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ARTICLE

Mechanism and Implementation of Oxygen Inhibition Suppression in Photopolymerizations by Competitive Photoactivation of a Singlet Oxygen Sensitizer

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ABSTRACT: Here, we report a novel method of suppressing oxygen inhibition while simultaneously performing photopolymerizations with a visible light photoinitiator. A singlet oxygen sensitizer, Zinc tetrakis(*tert*-butyl) phthalocyanine (Zn(ttp)), is used to excite oxygen at a rate greatly exceeding the initiation rate to promote the reaction of ground state oxygen preferentially with Zn(ttp). The inhibition times of such polymerizations decreased from 280 s for polymerization without Zn(ttp) to 40 s for Zn(ttp)-mediated polymerizations in air. Thermal polymerization studies shows that the suppression mechanism happens only when the formulation is exposed to visible light that is absorbed by Zn(ttp). The excited state of Zn(ttp) resulting from light absorption transfers its energy to oxygen, consequently exciting it to the singlet state. Because of the presence of deactivating mechanisms, the singlet oxygen decays back to its ground state and a quasi-steady state is established between the ground state and singlet state oxygen species. Because of the high rate of light absorption by Zn(ttp) as compared to the photoinitiator, the singlet state oxygen becomes the predominant oxygen species, thereby resulting in significant suppression of radical scavenging by ground state oxygen. Experimental results are corroborated with a mathematical model to describe the variation in inhibition times with changing Zn(ttp) concentration. The value of the characteristic lifetime of singlet oxygen calculated from the model is 1 ms, consistent with that which is reported in the literature for several organic monomers. Finally, optimal initiating conditions are designed to suppress oxygen inhibition while achieving high conversions in the most challenging condition of a sample equilibrated with a pure oxygen atmosphere.

Introduction

Oxygen inhibition is a commonly encountered issue while performing radical polymerizations. Many applications based on photopolymerizations namely paints, coatings, adhesives, photolithography, and dental resins are severely affected by oxygen inhibition.[1−4] In particular, surface-initiated polymerizations, performed with extremely low concentrations of surface-bound initiator,[5−8] are highly susceptible to oxygen inhibition. Without an inert gas purge such systems are often devoid of any significant polymerization.

Oxygen limits radical polymerizations by acting as a powerful radical scavenger, consuming radicals on a one radical to one oxygen molecule basis to form peroxy radicals that are practically incapable of continuing the polymerization, particularly in the absence of any chain transfer agents such as thiols or amines.[9] The final result is the presence of an induction period during which little polymerization occurs, and the initiating radicals consume oxygen. If diffusion of oxygen from the atmosphere or from noninitiating regions of the sample is more rapid than initiation, the inhibition time becomes effectively infinite and polymerization never proceeds to any significant extent. Otherwise, once the oxygen concentration drops to or below on the order of 10^{-6} M, the polymerization reaction begins in earnest.[10]

There have been a number of creative approaches to overcoming the problems of inhibition resulting from dissolved oxygen. Use of amines,[11,12] thiols,[13,14] singlet oxygen scavengers,[15−17] organoboranes,[18] organosilanes,[19] and reactive curing conditions[20] are some of the chemical means that have been employed to tackle this issue. Physical means comprise degassing the monomer formulation prior to polymerization or use of an inert gas purge chamber to perform polymerizations in an oxygen free environment. In all of these approaches the focus has been either driving the oxygen out of the system physically, consuming the oxygen prior to polymerization or scavenging peroxy radicals and transforming them into a more potent polymerization-capable radical.

Here, this work presents a scheme through which an alternative pathway for oxygen consumption is provided, thereby circumventing the reaction between oxygen and initiating radicals. This approach is illustrated in Scheme 1 where the competitive reaction pathway involving reaction of oxygen with the excited state singlet oxygen trapper occurs in parallel with the reaction of oxygen to form the peroxy radical that inhibits the polymerization. In the absence of the second parallel pathway, the rate of oxygen consumption by reaction with initiating radicals to form peroxy radicals is equivalent to the slowest reaction (rate-determining step) in the top reaction series, which is the initiation rate. By providing an alternative pathway for the reaction of oxygen that is much faster than the initiation rate, radical scavenging can be made negligible, and photoinitiator radicals are able to directly and efficiently initiate polymerization. It is precisely this technique that is employed in the present work to perform photopolymerizations in an oxygen rich environment.

Metallo-phthalocyanines (MPc) like zinc and aluminum phthalocyanines are used commonly in photodynamic tumor therapy because of their ability to produce reactive oxygen species (ROS) with a high quantum yield upon photoactivation.[21−23] Following photon absorption, the MPcs transition to their

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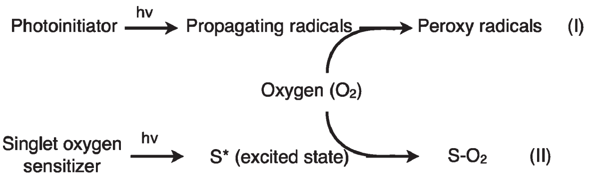
Scheme 1. Propagating Radicals Consumed in Pathway I by Oxygen To Form Weakly Initiating Peroxy Radicals.[a]



[a] Oxygen is consumed in a competitive pathway II via photoexcitation of a singlet oxygen sensitizer to promote the elimination or reduction of the inhibition time.

excited singlet state, which undergoes intersystem crossing to form the excited triplet state. Because the transition from the excited triplet state to the ground state is a spin forbidden process, the triplet lifetime is sufficient to enable energy transfer to oxygen resulting in excited singlet oxygen, also called singlet oxygen.[24] In contrast to ground state triplet oxygen, which by virtue of its biradical nature very efficiently reacts with radicals to form peroxy radicals, singlet oxygen is diamagnetic and not highly reactive with initiating or propagating radicals. Singlet state oxygen has a lifetime of about a millisecond in most acrylic monomers and decays back to its ground state.[17] Zn(ttp) has also been used previously as a photosensitizer of oxygen to increase the reactivity of oxygen toward reducing species like 9,10-dimethylanthracene, which acts as a trapper for the singlet oxygen.[17] This technique was successfully used to consume oxygen prior to polymerization as a means for eliminating any oxygen inhibition period. The focus of the work here is to show that suppression of oxygen inhibition can be enabled simply by direct photosensitization of oxygen. The fundamental mechanism of such a kinetic scheme is also elucidated.

Experimental Section

Materials. Poly(ethylene glycol) diacrylate (PEGDA) (M_n = 575), 1-vinyl-2-pyrrolidinone (VP), *N*-methyldiethanolamine (MDEA), zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (Zn(ttp)), zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25 -hexadecafluoro-29*H*,31*H*-phthalocyanine (ZnFPc), zinc 1,4,8,11,15,18,22,25-octabutoxy-29*H*,31*H*-phthalocyanine (Zn(oBPc)), Aluminum phthalocyanine hydroxide (AlPcOH), 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPO) 2,2′-Azobis(2-methylpropionitrile) (AIBN), Riboflavin and Camphorquinone were obtained from Sigma-Aldrich. PEGDA was purified twice using columns from Scientific Polymer Products that remove hydroquinone monomethyl ether (MEHQ). Irgacure-784 was purchased from CIBA.

Polymerizations. PEGDA was used as the monomer for all experiments. Small amounts of VP was also used to increase the mobility of the propagating radical as a result of the smaller size of VP while MDEA was used as the co-initiator in type II initiated systems. A Nicolet Magna-IR 760 E.S.P infrared spectrometer adapted with a horizontal sample holder was used to monitor polymerizations in real time tracking the 4465−4530 cm^{-1} peak . C=C conversion was calculated by measuring *in situ* changes in this peak area. Sample chambers were prepared using binder clips to clamp two glass slides on either side of a 100-μm thick sheet lining two edges. Where purging was performed, it was carried out by bubbling argon/oxygen through the monomer formulation before polymerization and transferred to the sample chamber quickly to prevent equilibration with the surroundings. Visible light irradiation of eosin was achieved with an in-house internal bandpass filter (350−650 nm) and an external 480 nm long-pass filter (Edmund optics) positioned at the end of a light guide and a collimating lens. A similar light setup was used for irradiation of camphorquinone, Riboflavin and Irgacure-784, except that the internal filter was a 400−500 nm bandpass filter (Exfo). Light Intensities were measured by an International Light radiometer. Thermal polymerizations were initiated with AIBN at 60 °C.

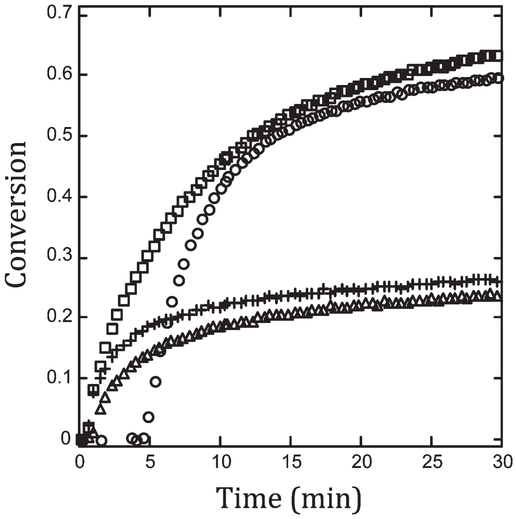


Figure 1. Conversion profiles for bulk polymerization of Poly(ethylene glycol) diacrylate (PEGDA) for various conditions: Addition of Zn(ttp) with (+) and without (Δ) argon purging, No Zn(ttp) added with (□) and without (O) argon purging. The monomer formulation used was 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP 0.87 μM Eosin, 2.9 × 10^{-4} M Zn(ttp). Light intensity was 75 mW/cm^2 of the wavelength range 480−650 nm.

Results and Discussion

Bulk Polymerization Studies. Eosin-initiated photopolymerizations were performed in laminated bulk samples both in purged and unpurged formulations both with and without the Zn(ttp). The inhibition times for different scenarios were compared, and the double bond conversion as a function of the irradiation time for these various experiments is shown in Figure 1. It is seen that when dissolved oxygen is present in the monomer formulations which are not purged with argon, an inhibition time of approximately 280 s is seen in the sample without any Zn(ttp). However, when Zn(ttp) is present in the monomer formulation the inhibition time is significantly decreased to approximately 40 s (Figure 1). Bulk polymerization with only Zn(ttp) in the monomer formulation and no eosin (not shown) did not exhibit any polymerization on these time scales, indicating that Zn(ttp) and its excited state products do not initiate polymerization under these conditions. Therefore, the reduction in inhibition time has other origins. When oxygen was eliminated through purging and photopolymerizations were initiated in the presence of Zn(ttp), the resulting conversion profile is very similar to the conversion profile of Zn(ttp) in the presence of oxygen. This behavior indicated that Zn(ttp) acts almost exclusively to suppress oxygen inhibition.

In addition to its beneficial effects on overcoming oxygen inhibition, it is also observed from the results presented in Figure 1 that Zn(ttp) affects the continuing polymerization rate and particularly the maximum conversion.

Comparing the photopolymerization conversion profiles for samples with and without Zn(ttp) in purged conditions (Figure 1), it is observed that the initial polymerization rates are similar but at higher conversion the rate decreases for the Zn(ttp) formulation, likely due to the participation of Zn(ttp) in promoting radical termination.

The effects of Zn(ttp) in oxygen rich conditions were also evaluated and the results are presented in Figure 2 where the conversion profiles are presented for the control and

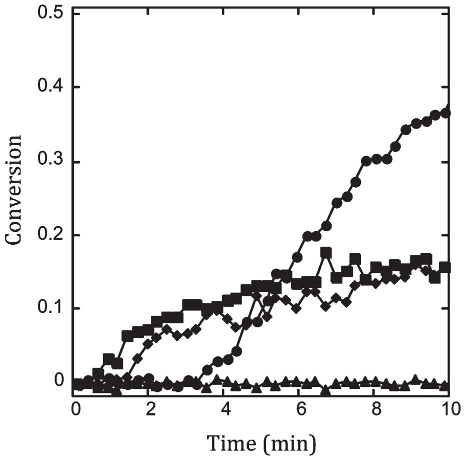


Figure 2. Behavior of Zn(ttp) mediated polymerization of PEGDA purged with pure oxygen to increase the dissolved concentration. The conditions are as follows: In the presence of Zn(ttp) with (◇) and without (□) an oxygen purge, No Zn(ttp) present with (Δ) and without (○) oxygen purge. The monomer formulation used was: 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 0.87 μM Eosin, 2.9×10^{-4} M Zn(ttp), Light intensity was 75 mW/cm^2 in the wavelength range 480−650 nm.

Table 1. Inhibition Times for Different Zn(ttp) Concentrations in the Presence of TEMPO[a]

Zn(ttp) concentration (M)	inhibition time (s)
0	126 ± 10
2.9×10^{-6}	129 ± 4
2.9×10^{-5}	135 ± 4
2.9×10^{-4}	114 ± 10

[a] The monomer formulation used was: 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 2.9 μM Eosin, and 130 μM TEMPO. Light intensity was 75 mW/cm^2 in the wavelength range 480−650 nm. Purged for 10 min with argon to remove oxygen.

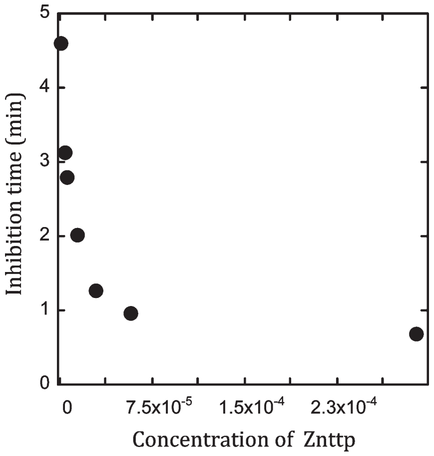


Figure 3. Effect of varying the concentration of Zn(ttp) on the bulk polymerization of PEGDA. Plotted is the inhibition time of polymerization in minuted (y axis) vs Zn(ttp) added in molar units (x axis). The monomer formulation used was 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 0.87 μM Eosin, and 2.9×10^{-4} M Zn(ttp); light intensity was 75 mW/cm^2 in the wavelength range 480−650 nm.

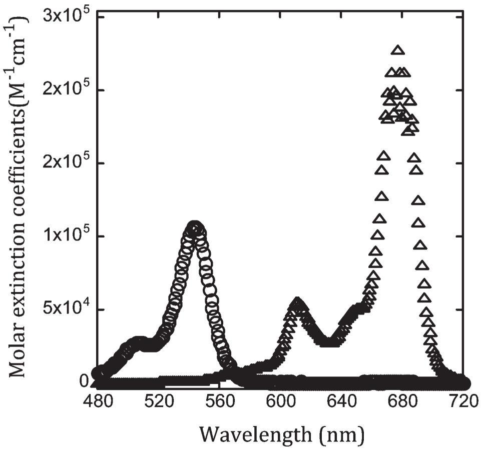


Figure 4. Absorption spectra of Zn(ttp) (Δ) and Eosin (○) in dimethyl sulfoxide.

Zn(ttp)-containing formulations in formulations equilibrated with oxygen-rich environments. Here, it is observed that oxygen purging results in complete inhibition of photopolymerization without Zn(ttp). This result is significant because it accentuates the ability of Zn(ttp) to promote photopolymerization under conditions of excess oxygen compared to the photoinitiator where polymerization is otherwise infeasible to any extent.

To understand whether this ability to suppress inhibition is applicable to other inhibition mechanisms through one of a variety of possible alternative mechanisms, TEMPO, a known radical scavenger was added as an inhibitor to the monomer formulation. Table 1 includes the inhibition times for photopolymerizations in the presence of TEMPO with varying Zn(ttp) concentration. Within error, the inhibition times in samples containing TEMPO (Table 1) are not different when compared to the significant reduction in inhibition times seen in formulations performed without TEMPO, but in the presence of oxygen (Figure 3). This clearly highlights the specific ability of Zn(ttp) in improving initiation in oxygen-inhibited photopolymerizations. However, the mechanism of this behavior is not well understood, and it is the intention of the following sections to address this topic.

Role of Photoactivation. Zn(ttp) is a light-absorbing compound, and its absorption characteristics are well-known. Figure 4 shows the absorption spectra of Zn(ttp) in the visible range. The incident light spans 480- 650 nm and even though the peak light absorption of Zn(ttp) does not fall in this range, the quanta of light absorbed are significant when incorporating high concentrations of Zn(ttp), as used in many of the experiments performed. To ascertain the importance of light, thermally initiated polymerizations were performed with and without Zn(ttp) for both simultaneous irradiation conditions as well as unexposed conditions. Figure 5 shows the polymerization kinetic profiles for these experiments. It is seen that in the unpurged conditions Zn(ttp) reduces the inhibition time only when the monomer formulation is exposed to light. This behavior confirms the hypothesis that light absorption by Zn(ttp) is necessary for overcoming the oxygen inhibition, even during thermal initiation. It can also be concluded that the effect on termination kinetics is a nonphotoactivated oxygen independent mechanism as the reduction in the long term polymerization kinetics and final conversion are observed whether there is simultaneous irradiation or not.

Behavior with Other Photoinitiators and Analogous Phthalocyanines. Eosin-initiated photopolymerizations in the presence of Zn(ttp) are different from conventional photopolymerizations because of the presence of two light absorbing compounds. It is therefore possible that the Zn(ttp) could be sensitized by eosin to lead to the observed behavior. If eosin sensitization is the primary mode through which the Zn(ttp) acts, then photopolymerizations initiated by type I photoinitiators would not exhibit similar suppression since

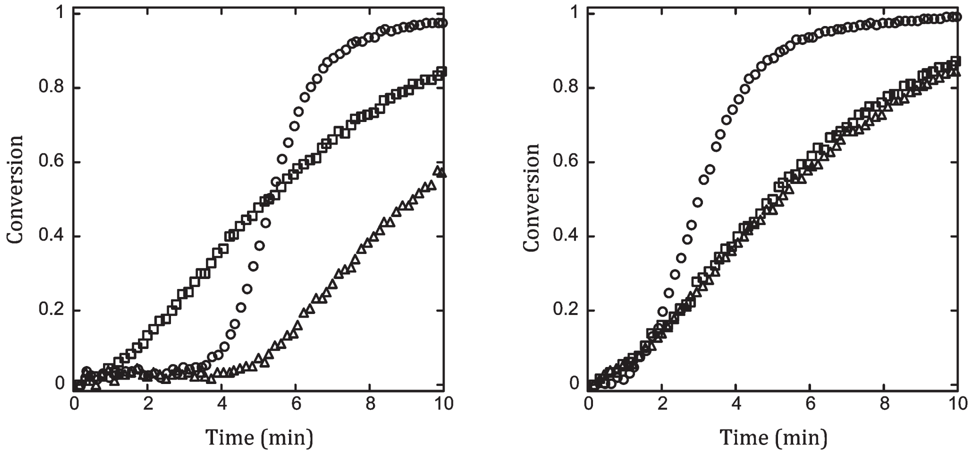


Figure 5. Thermal polymerization of PEGDA at 60 C with AIBN in unpurged (left) and purged (right) conditions. The conditions in both the conditions are as follows: No Zn(ttp) present with light exposure (O), in the presence of Zn(ttp) with (□) and without (Δ) light exposure. The monomer formulation is 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 0.85 wt % AIBN, and 5.8×10^{-4} M Zn(ttp); light intensity was 75 mW/cm^2 in the wavelength range 480−650 nm.

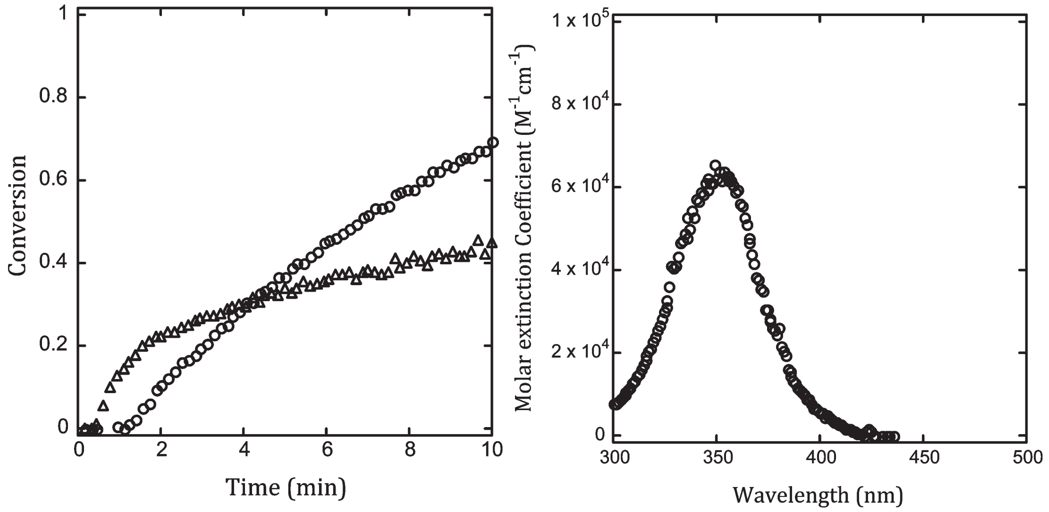


Figure 6. Bulk polymerization of PEGDA with (Δ) and without (O) the presence of Zn(ttp). The photoinitiator used is Irgacure-784. The monomer formulation is 1.8 M PEGDA, 35 mM VP, 150 μM I-784, and 2.9×10^{-4} M Zn(ttp), Light intensity is 10 mW/cm^2 in the wavelength range 400−500 nm. Absorption spectra for Zn(ttp) (right) in the wavelength range 300−500 nm.

their excited state generally cleaves rapidly, making the sensitization event unlikely. As presented in Figure 6, suppression of oxygen inhibition by the Zn(ttp) continues to be observed when the initiator is a type I photoinitiator as it was with both thermal initiators and with type II photoinitiators. Also, as shown in Figure 7, Zn(ttp) is effective in suppressing the inhibition time in the presence of numerous other initiators as well, including riboflavin and camphorquinone. In all cases, as the Zn(ttp) concentration increases, the inhibition time decreases.

It is common knowledge that metallo-phthalocyanines (MPc) like zinc and aluminum sensitize oxygen as a result of energy transfer from the triplet state of the MPc to ground state oxygen. Other MPcs that have unfilled valence shells are poor oxygen sensitizers as a result of their very short triplet state. Figure 8 shows the conversion profiles for zinc phthalocyanines with different ring substituents as well as aluminum phthalocyanine for the same concentrations of MPc. It is evident that the inhibition times in each of the phthalocyanines are significantly affected. In the Zinc-chelated Pcs, the magnitude of this change is observed to be in the same order as the total light absorbed by the Pc species (Table 1). Since varying the porphyrin ring substituents with the same metal center does not significantly affect the

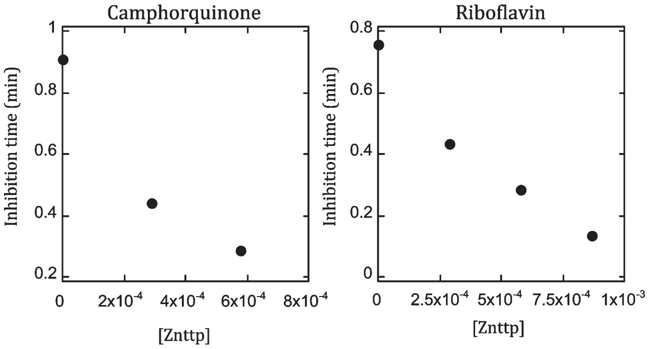


Figure 7. Effect of varying the concentration of Zn(ttp) on the inhibition time of polymerization of PEGDA for two different photoinitiators: camphorquinone (left) at a concentration of 700 μM and riboflavin (right) at a concentration of 1.6 μM. The monomer formulation used is 1.8 M PEGDA, 0.23 M MDEA, and 35 mM VP. Light intensity is 50 mW/cm^2 in the wavelength range 400−500 nm.

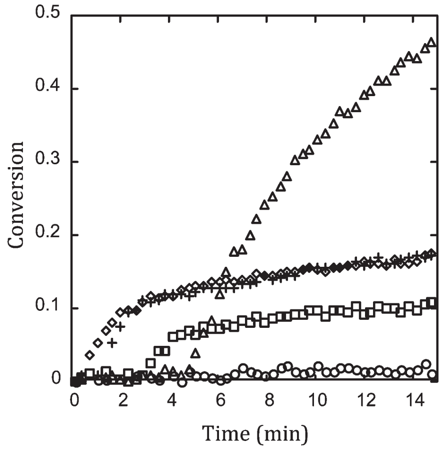
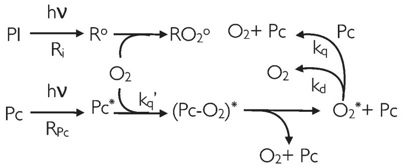


Figure 8. Conversion profiles for polymerization of PEGDA in the presence of different phthalocyanines: Zn(ttp) (◇), Zn(oBPc) (+), ZnFPc(□), AlPcOH (○) and without phthalocyanine (Δ). The monomer formulation used was 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 0.87 μM Eosin. 2.9×10^{-4} M Pc. Light intensity used was 75 mW/cm^2 of 480−650 nm light.

Scheme 2. Simplified Photoactivated Suppression of Oxygen Inhibition[a]



[a] R_{pc} is the rate of light absorption by the phthalocyanine and R_i is the rate of photoinitiation. k_d ($= 1/\tau$) is the decay constant of singlet oxygen, k_q is the quenching constant of singlet oxygen by the phthalocyanine, and k_q' is the quenching constant of excited phthalocyanine by oxygen.

quantum yield of oxygen,[25] it can be concluded that the rate of oxygen photosensitization by each of the Zinc-substituted phthalocyanines and hence the inhibition time follows the same order as th eir absorbances. Specifically the inhibition times for the Zn(ttp), ZnOBPc, and ZnFPc were found to be approximately 0.5, 1, and 2.9 min respectively while calculations indicate that the total number of photons absorbed under these conditions is approximately 6 times greater for Zn(ttp) and 3 times greater for ZnOBPc as compared to the ZnFPc. This latter calculation is based on the integration of light emission and absorption spectra of these three compounds in the wavelength range of interest. Uniquely, AlPcOH exhibits significantly enhanced termination, which leads to lower final conversions.

Further, when incomplete valence shell metal chelated phthalocyanines like Cu^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+} were used (not shown), the suppression of oxygen inhibition was absent. This behavior further validates the idea that sensitization of oxygen is the primary mechanism behind this remarkable suppression ability.

Kinetics of Photoactivated Suppression. To understand the mechanism of this photoactivated suppression, a quantitative study of the relationship between the inhibition time and the Zn(ttp) concentration was attempted. The simplified scheme of the proposed mechanism is shown in Scheme 2. Here, the phthalocyanine species (Pc) reacts with ground state oxygen upon absorption of light via its triplet state to form an excited complex (exciplex). This complex can return to the ground state through deactivating collisions or dissociate into singlet oxygen and ground state Pc. It is known that metal chelated phthalocyanines of transition metals are efficient quenchers of singlet oxygen.[24,26] Therefore, the singlet oxygen is either physically quenched by the phthalocyanine species, in this case Zn(ttp), or loses energy to the surrounding media with a characteristic lifetime ($\tau = 1/k_d$). Overall, this mechanism results in a pseudo steady state between ground state and singlet state oxygen, and the position of this pseudo steady state is determined by the concentration of the phthalocyanine species, the photon absorption rate and several other factors.

The rate-determining step for sensitization of oxygen by Zn(ttp) is photon absorption by Zn(ttp), since the oxygen quenching rate constant (k_q') is relatively large. The rate of photosensitization of oxygen by Zn(ttp) is calculated as,

$$R_{so} = \phi \sum_{\lambda} I_o(\lambda)\alpha(\lambda)C \times 10^3 e^{-\alpha(\lambda)Ct} = AC \qquad (1)$$

where R_{so} is the singlet oxygen photosensitization rate, $I_o(\lambda)$ is the wavelength-dependent incident light intensity, $\alpha(\lambda)$ is the wavelength dependent absorption coefficient, t is the thickness of sample, C is the concentration of Zn(ttp), and A is a constant. On the basis of previous work, the value for the singlet oxygen quantum yield is taken to be 0.4, and the oxygen quenching constant (ϕ) by phthalocyanine species (k_q') is 10^9 M^{-1} s^{-1}.[25]

The steady state is modeled by equating the generation rate of singlet oxygen, which is assumed to be the photosensitization rate of the singlet oxygen sensitizer, to the rate of disappearance of singlet oxygen as represented by the sum of the rates of singlet oxygen deactivation mechanisms mentioned earlier. The difference in inhibition time at a specific Zn(ttp) concentration, from its value at zero Zn(ttp) concentration provides a measure of the initial singlet oxygen concentration because it does not participate in radical scavenging. Although the concentration of singlet oxygen during the inhibition period changes as a result of small amounts of radical scavenging by oxygen, a single, approximate value is assumed to represent this concentration during the inhibition period. On the basis of this approach, the final form of the equations is given as

$$\begin{aligned} R_i \Delta t &= [O_2^1] \\ \frac{1}{\Delta t} &= \left(\frac{k_d R_i}{A}\right)\frac{1}{C} + \frac{k_q R_i}{A} \end{aligned} \qquad (2)$$

where Δt is equal to the quantity, $t_{inh}(C=0) - t_{inh}(C)$, $[O_2^1]$ is the singlet oxygen concentration. k_d is the singlet oxygen decay constant, k_q is the singlet oxygen deactivation constant, and R_i is the photoinitiation rate. According to eq 2, if the inverse of the change in inhibition time is plotted against the inverse of the Zn(ttp) concentration, the resulting curve should be linear. Figure 9 shows that it is indeed the case. Moreover, the kinetic constants k_d and k_q are readily calculated from the slope and intercept. The calculated value of k_d corresponds to an oxygen excited state lifetime of approximately a millisecond, near that which is reported for oxygen in most organic liquids and monomers.[17]

Optimization of Curing Conditions: Dual Wavelength Curing. In this section we demonstrate the capability of this technique to achieve high conversions and simultaneously suppress oxygen inhibition in highly inhibited environments. The primary effort was focused on making the undesirable termination reaction insignificant by altering the ratio of Zn(ttp) to propagating radicals. As a result, Zn(ttp) renders only a small fraction of the radicals inactive and most radicals continue to propagate, uninhibited by Zn(ttp). This outcome is enabled by

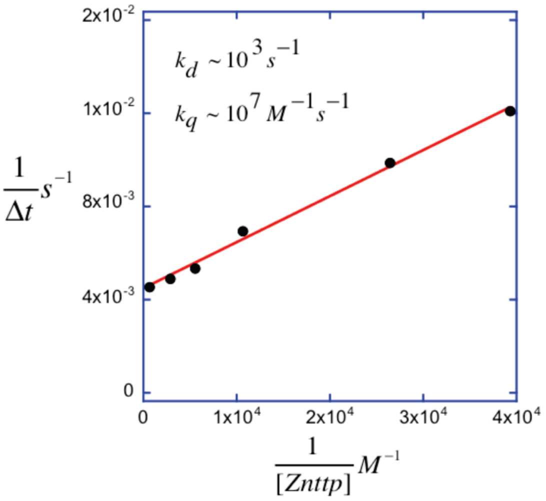


Figure 9. Validation of the mathematical representation of the proposed mechanism by fitting it with the experimental results. Δt represents the magnitude of the difference between the inhibition time for a specific concentration of Zn(ttp) and that at zero concentration of Zn(ttp). k_d and k_q are calculated from the slope and intercept respectively.

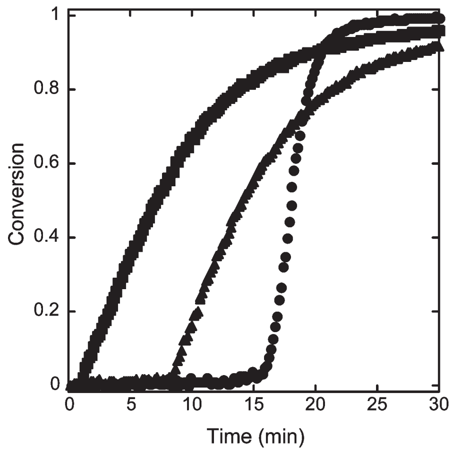


Figure 10. Conversion profiles for photopolymerization of PEGDA in oxygen saturated conditions: With Zn(ttp) and a single light source, 400−500 nm (△), With Zn(ttp) and two light sources, 400−500 nm and 600−650 nm (□), Without Zn(ttp) and two light sources, 400−500 nm and 600−650 nm (○). The monomer formulation used was 1.8 M PEGDA, 0.23 M MDEA, 35 mM VP, 44 μM Eosin, and 2.9×10^{-4} M Zn(ttp). Light intensity used was 7.5 mW/cm^2 of 400−500 nm light and 20 mW/cm^2 of 600−650 nm light. The monomer was purged with oxygen for 10 min prior to polymerization.

increasing the photoinitiator (Eosin) concentration and selecting wavelengths that promote effective singlet oxygen generation. Two independent light sources spanning 400−500 and 600−650 nm were chosen. The photoinitiator, eosin, has a negligible absorption in the 600−650 nm range whereas Zn(ttp) absorbs in both ranges, thereby providing an opportunity for nearly independent control of the oxygen photosensitization rates and the photoinitiation rate.

Figure 10 shows the conversion profiles of oxygen saturated monomer formulations for various scenarios. It is clear that when Zn(ttp) is absent, the conversion profile is characterized by an extended inhibition time followed by polymerization to complete conversion. The conversion profiles for Zn(ttp)-mediated polymerizations show significantly lower inhibition times while also enabling conversions of higher than 90%, even before the inhibition period in the conventional polymerization is complete! The difference between dual and single wavelength curing is obvious in the degree of reduction in inhibition time.

Conclusions

The ability of Zn(ttp) to reduce or eliminate oxygen inhibition in radical-mediated polymerizations has been shown. Moreover, the suppression happens simultaneously with polymerization. In particular, this ability was demonstrated to be most significant in highly inhibited environments where the oxygen concentration exceeds the photoinitiator concentration, a condition under which polymerization without Zn(ttp) is practically impossible. This approach facilitates the use of low initiator concentrations, even in oxygen rich media. Furthermore, the mechanism of this suppression has been shown to occur by photosensitization of oxygen by Zn(ttp). Therefore, with high rates of oxygen photosensitization, radical scavenging by oxygen and the associated polymerization inhibition are suppressed. Zn(ttp) also participates in increasing the termination kinetics via a nonphotoactivated mechanism and as a result decreases the overall conversion significantly under some conditions. This result was overcome by appropriately designing curing conditions that relatively reduce the termination reaction while still promoting singlet oxygen generation.

References and Notes

(1) Decker, C. Photoinitiated Curing of Multifunctional Monomers. *Acta Polym.* **1994**, *45*, 333–347.
(2) Decker, C. Kinetic study and new applications of UV radiation curing. *Macromol. Rapid Commun.* **2002**, *23*, 1067–1093.
(3) Andrzejewska, E. Photopolymerization kinetics of multifunctional monomers. *Prog. Polym. Sci.* **2001**, *26*, 605–665.
(4) Bowman, C. N.; Kloxin, C. J. Toward an enhanced understanding and implementation of photopolymerization reactions. *AIChE J.* **2008**, *54*, 2774–3037.
(5) Qian, T. C.; Li, Y. F.; Wu, Y. Z.; Zheng, B.; Ma, H. W. Superhydrophobic poly(dimethylsiloxane) via surface-initiated polymerization with ultralow initiator density. *Macromolecules* **2008**, *41*, 6641–6645.
(6) Hansen, R. R.; Avens, H. J.; Shenoy, R.; Bowman, C. N. Quantitative evaluation of oligonucleotide surface concentrations using polymerization-based amplification. *Anal. Bioanal. Chem.* **2008**, *392*, 167–175.
(7) Hansen, R. R.; Sikes, H. D.; Bowman, C. N. Visual detection of labeled oligonucleotides using visible-light-polymerization-based amplification. *Biomacromolecules* **2008**, *9*, 355–362.
(8) Sikes, H. D.; Hansen, R. R.; Johnson, L. M.; Jenison, R.; Birks, J. W.; Rowlen, K. L.; Bowman, C. N. Using polymeric materials to generate an amplified response to molecular recognition events. *Nat. Mater.* **2008**, *7*, 52–56.
(9) Hoyle, C. E.; Bowman, C. N. Thiol-Ene Click Chemistry. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540–1573.
(10) Decker, C.; Jenkins, A. D. Kinetic Approach of O-2 Inhibition in Ultraviolet-Induced and Laser-Induced Polymerizations. *Macromolecules* **1985**, *18*, 1241–1244.
(11) Davidson, R. S. *The role of amines in UV-curing*; Chapman and Hall: 1993; Vol. *III*.
(12) Miller, C. W.; Kess, R.; Iijima, T.; Hoyle, C. E. *Polym. Prepr.* **1997**, *38*, 258.
(13) Hoyle, C. E.; Lee, T. Y.; Roper, T. M. Thiol-Enes: Chemistry of the past with promise for the future. *J. Polym. Sci.: Polym. Chem. Ed.* **2005**, *42*, 530–5338.
(14) Gush, D. P.; Ketley, A. D. *Mod. Paint Coat.* **1978**, *11*, 68.
(15) Studer, K.; Decker, C.; Beck, E.; Schwalm, R. Overcoming oxygen inhibition in UV-curing of acrylate coatings by carbon dioxide inerting. Part I. *Prog. Org. Coat.* **2003**, *48*, 92–100.
(16) Decker, C. Novel Method for Consuming Oxygen Instantaneously in Photopolymerizable Films. *Makromol. Chem.—Macromol. Chem. Phys.* **1979**, *180*, 2027–2030.
(17) Gou, L. J.; B. Opheim, B.; Corestsopoulos, C. N.; Scranton, A. B. Consumption of the molecular oxygen in polymerization systems using photosensitized oxidation of dimethylanthracene. *Chem. Eng. Commun.* **2006**, *193*, 620–627.
(18) Lalevee, J.; M. A. Tehfe, M. A.; Allonas, X.; Fouassier, J. P. Boryl Radicals as a New Photoinitiating Species: A Way to

Reduce the Oxygen Inhibition. *Macromolecules* **2008**, *41*, 9057–9062.

(19) El-Roz, M.; J. Lalevee, J.; Allonas, X.; Fouassier, J. P. The silane-ene and silane-acrylate polymerization process: A new promising chemistry? *Macromol. Rapid Commun.* **2008**, *29*, 804–808.

(20) Awokola, M.; W. Lenhard, W.; Löffler, H.; Flosbach, C.; Frese, P. UV crosslinking of acryloyl functional polymersin the presence of oxygen. *Prog. Org. Coat.* **2002**, *44*, 211–216.

(21) Bonnett, R. Photosensitizers of the Porphyrin and Phthalocyanine Series for Photodynamic Therapy. *Chem. Soc. Rev.* **1995**, *24*, 19–33.

(22) Henderson, B. W.; Dougherty, T. J. How Does Photodynamic Therapy Work. *Photochem. Photobiol.* **1992**, *55*, 145–157.

(23) Nelson, J. S.; Liaw, L. H.; Orenstein, A.; Roberts, W. G.; Berns, M. W. Mechanism of Tumor Destruction Following Photodynamic Therapy with Hematoporphyrin Derivative, Chlorin, and Phthalocyanine. *J. Natl. Cancer Inst.* **1988**, *80*, 1599–1605.

(24) Wasserman, H. H., Murray, R. W., Eds. *Singlet Oxygen*; Academic Press: New York, 1979.

(25) Grofcsik, A.; Baranyai, N.; Bitter, I.; Csokai, V.; Kubinyi, M.; Szegletes, K.; Tatai, J.; Vidoczy, T. Triple state properties of tetrasubstituted zinc phthalocyanine derivatives. *J. Mol. Struct.* **2004**, *704*, 11–15.

(26) Schweitzer, C.; Schmidt, R. Physical mechanisms of generation and deactivation of singlet oxygen. *Chem. Rev.* **2003**, *103*, 1685–1757.