# Three-component dye sensitized systems- extending the initiation wavelength limit

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## Abstract

Three-component photo-initiator systems: photo-sensitizer (PS), electron-donor (ED), electron-acceptor (EA) can cure acrylic monomers more efficiently than their two-component counterparts. However, in most cases they display a limited stability at room temperature, i.e. initiation efficiency decreases over dark storage time, or spontaneous “dark” polymerization is promoted. The source of the instability can be correlated to basic chemical parameters such as ionization potential of ED and diffusivity of the components affecting the association and dissociation constants for the complex (instabilities) and exciplex (photopolymerization) intermediates. In many cases thermal stability is inversely proportional to photoinitiation efficiency, as dictated by photo-induced (PET) and ground state (ET) electron transfer mechanisms. In this work, thermal stability and photoinitiation efficiency are examined based on choice and concentration of the initiator components, as well as monomer/solvent properties. Thus, correlating thermodynamic and kinetic parameters of the PET and ET pathways with chemical structure and composition. Trends identified will aid in the design and development of improved photoinitiators sensitive to red light. Systematically designed three-component systems for visible light activated free radical curing could be very valuable in a wide range of applications from biomaterials to laser imaging technologies and lithography.

## Introduction

Three-component photoinitiators have gained interest as alternative to create long-wavelength curable photopolymerization systems. Visible light sources are becoming increasingly available, compared with UV-curing units, offering greater wavelength flexibility, less heat build-up and lower costs. Biological applications, including dental restorations, orthopedics, and tissue engineering[1–3], along with lithography and laser imaging technologies have a need for lower energy light sensitive formulations that do not compromise the photopolymerization efficiency. Even though several different systems studied both in the patent and academic literature have shown promising results regarding photopolymerization efficiency, their use has been limited due to the increase complexity in the mechanism leading to thermal instability.

Three-component photoinitiators are composed of a photosensitizer (PS), an electron donor (ED), and an electron acceptor (EA). These work through either one of three types of mechanisms: photo-reducible, photo-oxidizable or parallel. In this work only photo-reducible systems are considered. The two-component initiation mechanism (PS and ED) proceeds first through formation of an exciplex, followed by sequential electron-transfer (ET) and proton-transfer (if possible depending on the ED structure) from an alpha position to the heteroatom to produce active radicals. Prior work has

demonstrated dramatic increases in initiation efficiency from two to three-component systems[4–6]. Investigators have explained the enhanced polymerization rates by the participation of the EA in the photo-induced electron transfer (PET) mechanism, i.e. reduction of back-electron transfer, creation of a second active radical species per photon absorbed by the EA, and a means to recycle consumed PS. Three-component formulations can cure acrylates and methacrylates efficiently with comparable polymerization rates to some UV curing formulations[2,4,7,8]. Furthermore, it is a more practical and frequently more effective alternative than the, sometimes challenging, task of synthesizing a visible-light sensitive molecule to produce active radicals upon photocleavage. The major complication is these molecules have limited stability due to the fact that ground state (GS) reactions are thermodynamically feasible in the majority of the cases. And, as we increase the number of components we increase the complexity of these GS reactions. So, compared with one or two-component initiators, three-component systems commonly show reduced stability (shelf-lifetime), i.e. polymerization reactivity decreases after storage in the dark at room temperature (~ 23 ˚C; RT), or spontaneous polymerization occurs in the dark[9]. No work has been reported in instability analysis, and theoretical approaches to maximize both stability and photopolymerization efficiency in red-light sensitive formulations composed of a PS, a tertiary amine and an onium salt.

The goal of this study is to analyze general theoretical approaches to increase the stability of re-light sensitive three-component formulations composed of a PS, a tertiary amine as ED and an onium salt as EA. Example formulations are briefly analyzed to exemplify the complexity of both dark and photoinduced reactions in order to complement previously reported trends on the mechanisms involved.

This serves as guide for improving thermal stability in photopolymerization formulations without significantly compromising the photopolymerization efficiency gained by the addition of a third component (EA) to conventional dye-sensitized two-component systems. General methodologies proposed will aid implementation of novel three-component initiator systems with longer shelf lives and high initiating rates for use in a wide variety of industrial applications.

## Methods and experiments

### Materials

Methylene blue (MB), Camphorquinone (CQ), Diphenyliodonium chloride salt (DPI-Cl), Diphenyliodonium hexafluorophosphate (DPI-Ph), N,N-diisopropylethylamine (DIPEA) and 4-Ethyldimethylaminobenzoate (EDMAB) were used interchangeably for the initiating three-component system formulations. 2-Hydroxyethylmethacrylate (HEMA) was selected for this work because it is a methacrylate monomer in which components used are readily soluble. Methanol and acetonitrile were used as solvents. All materials were commercially obtained from Aldrich (Milwaukee, WI) in spectro grade, and used as received.

### Light source

A modified dental curing light unit (Max, DENTSPLY/Caulk, Milford, DE) was used for photopolymerizations. This halogen light, with its internal filter removed, emitted a broadband white light output of 400-800 nm. It was used with a 500 nm cut-off filter so that only MB is excited by the incident illumination (500-800 nm), i.e. no direct photochemical dissociation of DPI-Cl occurs.

Irradiance of the light source was measured before every experiment with a radiometer (6253, International Light Technologies, Peabody, MA).

**Ultraviolet-visible (electronic) spectroscopy (UV-Vis)**

A diode array spectrophotometer (Evolution 300, Thermo-Scientific, West Palm Beach, FL) was employed. Absorption spectra were collected in quartz cuvettes with a 1 cm pathlength (l). The $\lambda_{max}$ (665 nm) and maximum extinction coefficient ($\varepsilon_{max}$= 78,500 $cm^{-1}/M$) for MB were confirmed to match reported values[11]. DIPEA/DPI salt solutions were analyzed at room temperature and a volume of 3 $cm^3$ utilized for each collection. Collections were performed from 200 to 700 nm with a bandwidth of 1 nm.

**Fourier transform-infrared spectroscopy (FT-IR)**

HEMA bulk polymerization was monitored in real-time with a FT-Near-IR spectrophotometer (Nicolet Magna-IR Series II, Thermo Scientific, West Palm Beach, FL) by following the peak area of the first overtone absorption band for the methacrylate $=CH_2$ group ($\approx$6167 $cm^{-1}$). The spectrophotometer is equipped with a KBr beam splitter, a MCT/A detector, and an in-house fabricated horizontal stage adapted for in-situ photopolymerization experiments[16,17]. The distance between the light source and the sample was ~7 cm to ensure uniform irradiation over the sample with variable irradiance values. An 800 nm cut-off filter was used to protect the samples from the HeNe laser built in the IR as reference beam.

The sample holder for the in-situ polymerization, both in the dark and in the light, consisted of a 1 mm height, 1.6 cm diameter disc fabricated by sandwiching a perforated PDMS rubber shim in between two 1 mm thick glass slides held in place with metallic binder clips to prevent leakage of the injected monomer sample. Inhibition in the perimeter of the samples, i.e. where in contact with the PDMS rubber, was eliminated from the measurement by proper sample positioning and size. Temperature increase during polymerization of less than 10 ˚C was detected, confirming no thermally induced polymerization is possible upon heat build-up. Homogenous samples were prepared by vortexing.

**Differential Scanning Calorimetry (DSC)**

In this work, isothermal experiments were conducted to characterize the spontaneous polymerizations in the system in a DSC (Perkin-Elmer) adapted for photopolymerization experiments. Samples were place in an aluminum pan, and weighed to around 30 mg. Nitrogen was used to purge the chamber before every experiment. The nitrogen purge was set to 20 psi and started 10 min prior to the experiment in order to remove all oxygen present. Given the light sensitivity of the samples, every sample was weighed in a UV dark laboratory and exposure to visible-light was kept to a minimum. Additionally, a 5 min period at 20°C prior to the heating ramp was employed to identify any possible polymerization that could have started during the sample preparation process, none was observed. The heat of polymerization for HEMA, 49.8 kJ/mol, was used to convert the heat release data to the rate of polymerization.

## Results and discussion

### Photopolymerization efficiency

Three-component photoinitiators have been shown to efficiently produce neutral radicals active for the polymerization of (meth)acrylic monomers[3-5,16-18]. Photopolymerization of HEMA with the 3C initiation system is not only feasible, but also efficient, compared to a commonly used two-component initiator system, CQ/EDMAB (Figure 1- Left) (with equivalent photo activity of both formulations). Irradiation was started at t = 5 min. Polymerization rate is significantly enhanced with the addition of the DPI-Cl to the MB/DIPEA system[3]. In this particular case, the rate enhancement is very dramatic (Figure 1- Right). Concentrations of the initiating components were used based on typically used ratios. Amines are normally used in excess to increase quantum yield towards polymerization. MB is kept at a low concentration due to its high extinction coefficient and that it is expected to regenerate in the PET mechanism.

Modification of tertiary amine affects photopolymerization rate significantly. By changing the amine from DIPEA to EDMAB, lowering pKa value, no photopolymerization was observed. Neither amino nor aryl radicals are produced due to absence of PET between MB* and EDMAB. This indicates DPI-Cl does not produce aryl radicals by interacting with either MB*, MB or EDMAB. The EDMAB/DPI-Cl system in HEMA remained stable in the dark for months.

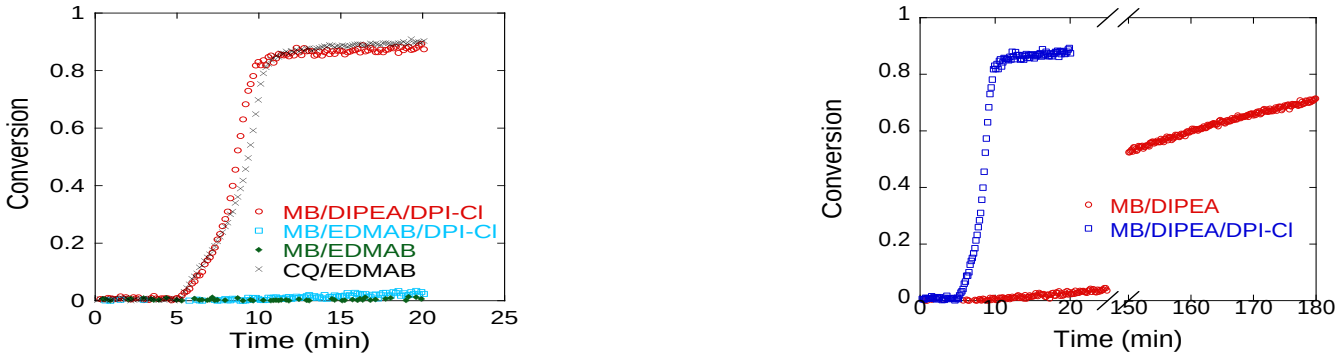


Figure 1. Left- Photopolymerization of HEMA: [MB] = 4 mM, [DIPEA] = [EDMAB] = 0.2 M, [DPI-Cl] = 0.04 M; [CQ] = 0.02 M, [EDMAB] = 0.05 M. Right- Photopolymerization of HEMA: MB systems- $I_a$ = 13 mW/cm^2 at λ= 500-800 nm; CQ systems- $I_a$ = 33 mW/cm^2 at λ= 400-500 nm.

### Thermal instability

MB/DIPEA/DPI-Cl system does not only initiate the methacrylate polymerization upon light exposure, but in the dark as well (Fig. 2- Left). Even though, dark reactions between amines and dyes have been mentioned since the development of dye-sensitized systems, only few have threated this or similar formulations[5,19]. Solutions prepared for the study of the photopolymerization of HEMA were not stable at RT for more than 24-48 h. In some cases, the final polymer material had a homogenous red-brown color; while in other samples a red-brown colored tacky surface remained over the colorless poly-HEMA. Several solutions were purged with argon (Ar) proving that the polymerization occurred even faster under these conditions than in the presence of oxygen. Other authors have reported DPI salts can

be broken into radicals after complexating with bases[6,20]. So, it is likely DIPEA and DPI-Cl form a 1:1 charge-transfer complex which leads to phenyl radicals, and iodobenzene.

In order to get a quantitative measurement of the extent of the spontaneous polymerization, the double bond concentration was monitored at RT within 24 h for all possible combinations of the initiating components. A standard mixing time of 10 min was used, during which no significant polymerization of HEMA was noticeable. Under these conditions (oxygen containing atmosphere), polymerization of HEMA occurred only when DIPEA and DPI-Cl were present. The effect of modifying or eliminating components is depicted, as well as the effect of storage time on the reactivity of DIPEA/DPI-Cl towards the radical polymerization (Fig. 2- Right).

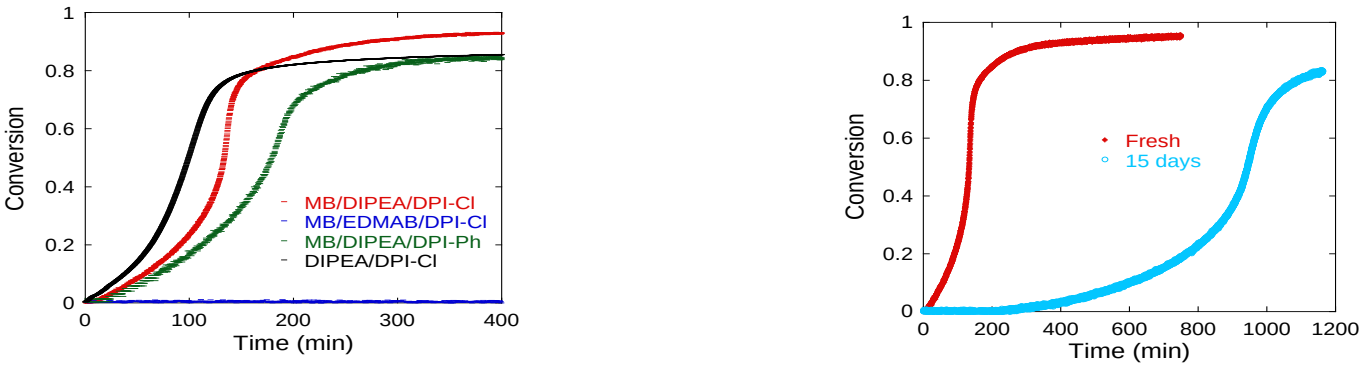


Figure 2. Left- Polymerization of HEMA (2C and 3C systems): [MB] = 4 mM, [DIPEA] = [EDMAB] = 0.2 M, [DPI-Cl] = [DPI-Ph] = 0.04 M. Right- Polymerization of HEMA (MB/DIPEA/DPI-Cl) at RT; no storage vs 15 days (2-4 ˚C) in the dark.

It can be seen that the addition of MB slows the spontaneous polymerization of the monomer. It is likely MB can function as a radical scavenger. Change from DIPEA to EDMAB completely eliminates the initiating reaction between ED and EA. This shows that both the PET and the GS ET processes involving the amine are equally or proportionally affected by the modification of the basicity of the amine. DPI-Ph seems to slow the polymerization rate, as a result of the increased counter-ion size.

Samples stored at 2-4 ˚C for weeks or months had a delayed onset of polymerization (after being templated to RT) and a reduced rate (Figure 4- Right). The latter could be related to a slow consumption of DIPEA and DPI-Cl during storage5. A change in coloration was also appreciable in stored samples with or without MB. This indicates reaction of DIPEA and DPI-Cl is the source of the change in reactivity with storage time in cases were the polymerization of the monomer is not thermodynamically preferred. The initiation of the HEMA seems to have a very narrow window for thermal stability (2-20 ˚C), but the reaction between excess DIPEA and DPI-Cl seems to have very low activation energy. Thus, this formulation seems to have a very low potential for reaching thermal stability. As could be expected, MB/DIPEA solutions also show a red-brown coloration after weeks dark storage without significant photobleaching of MB. But, interestingly, this GS reaction does not lead to polymerization of HEMA. So, it seems likely the DPI salt has the main role in active radical generation. And, amino radicals are not involved in the GS radical generation. To this point it is not clear if MB radicals formed are inactive for polymerization, or if the concentration is so low that inhibition is never overcome.

***Instability concentration dependence***

In order to establish whether the formulation could be made significantly more stable by adjusting the concentrations of DIPEA and DPI-Cl, the originally used concentrations were reduced and balanced stoichiometrically (Fig. 3- Left). The polymerization rate is decreased to the point were no spontaneous polymerization of HEMA is appreciable in a 48 h period in the dark at RT. The system was stable at 2-4 ˚C for months. But after storage, polymerization rate decrease significantly. The photopolymerization rate was noticeably decreased, in freshly made samples as well, compared to the formulation with higher DIPEA and DPI-Cl concentrations (Fig. 3- Right). Even if the radical concentration in the dark is not enough to effectively start the polymerization, DIPEA and DPI-Cl are being slowly consumed. GS reaction between DIPEA and DPI-Cl is thermodynamically feasible even at 2-4 ˚C with low concentrations.

In the photopolymerizations of stored (2-4 ˚C) samples with MB/DIPEA/DPI-Cl the final polymer had a red-brown residual tint upon MB photobleaching. Supporting the fact that even when no polymerization is observed during storage DIPEA and DPI-Cl are slowly reacting and changing the formulation potential reactivity upon light exposure.

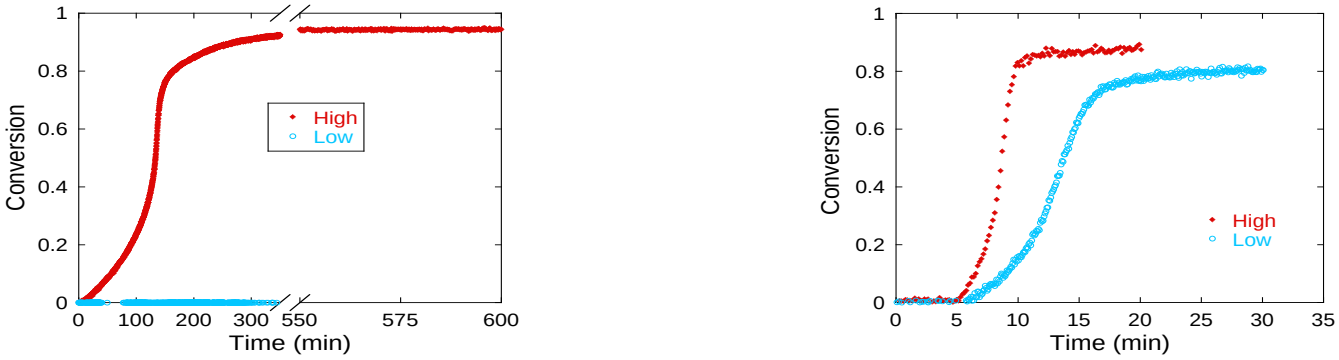


Figure 3. Left- Polymerization of HEMA (RT) (MB/DIPEA/DPI-Cl) : High) [MB] ≈ 4 mM, [DIPEA] ≈ 0.2 M, [DPI-Cl] ≈ 0.04 M; Low) [MB] ≈ 4 mM, [DIPEA] ≈ 0.05 M, [DPI-Cl] ≈ 0.02 M. Right- Photopolymerizations of fresh samples with $I_a$ = 13 mW/cm$^{\wedge 2}$ at λ= 500-800 nm.

***Temperature dependence of the ground state activation***

The GS reaction between the tertiary amine and the salt is proven to be highly temperature sensitive (Fig. 4). In these experiments, a nitrogen purge was used. No light activation was employed. With this we prove that dark redox activation is occurring in which DIPEA and DPI-Cl exchange an electron in their GS leading to the formation of one aryl radical upon dissociation of the GS complex. IN this formulation the latter is the only GS reaction that is capable of producing an active radical. So, it appears then that this redox-activated polymerization should follow as:

$$R_p = k_{red}[Amine]^{\alpha}[Onium\ Salt]^{\beta}$$

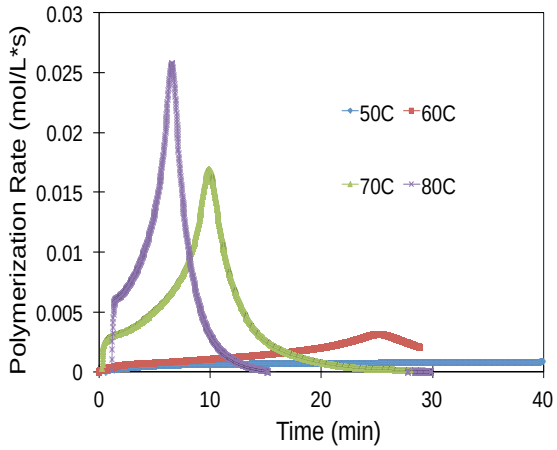


Figure 4- HEMA thermal polymerization rate as a function of time at 50°C, 60°C, 70°C and 80°C in the DSC.

***Non-polymerizing dark reactions***

There are not only radical producing dark reactions, but also those that consume the initiating species in the dark, thus decreasing the initiation rate with increasing storage time. Change from colorless to orange of DIPEA/DPI-Cl solutions (with excess DIPEA to DPI-Cl moles) is evident after dark storage within the time span of the spontaneous polymerization (< 24 h), in both polymerizable and non-polymerizable media. MeOH and HEMA have a similar polarity; thus, their UV/Vis absorption spectra are characterized by an increase in the near-UV tailing into the visible region (400-500 nm). In HEMA, the bathochromic shift extends further into the visible, correlating with the more intense orange coloration observed. In ACN, the change is faster and a clear broad peak arises in the visible, indicating a different intermediate is formed. MB/DIPEA solutions in HEMA also show an orange tint after dark storage without noticeable bleaching of MB. These UV-Vis results support the GS ET reaction via the formation of CT complexes for both DIPEA/MB and DIPEA/DPI-Cl solutions based on the broadness of the peaks evolving with time, and their intensities. A 1:1 DIPEA/DPI complex is expected to have an electronic absorption similar to that of any DPI salt, i.e. mostly independent of the counter-ion[24]. DIPEA absorbs at ~200 nm ($n \rightarrow \pi^*$ transition).

Polar aprotic acetonitrile DIPEA/DPI-Ph solutions change from colorless to blue in less than 20 min, then to black. Given its higher solubility, DPI-hexafluorophosphate was used (counter-ion size effect was negligible). After weeks of dark storage, an orange tint was noticeable. The greater the DIPEA excess used, the longer the orange tint is delayed. Appearance of the orange coloration was observed after weeks (5-100 times excess DIPEA). Formation of the broad structureless absorbance peak with a maximum at ~575 nm correlates to a 2:1 DPI/DIPEA complex, based on higher degree of $\pi \rightarrow \pi^*$ resonance. This long-wavelength absorption increases until equilibrium is rapidly attained, and then decreases as complex dissociation predominates. An isosbestic point indicates dissociation equilibrium is involved in the transition from blue complex to orange colored product[27]. The intermediate black coloration observed for [DIPEA]>>[DPI] could then be related to the transition from the DIPEA/DPI complex to DIPEA-based structure (orange resin). Benesi-Hildebrand analysis is difficult since sequential reactions are involved.

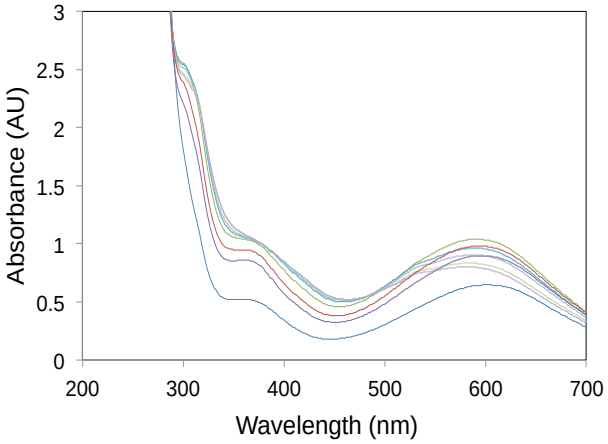


Figure 5. UV-Vis absorbance spectra with respect to time (24 h) of DIPEA/DPI-Ph in ACN vs wavelength; [DPI-Ph] = 3.4 mM, [DIPEA] = 153.4 mM.

**Improving thermal stability**

From Paczkowski et al. we know the photopolymerization rate of PET free radical initiation systems behaves as:

$$R_{ph} = -\frac{d[M]}{dt} = k_p[M]\left[\frac{2I_a}{k_t}10^{11}exp\left[-\left\{\frac{\left[\frac{\lambda}{4}\left(1+\frac{\Delta G\circ}{\lambda}\right)^2\right]}{RT}\right\}\right]^{\frac{1}{2}}\right]$$

Based on his analysis of the polymerization mechanism, it comes natural then to complement this equation with a similar relationship in the GS given that Markus theory also applies to the GS ET mechanism undergone by the ED and EA. As a result, instability rate, i.e. redox activated thermal polymerization rate, has to be similarly proportional to ΔG and the concentrations of amine and salt. As a result of this observation, then one can recognize the importance of the energy window of PS excitation, as considered by the Rehm-Weller equation: $\Delta G_{PET} = E_{ox}(D/D^+) - E_{red}(A/A^-) - E^*$.

$$R_{p-red} = -\frac{d[M]}{dt} = k_p[M][Amine]^{\alpha}[Onium\ Salt]^{\beta}\left[\frac{10^{11}}{k_t}exp\left[-\left\{\frac{\left[\frac{\lambda}{4}\left(1+\frac{\Delta G\circ}{\lambda}\right)^2\right]}{RT}\right\}\right]^{\frac{1}{2}}\right]$$

Given that Markus equation considers both the effects of the ionization potential, electron affinity and diffusivity of the species in solution, we can use these equations to find the appropriate combination to maximize both stability and photopolymerization efficiency. The latter should be adjusted for the non-polymerizing dark reactions based on the fact that the rate-determining step is the electron transfer between PS and tertiary amine, most likely.

## Conclusions

In this work we showed red-light sensitive three-component photoinitiators could be designed to parallel the photopolymerization efficiency of traditional UV curable one-component initiators. Only systems that undergo photoreducible mechanism involving electron transfer from a tertiary amine to the red-light sensitive photosensitizer were considered. Onium salts were chosen as well, to narrow the universe of combinations within the scope of this research. Then, we showed an example (MB/tertiary amine/onium salt) of different types of instabilities caused by components in this type of formulations. These are then theoretically related to three main parameters: ionization potential of tertiary amine (basicity), electron affinities of both PS and EA, and diffusivities of each one of the three components. Choice of either one of the ingredients will delimit the possibilities for the other two. Monomer or solvent environment will dictate the combinations that will extend the stability. Based on this, we propose general methods to maximize photopolymerization rate while extending their stability or shelf-lifetime. It seems possible to design practically stable three-component initiating systems by decreasing the ionization potential of the tertiary amine with respect to the electron affinity of both the dye and the onium salt. Rate of dark reactions can decrease by hindering the diffusion of the amine during polymerization so that only mobile excited state specie can collide to generate radicals. Electron affinity and diffusivities of PS and EA could also be modified with respect to the ED. But, tuning of amine ground-state reactivity seems like a more practical route. This needs to be done then with a specific monomer/solvent environment in mind because diffusivity of initiating species will change differently based on viscosity, polarity and hydrogen donating capabilities provided by the medium.

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