo-induced electron transfer process that produces active centers may, in many cases, also be thermally induced in the dark.[15] Therefore, the thermal stability and shelf life of fully formulated multi-component visible-light initiator systems in monomer is often less than that for the corresponding UV-activated material.

Despite their excellent benefits and potential to produce rapid and broad spectral sensitivity, dye-
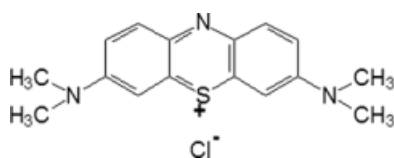

Figure 1 Chemical structure of MB.

sensitized initiating systems still have limitations in photoimaging applications.[15,16] Dark polymerization reactions between electron donor and the dye, the monomer, or other components of these systems often occur because the nucleophilic electron donor can deprotonate the dye, thereby changing its absorption spectrum and electron transfer characteristics.[15] For these reasons, many visible-light-induced initiator systems do not meet shelf-life stability requirements. For extended high shelf-life, each initiator component, individually and collectively, must have thermal and chemical stability.

In this study, we hypothesized that the shelf-life time of fully formulated reaction systems strongly depends upon the interactions and chemical structure of initiator systems. Therefore, once we retard any premature degradation or interactions among components of the initiator systems as well as between initiator and monomer, it may improve the storage stability of three-component initiator systems. We can speculate that a cationic dye does not engage in direct interactions with iodonium salt (which is also cationic) because of electrostatic repulsion. In addition, a basic dye also reduces direct interactions with nucleophilic electron donor as well. To test this hypothesis, methylene blue (MB) was selected as the photosensitizer because it is a cationic dye as well as MB a basic dye.

In this contribution, we investigated the effect of the electron donor's molecular structure on the thermal stability and dark storage stability for three-component initiator systems containing MB as the photosensitizer, four different amines as the electron donor, and diphenyl iodonium salt as the third component. Our studies will provide fundamental information regarding the effect of dye structure on the shelf-life time as well as suggest underlying guidelines for the selection of three-component initiator systems which lead to effective photoinitiators when illuminated, but remain stable in the absence of initiating light.

EXPERIMENTAL

Materials

The organic dye methylene blue (MB; Fig. 1) and diphenyliodonium chloride (DPI) were used in conjuction with a series of electron donors (DH): *N*-phenylglycine (NPG), *N*-methyldiethanolamine (MDEA),

N,N-diisopropyl-3-pentylamine (DIPA), and 1,4-diazabicyclo[2.2.2]octane (DABCO). 2-hydroxyethyl methacrylate (HEMA) was selected for these studies because it is a methacrylate monomer in which a wide variety of electron donors and electron acceptors are readily soluble. The hydroquinone inhibitor in the monomer was removed by treating it with a De-Hibit column (Polysciences).

UV-VIS Methylene blue (MB) dissolved completely upon addition to HEMA. The UV-vis absorption spectrum of the resulting solution was obtained using a Hewlett Packard 8452A diode array spectrophotometer. All UV-vis absorption experiments were performed at room temperature in neat HEMA. Figure 2 illustrates the absorption spectrum of MB. The maximum absorption peak of MB in HEMA is 662 nm. The figure illustrates that MB exhibits a broad, intense absorption between $\sim$ 500 and 700 nm, and an additional broad absorption band in the UV region between 300 and 350 nm. We observed the absorption spectrum of DPI exhibits absorption peaks between 300 and 360 nm and the four electron donors' absorb in the UV between 320 and 380 nm. Therefore, only MB exhibits any absorption in the visible region of the spectrum.

Shelf-lifetime experiments of three-component initiator systems

To investigate the effect of the electron donor on the shelf-life stability of three-component initiator systems, photo-differential scanning calorimetry (photo-DSC) was used to investigate the polymerization rate. The rate of polymerization was measured by a photo-DSC (Perkin-Elmer Photo-DSC 7) outfitted with a 200 W Oriel mercury-xenon (Hg:Xe) lamp as a photoinitiating light source. To control the atmosphere and to eliminate oxygen inhibition, the DSC
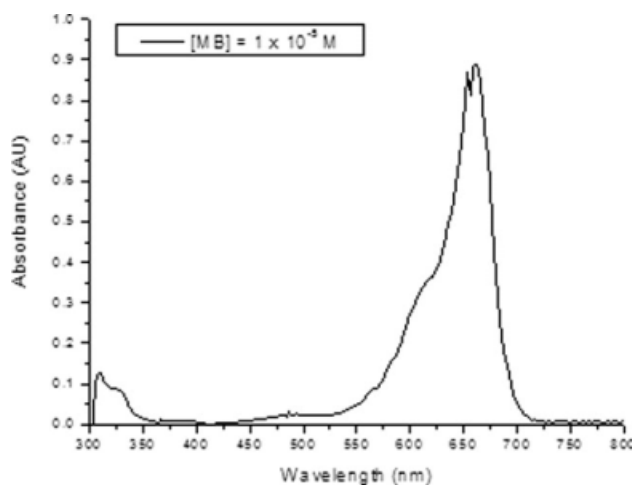

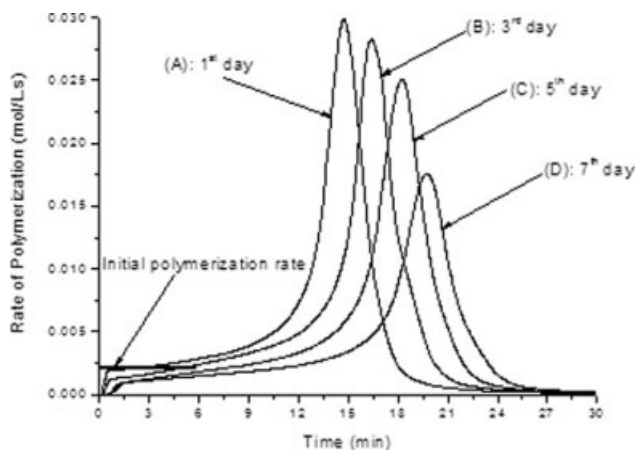**Figure 2** UV-vis absorption spectrum of MB dissolved in HEMA.

Figure 3 Representative photo-DSC reaction profiles to illustrate the initial polymerization rate and polymerization reaction profile changes as a function of storage time for shelf-lifetime studies with three-component initiator systems. The reaction profiles for (A), (B), (C), and (D) as a function of storage time were obtained for HEMA polymerizations in which the reactant concentrations are $[MB] = 5 \times 10^{-4}M$, $[DABCO] = 0.25M$, and $[DPI] = 0.015M$.

sample chamber was purged with nitrogen gas for 15 min prior to illumination, and throughout the reaction to eliminate oxygen inhibition of the polymerization. The flow rate of nitrogen gas was 20–30 cc/min. The incident irradiance of filtered light was ~ 55 mW/cm^2, as measured by graphite disc absorption. The average sample mass was approximately 12 mg and the reaction temperature was 50°C. For all samples, $[MB]_0 = 5 \times 10^{-4}M$, $[DH]_0 = 0.25M$ and $[DPI]_0 = 0.015M$ were used in neat HEMA. The output from the lamp was passed through a 400 nm bandpass filter and therefore, the photosensitizer (dye) is the only component that absorbs the transmitted visible light. The heat flow data were collected by the DSC and converted to the rate of polymerization using the heat of polymerization, which is 49.8 kJ/mol for HEMA.[4] For shelf-life experiments of three-component initiator systems, samples of the initiator systems were stored in the dark at room temperature and then initial polymerization rates were measured as a function of storage time as shown in Figure 3. From the photopolymerization reaction profile, the initial polymerization rate was obtained from each polymerization rate curve. For comparison of initiator systems, the initial rate of polymerization is practical because the initial rate of polymerization is directly proportional to the number of active centers created by the photoinitiator system.[7] Therefore, the initial polymerization rates were used as a kinetic parameter to characterize the kinetic effectiveness as well as to evaluate storage stability of the three-component initiator systems.

Thermal stability experiments of three-component initiator systems

To characterize the thermal stability of the initiator systems, DSC was also used to detect the onset of the exothermic polymerization as a function of temperature in the absence of light. Thermal stability temperatures of three-component initiator systems including MB as a photosensitizer (PS), an electron donor (DH) and diphenyl iodonium chloride (DPI) as an electron acceptor. Samples of the initiator systems in HEMA under a nitrogen purge in the dark were heated from 20°C to 100°C with 1°C/min for DSC sample chamber. For all samples, $[MB]_0 = 5 \times 10^{-3}M$, $[DH]_0 = 0.02M$ and $[DPI]_0 = 0.015M$ were used in neat HEMA. Figure 4 illustrates a representative temperature scan profile obtained using DSC, and shows the temperature of polymerization onset. The data was used to evaluate the electron donor structure effect on thermal stability of the three-component initiator systems.

RESULTS AND DISCUSSION

Effect of electron donor structure on the polymerization kinetics of three-component photoinitiator systems

A number of investigators have reported that three-component systems have consistently been found to be faster, more efficient, and more sensitive than their two-component counterparts[4–7]; photosensitizer
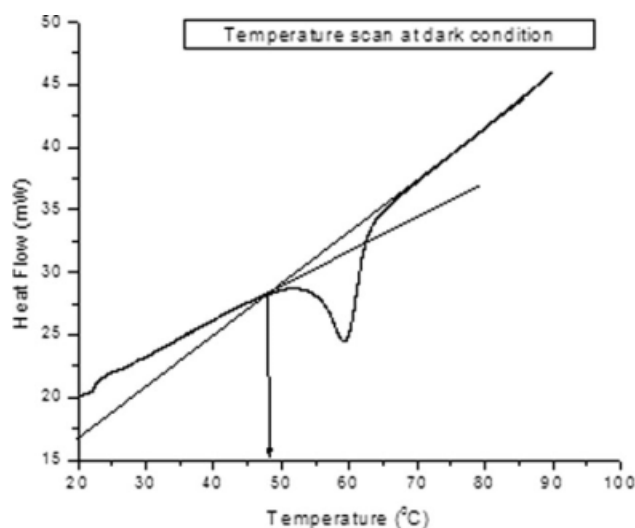

Figure 4 Representative thermal scan with DSC under completely dark conditions to illustrate effect of electron donor structure on the thermal stability of three-component initiator systems. The temperature scan was performed from 20°C to 100°C at 1°C/min. The temperature scan profile was obtained for the HEMA polymerization in which the reactant concentrations are $[MB] = 5 \times 10^{-4}M$, $[NPG] = 0.25M$, and $[DPI] = 0.015M$. MB/NPG/DPI initiator shows the temperature of onset of polymerization is 48°C ± 1.
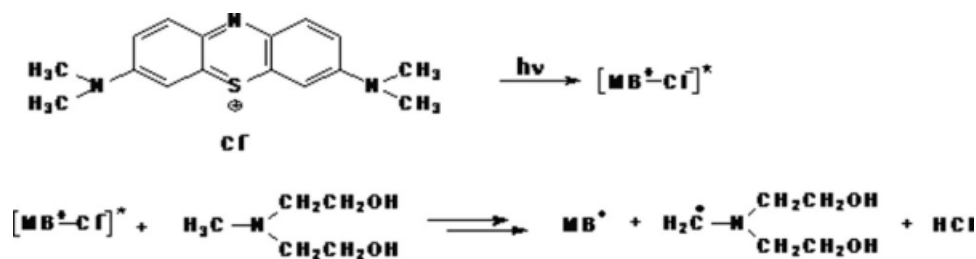
Figure 5 Visible-light activated initiation mechanism of a two-component initiator system with MB as a light-absorbing photosensitizer and MDEA as an electron donor. The two-component initiator system (MB/MDEA) shows that primary photo-reaction involves photo-induced electron transfer reactions between photo-excited MB dye and an electron donor, MDEA.

with either electron donor or electron acceptor. For example, Figure 5 illustrates the initiation mechanism of visible-light activated two-component initiator system with MB as a light-absorbing photosensitizer and MDEA as an electron donor. The two-component initiator system (MB/MDEA) undergoes primary photo-induced electron transfer reactions between the excited state of the MB dye and the electron donor. After electron transfer from the electron donor to the photo-excited MB dye, an initiating free radical active center (D·) is produced through a series of events which include separation of the radical pair that was created by the electron transfer step and proton transfer from the electron donor radical cation. The overall products are neutral amine radical (D·) capable of initiating polymerization, the neutral MB radical, an electron donor radical and HCl.[4] However, the MB/MDEA combination does not show effective initiation kinetics, leading to insufficient reaction kinetics and final conversions. These practical limitations lead to the development of visible-light-induced three-component initiators.

For example, Padon and Scranton[4] have illustrated that the initiation efficiency or reaction kinetics of a two-component electron transfer initiator system can be enhanced by the addition of a third component, such as an iodonium salt, which introduces a secondary reaction step as shown in Figure 6. Based upon kinetic trends and steady-state methylene blue fluorescence intensity, Padon and Scranton[4] concluded that DPI consumes an inactive MB radical and produces an active phenyl radical, and simultaneously regenerates the original MB, which leads to enhanced effectiveness of the three-component initiator systems for the production of free radical active centers. In this secondary reaction step, once the DPI accepts an electron, it fragments to produce an active, initiating phenyl radical along with a phenyl iodide molecule, which prevents back electron transfer.[7]

The selection criteria of the four different electron donors (amines) used in this shelf-life stability study are based on the radical/cation persistence and the proton transfer efficiency. We hypothesize that electron donors with high radical/cation persistence and/or limited ability for proton transfer may be efficient for extended storage stability. For efficient electron transfer and proton transfer reactions, the α—C—H bond of the electron donor must be eclipsed with the nitrogen lone pair orbital.[19–23] Since the radical/cation formed by the first electron transfer step can be stabilized by conjugation between the unpaired electron and the nitrogen lone pair of the electron donor, the amine assumes a 2-center-3 electron bonding after proton loss.[19–23] However, electron donors containing a rigid bicyclic structure such as DABCO have α-C-H bonds, which are conformationally frozen into a 60° orientation with respect to the amine lone pairs. This restriction prevents the 2-center-3 electron bonding after proton transfer.[24,25] It is also notable that the DABCO radical/cation shows extremely high radical cation persistence because the formation of a three-electron σ bond involves the positive charge being delocalized over both nitrogen atoms. For example, McKinney and Geske[26] demonstrated that DABCO produces unusual radical cation persistence in solution ($t_{1/2} \sim 1$ s in CH$_3$CN at 25°C).

In addition, DIPA has unusually high radical/cation persistence because the electron donor does not easily allow proton transfer due to its bulky substituents. Raumer and et al.[22] reported that while they observed unusual ionic transients in the presence of DABCO or DIPA in the quenching of triplet benzophenone (BP), this ionic transient could not be observed in the presence of typical tertiary amine such as triethylamine (TEA). Based upon transient absorption and transient photocurrent, these authors
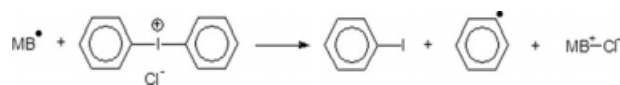

Figure 6 Electron transfer from the neutral methylene blue radical (MB$^\bullet$) to the iondonium chloride (DPI) in the secondary reaction step.
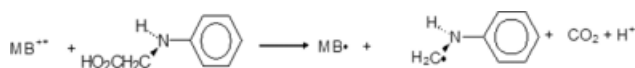
Figure 7 Schematic of the electron-transfer reaction from NPG to MB. The unimolecular fragmentation involving decarboxylation of the radical/cation of *N*-phenyl leads to the NPG radical.

concluded that this result arises from the particular structure of these amines, which influences the proton transfer efficiency. Furthermore, Raumer and et al.[22] reported that proton transfer of the sterically hindered DIPA does not occur easily despite the favorable geometrical arrangement of the α-C-H bond with respect to the axes of the N-lone pair.

In contrast, NPG shows high proton transfer efficiency of the radical/cation because once NPG donates an electron, the radical/cation of NPG formed by electron transfer decomposes rapidly to yield CO_2, a proton and a radical fragment[16,18,27,28] as shown in Figure 7. From the unusual unimolecular fragmentation reaction, NPG demonstrates extremely high proton transfer efficiency and the decarboxylation of the radical/cation of N-phenyl-substituted amino acid is extremely rapid. Finally, MDEA was selected as a standard tertiary amine. Hence, we may expect the order of efficiency of proton transfer from the electron donor as NPG > MDEA > DIPA > DABCO, which is opposite the order of radical/cation persistence.

Before characterizing the effect of electron donors on the polymerization rates, the thermodynamic feasibility of the photo-induced electron transfer reaction was verified using the Rehm-Weller equation[29,30] for each of the photoinitiator systems. Table I demonstrates the oxidation potentials of electron donors and the Gibbs free energy changes for photo-induced electron transfer reactions with MB. It confirms that the photo-induced electron transfer is indeed thermodynamically feasible for all of the selected electron donors. As expected, Table II demonstrates that the order of the initial polymerization rates coincide with the proton transfer efficiency of the electron donors; NPG > MDEA > DIPA > DABCO. The initial photopolymerization rates (Fig. 3), which were obtained from the Photo-DSC polymerization rate curves, are useful to characterize the number of active centers initially formed by the photoinitiator system.[7] As described above, because NPG undergoes an essentially irreversible unimolecular fragmentation reaction after it has donated an electron, the MB/NPG/DPI three-component initiator produced the highest initial polymerization rate. In contrast, MB/DABCO/DPI three-component initiator generated the lowest initial polymerization rate because of the lack of proton transfer from DABCO. The MB/DIPA/DPI initiator produced a lower initial polymerization rate than the MB/MDEA/DPI initiator due to its lower proton transfer efficiency as previously described.

TABLE I
Thermodynamic Data for the Photo-Induced Electron Transfer Reaction

Electron donor	Chemical structure of electron donor	E_{ox} (V vs. SCE)	ΔG_{et} kJ/mol
N-phenylglycine (NPG)		0.77[28]	−33
N-methyldiethanolamine (MDEA)		0.72[2]	−38
N,N-diisopropyl-3-pentylamine (DIPA)		0.72[20]	−38
1,4-diazabicyclo[2.2.2]octane (DABCO)		0.57[19]	−52

For these calculations, the reduction potential of MB is −0.32 V[31] relative to a saturated calomel electrode (SCE) and the energy of the triplet excited state of the MB, 138 kJ/mol,[32] relative to the ground state. The oxidation potentials of electron donors were taken from literature and converted to those relative to SCE. These values are used for calculation of free energy changes by Rehm-Weller[29,30] equation; $\Delta G_{et} = F [E_{ox}(D/D^+) - E_{red}(A/A^-)] - E^*$.

**The Effect of Electron Donor Structure on the Initial Polymerizations Rate for Initiator Systems Containing
Methylene Blue (MB) as a Photosensitizer (PS), an Electron Donor (DH) and
Diphenyl Iodonium Chloride (DPI) an Electron Acceptor**

MB/DH/DPI	NPG	MDEA	DIPA	DABCO
Initial Polymerization Rate (mol/L s)	0.0234 ± 0.0007	0.0069 ± 0.0006	0.0052 ± 0.0005	0.0021 ± 0.0005

For all systems, [MB] = 5 × $10^{-4}M$, [DH] = 0.25M, and [DPI] = 0.015M, in neat HEMA. Light intensity = ~ 55 mW/cm^2 (400 nm−800 nm); Temperature = 50°C.

Effect of electron donor structure on the shelf-life of three-component photoinitiator systems

To investigate the effect of electron donor structure on the shelf-life storage stability of three-component initiator systems, we measured the polymerization reaction profiles for the four different initiator systems as a function of dark storage time. We observed that the order of the dark storage stability of the three-component initiator systems is reverse that order of the proton transfer efficiency of the electron donors. For example, the MB/NPG/DPI initiator exhibited very low shelf-life stability with a decrease to approximately 50% of its initial reactivity after 24 h storage. This result is consistent with the reported trends for reduced activity in MB/NPG initiated polymerizations.[14,16] The decarboxylation of the radical/cation of the N-phenyl-substituted amino acid is extremely rapid, which is very effective for initiation kinetics but also lead to decreased shelf-life. Thus, MB/NPG/DPI demonstrates an extremely high proton transfer efficiency but provides a poor shelf-life time. In contrast, the MB/DABCO/DPI initiator produced the lowest initiation kinetics but resulted in excellent storage stability.

Figure 3 illustrates the effect of electron donor structure on the shelf life as a function of dark storage time obtained using photo-DSC. This figure demonstrates the systematic decrease in both the initial and the maximum polymerization rates with the MB/DABCO/DPI initiator as a function of storage time up to one week. To analyze the kinetic changes as a function of storage time more quantitatively, we assume that the initial polymerization rates decrease exponentially and that a shelf-lifetime constant (k) of three-component initiator systems may be determined from the exponential decay of initial polymerization rate. Based upon this assumption, we suggest the following equation to characterize the shelf-lifetime constant (k):

$$R_i(t) = R_{i,\infty} + R_{i,s} \exp(-t/k) \qquad (1)$$

where, R_i (t): initial polymerization rate based on shelf-life, (mol/L s); t: time (h); $R_{i,\infty}$: initial polymerization rate at $t \to \infty$, (mol/L s); $R_{i,s}$: decay gradient of initial polymerization rate, (mol/L s); k: shelf-lifetime constant (h).

For example, the initial polymerization rates as a function of storage time (from Fig. 3) were fit to this equation using nonlinear regression, to yield values for the shelf-life time constant (k), the infinite initial polymerization rate ($R_{i,\infty}$), and the decay gradient of initial polymerization rate ($R_{i,s}$). The results of this analysis are shown in Figure 8, which contains the nonlinear least squares fit superimposed on the original data of the initial polymerization rates. The figure illustrates that both the experimental data and the best-fit curve exhibit a characteristic shape in which the initial polymerization rate decreases exponentially with increasing storage time. The good fit of the regression indicates that our assumption over the time scale of this experiment is reasonable and the equation of initial polymerization rates of shelf-life time is valid for three-component initiator system.

The shelf-lifetime constant for three-component initiator systems (Table III) illustrates that tremendous effect of electron donor structure. The data clearly indicate DABCO is the most effective electron donor for good storage stability with high shelf-lifetime (121 h): 1.3–4.8 times higher than the other electron donors. The effectiveness of DABCO may arise
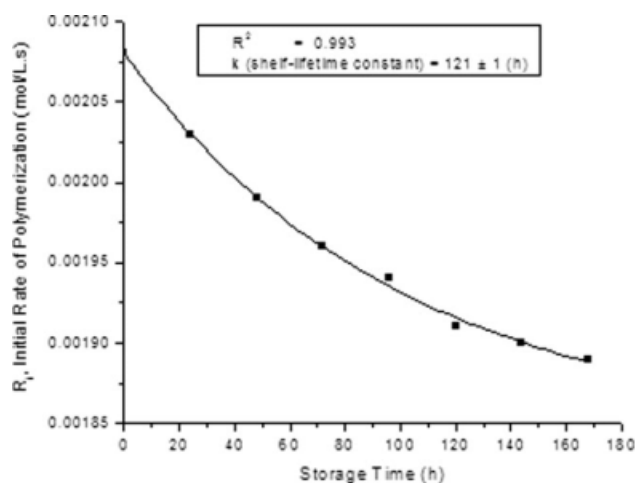

Figure 8 Nonlinear least squares fit to determine the shelf-lifetime constant (k), infinite initial polymerization rate of shelf-life at $t \to \infty$ ($R_{i,\infty}$), and decay gradient of initial polymerization rate of shelf-life ($R_{i,s}$). Initial polymerization data were taken as a function of storage time for MB/DABCO/DPI initiator system.

TABLE III
Effect of Electron Donor Structure on the Shelf-Lifetime for Initiator Systems Containing Methylene Blue (MB) as a Photosensitizer (PS), an Electron Donor (DH) and Diphenyl Iodonium Chloride (DPI) an Electron Acceptor

Initiator systems	k (shelf-life time constant, h)	$R_{i,s}$ (mol/L s)	$R_{i,\infty}$ (mol/L s)	R^2
MB + NPG + DPI	24.98 ± 5.36	$2.05 \times 10^{-2} \pm 2.71 \times 10^{-3}$	0	0.947
MB + MDEA + DPI	52.51 ± 2.43	$1.72 \times 10^{-3} \pm 3.00 \times 10^{-5}$	$5.19 \times 10^{-3} \pm 2.0 \times 10^{-5}$	0.999
MB + DIPA + DPI	90.0 ± 1.0	$6.00 \times 10^{-4} \pm 3.00 \times 10^{-5}$	$5.38 \times 10^{-3} \pm 1.0 \times 10^{-5}$	0.988
MB + DABCO + DPI	121.0 ± 1.0	$2.60 \times 10^{-4} \pm 8.91 \times 10^{-6}$	$1.82 \times 10^{-3} \pm 5.32 \times 10^{-6}$	0.993

Samples of the various initiator systems in HEMA were stored under completely dark conditions and then initial polymerization rates were measured as a function of storage time. For all systems, $[MB] = 5 \times 10^{-4}M$, $[DH] = 0.25M$, and $[DPI] = 0.015M$, in neat HEMA.

from its unusual radical/cation persistence. The order of shelf-life stability is consistent with the order of magnitude of the radical/cation persistence; DABCO > DIPA > MDEA > NPG, but is entirely opposite the order of proton transfer efficiency for the of electron donors. Specifically, as a standard tertiary amine, the MDEA initiator system yields a shelf-lifetime ~ 52 h but DIPA and DABCO initiator systems, with higher radical/ cation persistence, show ~ 90 h and ~ 121 of shelf-life, respectively. It is notable that the observed experimental shelf-lifetime (~ 24 h) for MB/NPG/DPI is consistent with our shelf-lifetime analysis value (~ 25 h) as shown in Table III. The result suggests that eq (1) is valid to characterize shelf-life time of three-component initiator systems. In fact, we observed that HEMA formulated with MB/NPG/DPI did not generate any perceptible polymerization because the formulation had already begun to polymerize within 24 h.

In Table III, the effect of electron donor structure on the observed decay gradient of initial polymerization rate of shelf-life ($R_{i,s}$) reflects the proton transfer efficiency in Table II. For example, Figure 8 illustrates that both the experimental data and the best-fit curve exhibit a characteristic shape in which the initial polymerization rate decreases gradually with increasing storage time, which indicates DABCO initiator system shows the lowest value of $R_{i,s}$. In contrast, the initial polymerization rate of NPG initiator system decreases sharply within 24 h, which provides the highest value of $R_{i,s}$.

Also Table III shows the effect of electron donor structure on the observed the infinite initial polymerization rate of shelf-life at $t \to \infty$, $R_{i,\infty}$. It is interesting to note that the $R_{i,\infty}$, value initial polymerization rate of shelf-life of the NPG initiator system shows zero, which indicates this initiator system is very unstable. In addition, the $R_{i,\infty}$ data of the DIPA initiator system is relatively higher than that of MDEA initiator system. This result suggests that while polymerization kinetics of the MDEA initiator system is more efficient than the DIPA initiator system, the latter is characterized by greater initiator stability. Furthermore, although the DABCO-based initiator system is very

stable, it also shows a low value of infinite initial polymerization rate. Because DABCO generates only one free radical active center, this initiator system produces a low initial polymerization rate and a low infinite initial polymerization rate.

Effect of electron donor structure on the thermal stability

To more convincingly support the shelf life results, a series of experiments were carried out to investigate the effect of electron donor structure on the thermal stability of three-component initiator systems. Under the completely dark conditions, thermally induced reaction profiles were obtained using differential scanning calorimetry (DSC) in a standardized thermal ramp mode. The temperature at which reaction starts is characterized by the intersecting slopes of reaction profile as shown in Figure 4. The onset temperatures are shown in Table IV. These thermal stability results are consistent with the trends obtained with the photo-based reaction shelf-life results as might be anticipated from time-temperature correlation studies.

As anticipated, the NPG initiator system showed the lowest thermal stability with a thermally induced reaction onset of 47–49°C. On the other hand, MB/

TABLE IV
Thermal Stability Temperatures of Three-Component Initiator Systems Including Ethylene Blue (MB) as a Photosensitizer (PS), an Electron Donor (DH) and Diphenyl Iodonium Chloride (DPI) as an Electron Acceptor

Electron Donor	Temperature (°C)
N-phenylglycine (NPG)	48 ± 1
N-methyldiethanolamine (MDEA)	59 ± 3
N,N-diisopropyl-3-pentylamine (DIPA)	78 ± 3
1,4-diazabicyclo[2.2.2]octane (DABCO)	83 ± 3

Samples of the initiator systems in HEMA under a nitrogen purge in the dark were heated from 20 to 100°C with 1°C/min for DSC sample chamber. For all samples, $[MB] = 5 \times 10^{-3}M$, $[DH] = 0.02M$, and $[DPI] = 0.015M$, in neat HEMA.

DIPA/DPI and MB/DABCO/DPI initiator systems exhibited relatively high thermal stability with reactions initiating at 76–81°C and 80–85°C, respectively. From these results, we expect that DIPA and DABCO may be used for elevated-temperature photoinitiator systems such as hot-melt processes. The MB/MDEA/DPI initiator provided an intermediate thermal stability temperature of 56–62°C.

Accordingly, these overall results illustrate the tremendous impact of the effect of electron donor structure on the reaction kinetics, shelf life and thermal stability of initiator systems. Specifically, the order of initial polymerization kinetics is the same order of proton transfer efficiency of electron donor; NPG > MDEA > DIPA > DABCO. However, the order of high shelf-lifetime and thermal stability is opposite the order of proton transfer efficiency of the electron donor because shelf-lifetime and thermal stability are strongly dependent on the magnitude of the radical/cation persistence. Therefore, while MB/NPG/DPI initiator showed the highest polymerization kinetics, it also led to the lowest shelf-lifetime and thermal stability. In contrast, the MB/DABCO/DPI initiator showed the lowest polymerization kinetics along with the highest shelf-lifetime and thermal stability.

CONCLUSIONS

In this study, we investigated the effect of electron donor structures on the shelf-life of three-component visible light initiator systems based on MB as a photosensitizer, DPI as an electron acceptor and a variety of amine electron donors. To characterize the shelf-life, the change in the polymerization reaction profiles of each of the initiator systems were obtained using photo-DSC following varied dark storage times. To analyze the kinetic changes as a function of storage time more quantitatively, we suggest an equation and characterized the shelf-lifetime constant (k) of three-component initiator systems. From the experiments and analysis, we concluded that shelf-life stability is consistent with the order of radical/cation persistence (DABCO > DIPA > MDEA > NPG) and inversely related to the proton transfer efficiency for the electron donors, which correlates the order of initial photopolymerization reaction kinetics. To further support the shelf-lifetime results, the thermal stability results of HEMA containing the different three-component initiator systems were analyzed and found to be in agreement with the shelf-life experimental results. Finally, we suggest the need to find an appropriate compromise between reactivity and stability for the rational design of three-component visible-light initiator systems.

References

 1. Grotzinger, C.; Burget, D.; Jacques, P.; Fouassier, J. P. Polymer 2003, 44, 3671.
 2. Kim, D.; Stansbury, J. W. J Polym Sci Part A: Polym Chem 2009, 47, 887.
 3. Kim, D.; Scranton, A. B., Stansbury, J. W. J Polym Sci Part A: Polym Chem 2009, 47, 1429.
 4. Padon, K. S.; Scranton, A. B. J Polym Sci Part A: Polym Chem 2000, 38, 2057.
 5. Bi, Y.; Neckers, D. C. Macromolecules 1992, 25, 541.
 6. Padon, K. S.; Kim, D.; El-Maazawi, M.; Scranton, A. B. Photoinitiated Polymerization; ACS Symposium Series 847, American Chemical Society: Washington, D.C., 2003; pp 15–26.
 7. Kim, D.; Scranton, A. B. J Polym Sci Part A: Polym Chem 2004, 42, 5863.
 8. Oxman, J. D.; Jacobs, D. W.; Trom, M. C.; Sipani, V.; Ficek, B.; Scranton, A. B. J Polym Sci Part A: Polym Chem 2005, 43, 1747.
 9. Yeniad, B.; Albayrak, A. Z.; Olcum, N. C.; Avci, D. J Polym Sci Part A: Polym Chem 2008, 46, 2290.
10. Catel, Y.; Degrange, M.; Pluart, L. L.; Madec, P. J.; Pham, T. N.; Picton, L. J Polym Sci Part A: Polym Chem 2008, 46, 7074.
11. White, T. J.; Natarajan, L. V.; Tondiglia, V. P.; Lloyd, P. F.; Bunning, T. J.; Guymon, C. A. Polymer 2007, 48, 5979.
12. Liu, V.A.; Bhatia, S. N. Biomed Microdev 2002, 4:4, 257.
13. Burdick, J. A.; Peterson, A. J.; Anseth, K. S. Biomaterials 2001, 22, 1779.
14. Crivello, J. V.; Dietliker, K. Photoinitiators for Free Radical Cationic and Anionic Photopolymerizations, 2nd ed.; Wiley: New York, 1998; Vol. 3, p 229.
15. Monroe, B. M.; Weed, G. C. Chem Rev 1993, 93, 435.
16. Eaton, D. F. Photogr Sci Eng 1979, 23, 150.
17. Paczkowski, J.; Kucybala, Z. Macromolecules 1995, 28, 270.
18. Gould, I. R.; Lenhard, H. R.; Muenter, A. A.; Godleski, S. A.; Farid, S. J Am Chem Soc 2000, 122, 11934.
19. Hub, W.; Schneider, S.; Dörr, F.; Oxman, J. D.; Lewis, F. D. J Am. Chem Soc 1984, 106, 701.
20. Pischel, U.; Zhang, X.; Hellrung, B.; Haselbach, E.; Muller, P. A.; Nau, W. M. J Am Chem Soc 2000, 122, 2027.
21. Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. J Am Chem Soc 1981, 103, 619.
22. Raumer, M. V.; Suppan, P.; Haselbach, E. Chem Phys Lett 1996, 252, 263.
23. Viswanathan, K.; Hoyle, C. E.; Jönsson, E. S.; Nason, C.; Lindgren, K.; Macromolecules 2002, 35, 7963.
24. Lewis, F. D.; Ho, T. I. J Am Chem Soc 1980, 102, 1751.
25. Nelsen, S. F.; Gannett, P. M. J Am Chem Soc 1982, 104, 4698.
26. McKinney, T. M.; Geske, D. H. J Am Chem Soc 1965, 87, 3013.
27. Crivello, J. V.; Dietliker, K. Photoinitiators for Free Radical Cationic and Anionic Photopolymerizations, 2nd ed.; Wiley: New York, 1998; Vol. 3, p 247.
28. Kucybala, Z.; Pietrzak, M.; Paczkowski, J.; Lindén, L.-Å.; Rabek, J. F. Polymer 1996, 37, 4585.
29. Rehm, D.; Weller, A. Ber BunsenGes Phys Chem 1969, 73, 834.
30. Rehm, D.; Weller, A. Isr J Chem 1970, 8, 259.
31. Kojima, M.; Kuriyama, Y.; Sakuragi, H.; Tokumaru, K. Bull Chem Soc Jpn 1991, 64, 2724.
32. Murov, S. L.; Carmichael, I.; Hug, G. L. Handbook of Photochemistry, 2nd ed., Marcel Dekker, Inc.: New York, 1993; p 30.