Extensive Dark Cure from Controlled Polymerization Based on a Method Using Visible-Light Activated Initiator System

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ABSTRACT

Free-radical photopolymerization has been widely used for polymeric biomaterials because of rapid reaction, excellent mechanical properties and the versatility available with a broad array of monomers. In contrast, cationic polymerization shows greater sensitivity to trace impurities and involves a much more restrictive selection of monomers; however, cationic polymerization allows significant dark curing because of long active center lifetimes. The dark curing process is one of the distinct differences between cationic and free-radical photopolymerization. In this contribution, we report the development of a photo-initiator system that allows extensive dark curing from visible light-initiated controlled radical polymerization. The photo-initiator is a radical-based, three-component initiator system that includes a light-absorbing photosensitizer (PS), an electron donor and an electron acceptor, which is usually an onium salt. In this system, 5,10,15,20-tetraphenyl-21H,23H-porphyrin zinc (Zn-tpp) is used as a PS, diazabicyclooctane (DABCO) is used as an electron donor and diphenyliodonium hexafluoroarsenate (DPI) is used as an electron acceptor. The three-component initiator system, Zn-tpp/DABCO/DPI produced a limiting conversion of 93.3 % conversion in 2-hydroxyethyl methacrylate (HEMA) upon full exposure time over 90 min. Real time conversion was monitored using near-infrared spectroscopy while photopolymerizations were conducted with a 100 W halogen lamp at an irradiance of 0.15 mW/cm^2.

Remarkably, three-component initiator system did not exhibit rapid termination of HEMA polymerization when the irradiation source was turned off. For example, only 30, 60 or 300 sec partial illumination coincided with conversion of 1.7 %, 4.3 % and 30.7 % respectively, but the final conversions reached 81.5 %, 84.7 % and 93.3 % respectively, at 90 min. These conversion kinetic results illustrate a unique controlled radical dark polymerization where the radical active centers are not terminated even when the light source is extinguished. Among many applications, this approach has practical significance for polymeric biomaterials including dental composite materials and bone cements where depth of cure and shadow cure are important considerations.

Introduction and Motivations

Free radical photopolymerization serves as the industry standard due its excellent efficiency across broad classes of vinyl-based monomers. However, the free radical process produces short propagating radical lifetimes due to termination reactions which means continuous initiation is required to maintain active polymerization. The result is a rapid cessation of polymerization when the irradiation source is extinguished or more simply, very limited dark cure potential. As such, complete polymerization requires either repeated incremental exposures or continuous irradiation throughout the course of

polymerization. In contrast, cationic photopolymerization allows significant dark curing because of long active center lifetimes; however, compared with radical polymerizations, there are few monomers compatible with the cationic curing process[1]. The dark curing behavior is one of the distinct differences between cationic and free-radical photopolymerization. The prospect of removing this dark cure limitation from radical-based polymerizations with conventional monomers is highly significant since effective dark curing could be useful by allowing reduced processing times and lower initiator concentrations as well as achieving photocuring into shadow regions, enhanced depths of cure and photocuring of pigmented or highly filled systems using radical polymerizations.

Recently, we have identified visible-light activated three-component initiator systems that provide dramatic dark cure behavior with conventional monomers. The initiator system includes a light-absorbing photosensitizer, an electron donor and an electron acceptor[2-11]. Although a number of three-component initiator systems have been reported, no studies have attempted to provide extensive dark polymerization kinetic results using of three-component initiator systems. In this contribution we report a series of kinetic studies of radical dark polymerizations[12,13] of three-component initiator systems. We performed dark polymerization experiments as a function of iodonium salt counter anion size. For this research 5,10,15,20-tetraphenyl-21H,23H-porphyrin zinc (ZnTPP) dye was chosen as a photosensitizer (PS) due to the thermodynamic and kinetic considerations.

Experimental Methods
Materials.

The organic dye 5,10,15,20-tetraphenyl-21H,23H-porphyrin zinc (ZnTPP) was purchased from Aldrich Chemical Company and were used as received. The chemical structures of Zn-ttp and CQ are shown in Figure 1. The monomer 2-hydroxyethyl methacrylate (HEMA) was obtained from Aldrich and used as model monomer systems. 1,4-diazabicyclo[2.2.2]octane (DABCO) was purchased from Aldrich and were used as electron donors (DH). Four different iodonium salts were used as a function of counter anion size (e.g. Cl⁻, PF_6^- AsF_6^- long chain structure with SbF_6^-) were purchased from Aldrich. All chemicals were used without further purification.
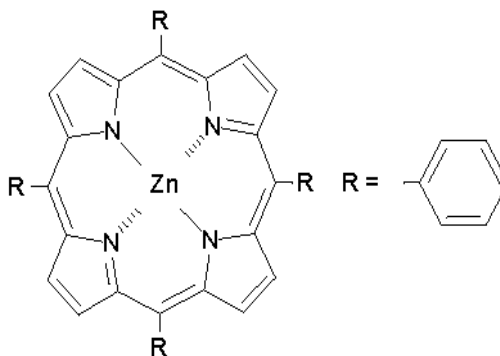

Figure 1. Chemical structures of 5,10,15,20-tetraphenyl-21H,23H-porphine zinc (Zn-ttp).

Methods
Real-time FT-near-infrared (NIR) spectroscopy.

The HEMA polymerization conversion profile was monitored *in situ* by FT-near-infrared (NIR) spectroscopy (Nicolet Nexus 670, Nicolet Instrument Corp., Madison, WI) equipped with an extended KBr beam-splitter and an MCT/A detector. To initiate photopolymerizations, a 385 - 800 nm light source (Oriel Model 77501 Fiber Optics Source, Stratford, CT) was used. The visible light source contains an adjustable iris, a manual shutter and a 100 W quartz halogen lamp outfitted with 3.2 mm diameter and 0.9 m length silica fiber optic cable. The output from the light source was passed through IR blocking filter to remove IR light (wavelengths greater than 800 nm). The filtered light irradiance reaching the sample was ~ 0.15 mW/cm^2, as measured by a calibrated diode array spectrometer. Samples with a variety of photoinitiator compositions were prepared in a rectangular mold made by glass slides at a thickness of 0.5 mm. To judiciously characterize kinetics, very mild reaction conditions were selected; all photopolymerizations were conducted at room temperature with ~ 0.15 mW/cm^2 incident light intensity. Samples with a series of photoinitiator component were place in a rectangular mold made by glass slides at a thickness of 0.5 mm. For all samples, [Zntpp] = 2.32 × 10^{-3} M [DABCO] = 0.25 M, [DPI] = 0.02 M in HEMA. All photopolymerizations were conducted at room temperature. The absorbance peak area method was used to calculate conversion. The $=CH_2$ first overtone absorption band at ~ 6167 cm^{-1} in the NIR region was used to characterize the concentration of the HEMA double bond. For each initiator system, at least three independent measurements were made, and the average values are reported.

Results and Discussion
Effect of selection of PS on the radical dark polymerization kinetics.

Extensive dark curing from a visible-light initiated controlled radical polymerization has been demonstrated where the radical active centers are not terminated even when the light source is extinguished. For example, when 5,10,15,20-tetraphenyl-21H,23H-porphyrin zinc (Zn-tpp) as a photosensitizer (PS), diazabicyclooctane (DABCO) as an electron donor and diphenyliodonium hexafluoroarsenate (DPI) as an electron acceptor are used as three-component initiator system, dramatic dark cure with a conventional methacrylate monomer was observed. Remarkably, the three-component initiator system did not exhibit rapid termination of 2-hydroxyethyl methacrylate (HEMA) polymerization when the irradiation source was turned off. Specifically, 30, 60 or 300 seconds partial illumination coincided with conversion values of 1.7 %, 4.3 % and 30.7 % respectively, at the time the curing light was extinguished; however, polymerization continued very efficiently in the dark and the final conversion values attained were 81.5 %, 84.7 % and 93.3 % respectively, at 90 min. The Zn-tpp/DABCO/DPI produced a limiting conversion of 93.3 % conversion in 2-hydroxyethyl methacrylate (HEMA) upon full exposure time over 90 minutes as shown in Figure 2. The same monomer polymerized with conventional photoinitiators provides very limited (< 5 %) additional dark cure conversion once the light exposure is ended due to efficient biradical termination mechanisms that rapidly consume the active radical centers.

We also report preliminary selection criteria of three-component initiator system and monomers for efficient controlled radical dark polymerizations. For example,

significant improvement in conversion under the dark polymerization condition was obtained with photo-oxidizable PS, electron donors with high radical cation persistence, electoron acceptors with larger counter anions and in hydrogen abstractable monomers. Notably, the initiator systems including photo-reducible PS such as camphorquinone (CQ) and methylene blue (MB) as the PS did not produce any controlled radical dark polymerization behavior, which means that these initiator systems showed typical rapid cessation of polymerization under dark polymerization conditions as illustrated in Figure 3.
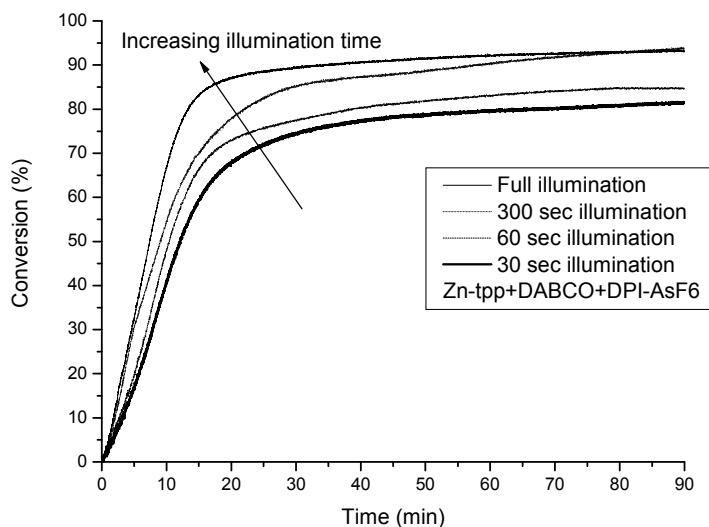

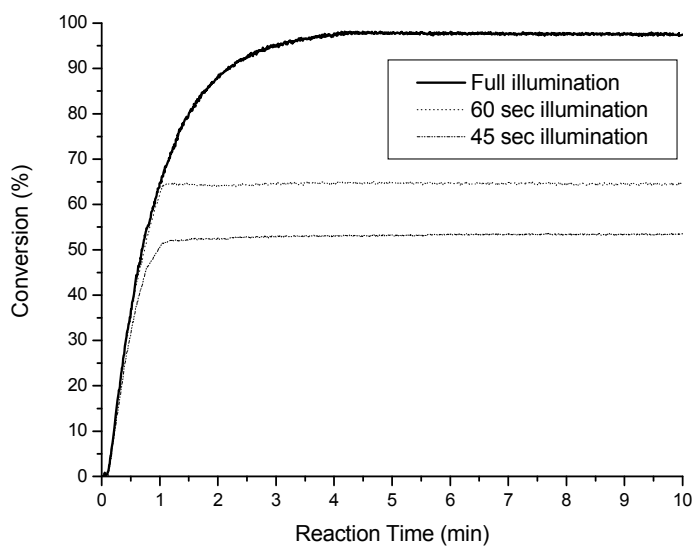**Figure 2.** Conversions of HEMA polymerizations as a function of illumination time with Zntpp/DABCO/DPI-AsF$_6$, as measured by NIR at room temperature with an incident light intensity of 0.15 mW/cm^2. For all samples, [Zn-tpp] = 2.32 × 10^{-3} M, [DABCO] = 0.25 M and [DPI-AsF$_6$] = 0.02 M, in neat HEMA.

Figure 3. Conversions of HEA polymerizations as a function of illumination time with CQ/DABCO/DPI-AsF$_6$, as measured by NIR at room temperature with an incident light intensity of 440 mW/cm^2. For all samples, [CQ] = 0.5 M, [DABCO] = 0.25 M and [DPI-AsF$_6$] = 0.02 M, in neat HEA.

Effects of counter anion size and electron density of iodonium salts on the radical dark polymerization kinetics

The conversion data illustrated that size and electron density of counter aniom of iodonium salt plays an important role in the photopolymerization reaction under full illumination as shown in Figure 4. This conversion data showed both initiation and propagation step are dependent on both size and electron density of counter aniom of iodonium salt. For these reasons, ZnTPP/DABCO/DPI-AsF$_6^-$ initiator system shows highest conversion (~ 90 % conversion at 20 min). As a result, as counter aniom size decrease, the time to reach final conversion increase and final conversion decreases. This data also showed electron density of counter anion influenced the conversions.
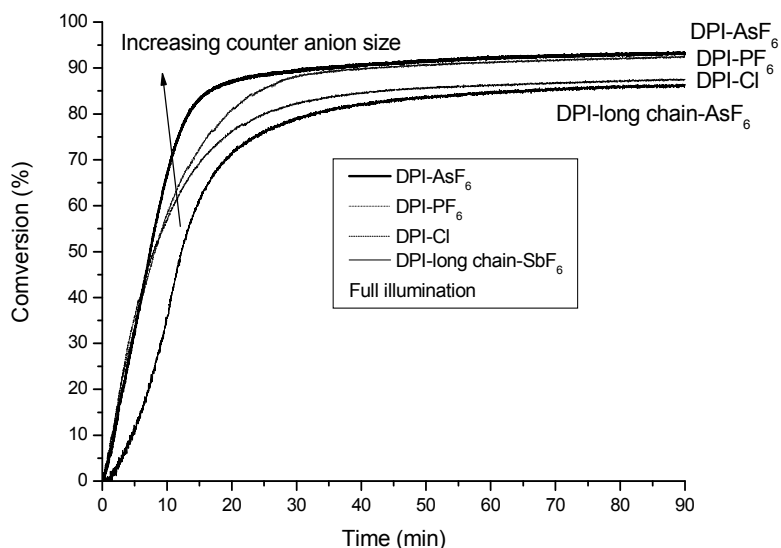

Figure 4. Conversions of HEMA polymerizations with Zn-tpp/DABCO/DPI-Xn, as measured by NIR at room temperature with an incident light intensity of 0.15 mW/cm^2. For all samples, [Zn-tpp] = 2.32 × 10^{-3} M, [DABCO] = 0.25 M and [DPI-Xn] = 0.02 M, in neat HEMA.

Under the 30 sec illumination and dark polymerization conditions, size and electron density of counter aniom of iodonium salt plays the same role in the both initiation and propagation step of dark polymerization reaction as shown in Figure 5. ZnTPP/DABCO/DPI-AsF$_6^-$ initiator system shows the most dramatic conversion efficiency under the 30 sec illumination. The initiator system produced ~ 75 % conversion at 30 min under dark polymerizations with 30 sec illumination. However, as the counter anion size was decreased, final conversion obviously decreased. In addition, electron density of counter anion also influenced the conversions. From the data in Figure 4 and Figure 5, we observed that ZnTPP/DBCO/DPI-AsF$_6^-$ initiator system is the most efficient initiator system under both full illumination and dark polymerizations with 30 sec illumination. Figure 5 illustrates the effect of size and electron density of counter

aniom of iodonium salt on the conversion profile. Unlike cationic polymerizations, typical radical polymerizations do not exhibit long-lived life time of radical active centers. As a result dark polymerizations generally are not on the radical polymerizations. Therefore, these kinetic data are significantly important for radical polymerizations.
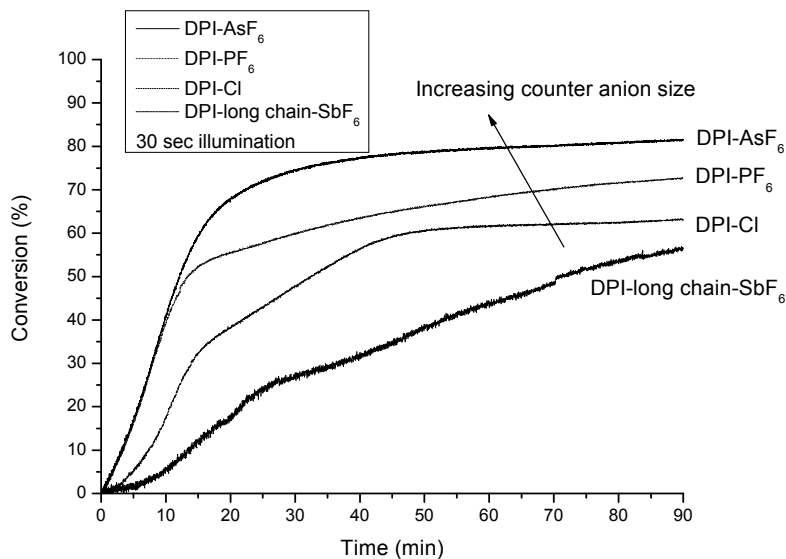

Figure 5. Conversions of HEMA polymerizations under 30 sec illumination time with Zntpp/DABCO/DPI-Xn, as measured by NIR at room temperature with an incident light intensity of 0.15 mW/cm^2. For all samples, [Zn-tpp] = 2.32 × 10^{-3} M, [DABCO] = 0.25 M and [DPI-Xn] = 0.02 M, in neat HEMA.

Conclusions

The photo-initiator is a radical-based, three-component initiator system that includes a light-absorbing photosensitizer (PS), an electron donor and an electron acceptor, which is usually an onium salt. In this system, 5,10,15,20-tetraphenyl-21H,23H-porphyrin zinc (Zn-tpp) is used as a PS, diazabicyclooctane (DABCO) is used as an electron donor and diphenyliodonium hexafluoroarsenate (DPI) is used as an electron acceptor. The three-component initiator system, Zn-tpp/DABCO/DPI produced a limiting conversion of 93.3 % conversion in 2-hydroxyethyl methacrylate (HEMA) upon full exposure time over 90 min. Real time conversion was monitored using near-infrared spectroscopy while photopolymerizations were conducted with a 100 W halogen lamp at an irradiance of 0.15 mW/cm^2. Remarkably, the three-component initiator system did not exhibit rapid termination of HEMA polymerization when the irradiation source was turned off. For example, only 30, 60 or 300 sec partial illumination coincided with conversion of 1.7 %, 4.3 % and 30.7 % respectively, but the final conversions reached 81.5 %, 84.7 % and 93.3 % respectively, at 90 min. These conversion kinetic results illustrate a unique controlled radical dark polymerization where the radical active centers are not terminated even when the light source is extinguished.

References

1. 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, 1747-1756.

2. Kim, D.; Scranton, A.B., *J. Polym. Sci. Part A: Polym. Chem.,* 2004, 42, 5863-5871.

3. Padon, K.S.; Scranton, A.B.; Pandalai, S. G., Ed.; *Transworld Research Network*: Trivandrum, India, 1999, Vol. 3, 369-385.

4. Padon, K. S.; Scranton, A. B., *J. Polym. Sci. Part A : Polym. Chem.,* 2000, 38, 3336-3346.

5. Padon, K. S.; Scranton, A. B., *J. Polym. Sci. Part A : Polym. Chem.,* 2001, 39, 715-723.

6. Oxman, J.D.; Ubel, F.A.; Larson, E.G., US Patent, 1989, 4,828,583.

7. Palazzotto, M.C.; Ubel, F.A.; Oxman, J.D.; Ali, Z.A.; US Patent, 2000, 6,017,660.

8. Oxman, J.D.; Jacobs, D.W., US Patent, 1999, 5,998,495.

9. Oxman, J.D.; Jacobs, D.W., US Patent, 2000, 6,025,406.

10. Erddalane, A.; Fouassier, J. P.; Morlet-Savary, F.; Takimoto, Y., *J. Polymer Sci., A: Polym. Chem.,* 1996, 34, 633-642.

11. Fouassier, J. P.; Wu. S. K., *J. Appl. Polm. Sci.,* 1992, 44, 1779-1786.

12. Lalevee, J.;.El-Roz, M.; Allonas, X.; Foussier, J. P. *Journal of Polymer Science Part A-Polymer Chemistry* 2007, 45: 2436-2442.

13. Kilambi, H.; Reddy, S. K.; Schneidewind, L.; Stansbury, J. W.; Bowman, C. N.. *Polymer* 2007, 48: 2014-2021.