

# A Photochemical Method to Eliminate Oxygen Inhibition in Photocured Systems

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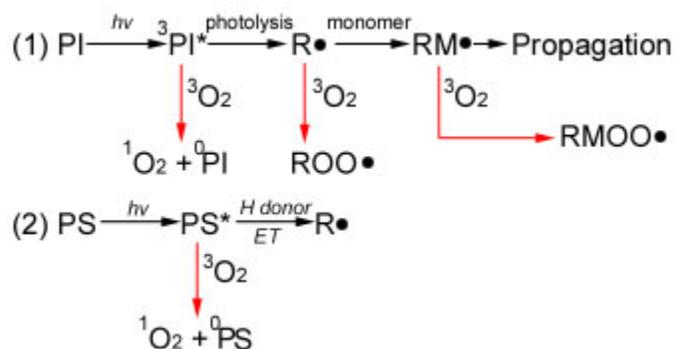
## Abstract

This paper provides a unique and practical solution to a major problem in photocured acrylate coatings: oxygen inhibition at the coating surface. The strategy involves the inclusion of two specially selected components in the reactive formulation: 1) a light-absorbing molecule (the singlet oxygen generator), which interacts with the ground state (triplet) oxygen to produce an excited singlet state of oxygen, and 2) a second compound (the singlet oxygen trapper) which reacts with the singlet oxygen thereby removing it from the system. A variety of photo-induced singlet oxygen generators with different light absorption spectra may be used in this method, however porphyrins were found to be especially attractive because they allowed singlet oxygen to be produced using light in the red or the near IR regions of the spectrum. Therefore, the oxygen-consumption reaction can be initiated using a different wavelength than the photopolymerization, and the oxygen can be consumed before the reaction has begun. The experimental results illustrate that this method can be used to reduce or eliminate the inhibition period, and enhance the photopolymerization rate for reactions carried out in air.

## Introduction

Oxygen inhibition is perhaps the most important unsolved problem in free radical polymerizations. Molecular oxygen, with its extraordinary biradical structure and the high reactivity towards electron rich groups, participates in numerous chemical and biochemical processes which in some degree determine the ultimate outcome of these reactions. The presence of oxygen in free-radical polymerization system known to be a primary cause of an inhibition period and will ultimately affect the attainable properties of polymer and lower the rate of polymerization. It is believed that major reactions of oxygen in light induced polymerization through two mechanisms as illustrated in Figure 1: quenching of the triplet state of photoinitiator or dye and scavenging of free radicals. For the first mechanism, the triplet ground state of molecular oxygen tends to undergo triplet-triplet annihilation with the excited triplet state of photoinitiator or photosensitizer and form singlet oxygen. This effect is especially pronounced in the second type of photoinitiators due to their prolonged lifetime of triplet state.<sup>[1],[2]</sup> In the second mechanism, the characteristic biradical structure of oxygen render it extremely high reactivity towards free radicals, therefore the primary radical or the propagating chain will be terminated efficiently in the presence of oxygen. The resulting peroxide radicals are non-reactive in initiating the polymerization and ready to abstract a hydrogen atom to form hydroperoxide.<sup>[1][2]</sup>

Discovering an efficient way to eliminate oxygen inhibition has been a long-standing goal of the polymerization industries, especially for polymerization of thin films and coatings, where the presence of oxygen will lead to the formation of a tacky surface on the top of the



**Figure 1:** Oxygen quenching of free radicals and triplet excited state of photoinitiators. PI: Photoinitiator; PS: Photosensitizer; ET: Electron transfer; R: free radical.

product. Several approaches have been proposed to reduce the detrimental oxygen effect, including addition of oxygen scavengers (thiols, phosphines, acrylic amines) or photoinitiators in their triplet state, using paraffin wax to exclude oxygen and applying chemicals which are capable of forming an indiffusible film on the top surface of the sample. [2] However, they are either difficult to control or not efficient in blocking the diffusion of oxygen. As a result, many companies perform polymerization under an inert nitrogen atmosphere using expensive inerting equipment. In this project we aim to develop an improved understanding of the effects of oxygen on both the initiation and propagation steps of the polymerization. Mitigation of oxygen's effects will be attempted through the application of different initiation system including photo-cleavage, three component initiator systems and the presence of highly abstractable hydrogens.

Our strategy for overcoming the oxygen inhibition of free radical polymerizations involves the inclusion of two specially selected components in the reactive formulation: 1) a light-absorbing molecule which interacts with the ground state (triplet) oxygen to produce an excited (singlet) state of oxygen (hereafter this compound will be called the singlet oxygen generator), and 2) a second compound which reacts with the singlet oxygen thereby removing from the system (this compound will hereafter be called the singlet oxygen trapper). A variety of photo-induced singlet oxygen generators with different light absorption spectra may be used in this method, and criteria for the selection of both components will be discussed. Porphyrins were found to be attractive because they allowed singlet oxygen to be produced using light in the red or the near IR regions of the spectrum. Therefore, the oxygen-consumption reaction can be initiated using a different wavelength than the photopolymerization, and the oxygen can be consumed before the reaction has begun.

The application of this method is very flexible since it allows the oxygen to be consumed either before the polymerization is initiated (by a pre-illumination step using red or near-IR light), or simultaneously with the polymerization (by simultaneous illumination with one set of wavelengths that excite the singlet oxygen generator and a second set of wavelengths absorbed by the initiator). This method can be used in conjunction with nearly any current free radical photoinitiator or thermal initiator, and any free radical polymerizable monomer. In addition, since our approach allows the oxygen to be consumed before the polymerization is begun, it may lead to an increase in the primary polymer chain length. Finally, since the

product of the oxygen-consumption reaction is a peroxide (which may decompose to produced radicals, there is the potential that the oxygen is essentially converted into new active centers.

## Selection of the singlet oxygen generator

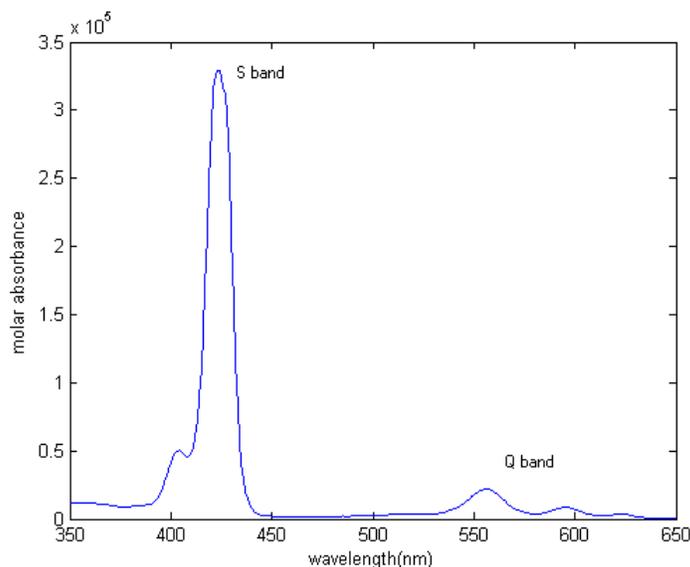
**The electronic states of oxygen.** The high reactivity of ground state oxygen towards radicals and electron-rich groups can be explained by its electronic configuration, which is often represented by  $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2$ . The antibonding  $\pi_g^*$  frontier orbitals of the ground state oxygen are singly occupied by electrons with parallel spins, therefore the ground state is a triplet state. There are two lowest energy excited states of oxygen,  $S_1$  ( $^1\Delta_g$ ) (95 kJ/mol above the ground state) and  $S_2$  ( $^1\Sigma_g^+$ ) (155 kJ/mol above the ground state). In the  $S_1$  state, one of the antibonding  $\pi$  orbitals is occupied by two paired electrons, and the other is empty. The frontier orbitals of the  $S_2$  state are singly occupied by two anti-parallel electrons. The electron transitions  $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$  and  $^1\Delta_g \rightarrow ^3\Sigma_g^-$  are quantum mechanically forbidden. Consequently, both singlet states of molecular oxygen have relatively long lifetimes (typically on the order of milliseconds in the liquid state). However, the significance of the 2<sup>nd</sup> singlet state is greatly reduced in the condensed phase because of the increase chance of the collapse to the 1<sup>st</sup> singlet state. Therefore, the first singlet state ( $S_1$ ) plays a more important role in our proposed method and will be referred to singlet oxygen. [3]

**Overview of the properties of porphyrins.** Porphyrins and their derivatives have been widely used in many important applications such as photodynamic therapy, catalysis of multi-electron redox reactions, modeling of photosynthesis, etc. Their ability to produce singlet oxygen has been well established and documented. The quantum yield of singlet oxygen for different kinds of porphyrin, which is essential for this research, is typically close to unity, and can be directly obtained from published reports and papers. Porphyrin consists of four pyrrole rings; their highly conjugated structure renders them the ability to undergo a number of chemical reactions typical of aromatic compounds. In addition, porphyrins exhibit unique absorbance characteristics and photochemical properties. [4]

The exact absorption spectrum of a given porphyrin will depend upon its chemical structure, however porphyrins generally exhibit two absorption bands. The higher energy absorption band is in the near UV region (typically 400-430 nm) and is called the Soret band. This absorption band corresponds to a transition from the ground singlet state,  $S_0$ , to the second excited singlet state,  $S_2$ . The second absorption band generally exhibited by porphyrins occurs at longer wavelengths, and is called the Q band. This absorption band corresponds to a transition from the ground singlet state,  $S_0$ , to the first excited singlet state,  $S_1$ . The relative intensities of the Soret band and the Q band depend upon the chemical structure of the porphyrins. For example, in the case of phthalocyanine derivatives of porphyrins, the Q band absorption is generally higher than the Soret band, while many other classes of porphyrins exhibit a more intense Soret band. In any case, the  $S_2$  state of all porphyrins and their derivatives is separated by a large energy gap from the lowest excited state ( $S_1$ ). This large energy gap means that radiationless deactivation of the  $S_2$  to the  $S_1$  state is slow enough to allow competing processes to occur. The two absorption bands make it possible to achieve desired photochemical results through applying different wavelengths of incident light. Notably, it is  $S_1$  state that is responsible for singlet oxygen generation, [10] therefore the Q absorption may be used for photochemical elimination of oxygen. In addition,

the  $S_1$  state generally does not participate in electron transfer reactions with more organic molecules, while the  $S_2$  state may participate in many more electron transfer reactions. This is significant since the higher energy  $S_2$  absorption could be used to consume the porphyrin after the oxygen consumption is complete. [4]

Porphyrins produce singlet oxygen through a well-known triplet-triplet annihilation process. After this first excited singlet state is populated by absorption, the porphyrins undergo intersystem crossing to the first excited triplet state. Porphyrins are effective singlet oxygen generators because they meet the following requirements: (a) their triplet excited state is sufficiently long-lived to encounter the dissolved oxygen during its lifetime; (b) the triplet state energy is around 100 kJ/mol (slightly higher than the 95 kJ/mol energy of singlet oxygen) allowing these compounds to give efficient  $^1O_2$  production without efficient back reaction. [4]



**Figure2:** UV-Vis absorption spectra of 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc

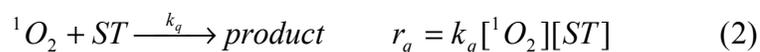
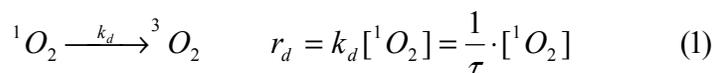
The unique absorption characteristics and photochemical properties described above make porphyrins and their derivatives ideal for a new photochemical method to eliminate oxygen inhibition in free radical polymerizations.

### **Selection of the singlet oxygen trapper**

Once the high-energy singlet oxygen is produced through the TTA process, it can undergo relaxation through photochemical or photophysical pathways. A chemical quencher that can rapidly react with the singlet oxygen (singlet oxygen trapper or ST) is needed to stabilize the singlet oxygen before it is physically deactivated and forms the inhibiting ground state oxygen again. The singlet oxygen is more electrophilic than the ground state oxygen and is capable to participate in a variety of reactions with organic compounds, such as cycloaddition to carbon double bonds to produce cyclic peroxides, cycloaddition with 1,3-dienes and polynuclear aromatics to produce endoperoxides, the “ene” reaction with carbon double bonds to produce hydroperoxides. The rate of singlet oxygen addition to the double

bond depends on a number of factors including the electron density of the double bond, and substituents attached to the carbon atoms. <sup>[3][6]</sup> Some classes of organic compounds that exhibit high reaction rates with singlet oxygen are, for example, enamines, polynuclear aromatics, pyrroles, furans, and alkenes containing one or more allylic hydrogens, *etc.* However not all of the compounds that will react with singlet oxygen are appropriate for this method due to other considerations and limitations. The general criteria that must be applied to identify appropriate singlet oxygen trappers are listed below:

1. The reaction rate between singlet oxygen and the singlet oxygen trapper must be fast enough (note that the reaction rate depends upon both the rate constant for the reaction and the concentration of the singlet oxygen trapper); The competing chemical reactions and the resulting constraints on the reaction rate constants are illustrated by equations 1 through 4 below.



$$\text{Criteria:} \quad r_q > r_d \Rightarrow k_q[{}^1O_2][ST] > \frac{1}{\tau} \cdot [{}^1O_2] \quad (3)$$

$$\text{therefore:} \quad k_q > \frac{1}{\tau \cdot [ST]} \quad (4)$$

In these equations:

${}^1O_2$  represents the excited singlet state oxygen;

${}^3O_2$  represents the ground triplet state oxygen;

ST represents the ST;

$r_d$  is the rate of singlet oxygen deactivation in pure solvent;

$k_d$  is the rate constant of singlet oxygen deactivation;

$\tau$  is the lifetime of the excited singlet oxygen ;

$r_q$  is the rate of reaction between ST and singlet oxygen; and

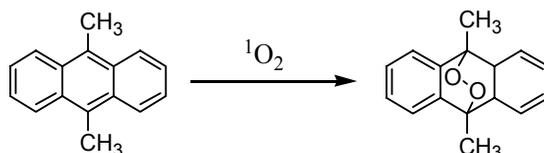
$k_q$  is the rate constant of ST.

Where the value of  $\tau$  (the singlet oxygen lifetime) in organic liquids is typically on the magnitude of  $10^{-3}$  seconds and the concentration of the ST should be on order of  $10^{-3}$  M (slightly higher than the oxygen concentration). Therefore, the  $k_q$  should be on the order of  $10^6 \text{ M}^{-1}\text{sec}^{-1}$  or higher.

2. The singlet oxygen trapper should not react with the ground state (triplet) oxygen;
3. The singlet oxygen trapper must be stable in air-saturated monomer

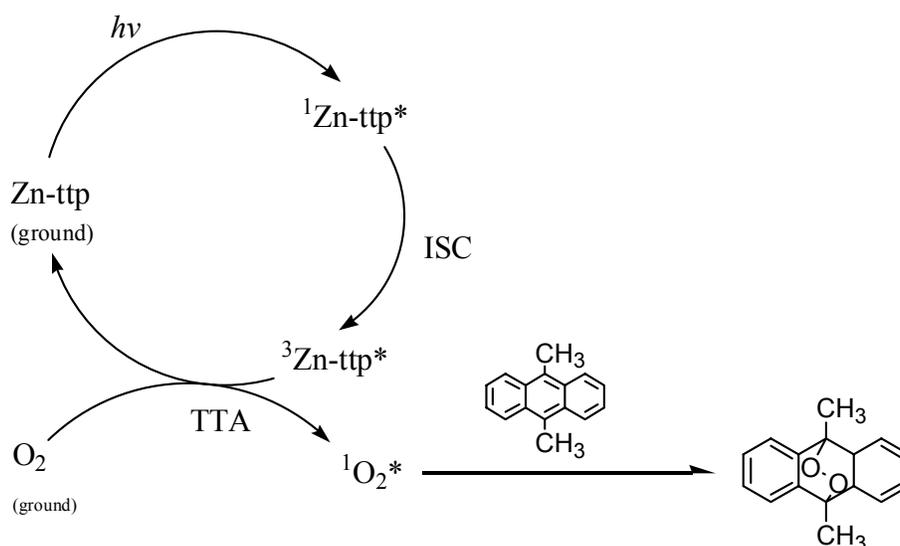
A compound such as diphenylisobenzofuran (DPBF), which is a most commonly used ST<sup>[5]</sup>, meets the first criterion, but does not meet the second and third criteria. Preliminary results showed that DPBF decays rapidly in both air-saturated monomer and the Argon-purged monomer, which suggests that it can react with ground state oxygen or unsaturated monomer (possibly through Diels-Alder scheme <sup>[7]</sup>). Extensive work had been carried out to characterize the potential STs from electron rich compounds such as enamines, polynuclear aromatics, pyrroles, furans, and the three compounds that do meet all three of these criteria are: 9,10-

dimethylantracene (DMA), 9,10-diphenylanthracene, and rubrene. In this study, DMA is selected as ST because it has higher solubility in a wider range of monomers. The DMA has been proved experimentally to have much higher stability in the unsaturated acrylate monomers than previously reported DPBF, and the reaction scheme of DMA and singlet oxygen is well established<sup>[8]</sup> (Figure 3). More importantly, the rate constant for the reaction between DMA and singlet oxygen is reported as high as  $2.4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  which, according to the first criteria, makes DMA a very efficient ST.



**Figure 3:** [4+2]cycloaddition reaction between DMA and singlet oxygen

According to the previous discussion, Zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (Zn-ttp) was selected as the SG for these studies, and dimethylantracene (DMA) was selected as the ST. Based upon these components, the proposed reaction mechanism by which the singlet oxygen is measured is illustrated in Figure 4.

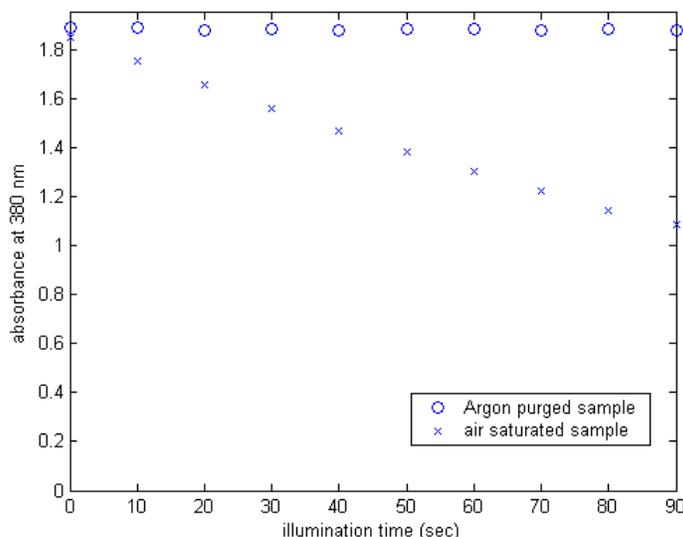


**Figure 4:** Proposed mechanism of the singlet oxygen generation and trapping processes in the photochemical method to measure oxygen concentration.

**Endoperoxide, hydroperoxide and dioxetane:** In general, the reactions between singlet oxygen and the trapper results in the production of hydroperoxides, endoperoxides, or dioxetanes. For example, DMA results in the production of an endoperoxide while alkenes containing allylic hydrogens result in the production of hydroperoxides. Because of the weakness of the O-O bond, these peroxide products can undergo homolysis of peroxy linkage photochemically or thermally to yield free radicals which are capable to attach nearby C-C double bonds to induce another round of propagation.<sup>[6]</sup>

## Results and Discussion

**Preliminary studies.** A series of control experiments was performed to verify that DMA is consumed only through the photo-oxidation reaction with singlet oxygen. The experimental results revealed that the DMA concentration decreased with time only for the experiment in which both Zn-ttp and DMA are present in the oxygen-saturated monomer. The sample containing both Zn-ttp and DMA in the argon-purged (oxygen-depleted) monomer exhibited a DMA absorbance that did not change with time. These results illustrate clearly that oxygen must be present for the DMA to be consumed upon illumination with 556 nm light. In addition, no change in the DMA concentration was observed for the samples containing only Zn-ttp or only DMA. Together, these results suggest that oxygen plays a key role in the consumption of DMA upon illumination with light absorbed by Zn-ttp. For systems containing all three compounds: oxygen, Zn-ttp and DMA, absorption of light by Zn-ttp results in the consumption of DMA. If any one of these three components is missing, there is no change in DMA concentration upon illumination with 556 nm light. These results are consistent with the reaction scheme shown in Figure 4 which Zn-ttp produces singlet oxygen and DMA reacts with the singlet oxygen to produce an endoperoxide.



**Figure 5:** Overlaid absorbance at 380 nm as function of illumination time for air-saturated sample and Argon purged sample. Both samples contain  $1 \times 10^{-4}$  M Zn-ttp and  $2 \times 10^{-3}$  M DMA in HEMA, and the integrated intensity of the incident light ( $556 \pm 10$  nm) was  $0.146 \text{ mW/cm}^2$ .

**The effect of a singlet oxygen quencher.** The presence of 1,4-diazabicyclo [2.2.2] octane (DABCO) in the system will lead to the inhibition of the reaction between singlet oxygen and the trapper. DABCO is well known for the physical quenching of the singlet oxygen and is capable of returning it to its ground state without undergo any chemical transformation. Experiments performed in the presence of  $1 \times 10^{-3}$  M DABCO showed that the addition of this singlet oxygen quencher significantly decreased the rate of DMA absorption decay, which suggests that singlet oxygen has indeed been generated through the TTA process as proposed in Figure 4.<sup>[9]</sup>

**Dissolved oxygen concentration measurement.** The excess amount of ST (DMA) is not favored by this method since the absorption of DMA overlaid with PI's absorption, therefore a reliable data of the dissolved oxygen (DO) concentration is required to determine the range of the ST concentration base on the established reaction scheme between the ST and singlet oxygen.

The experiments to measure the dissolved oxygen (DO) concentrations in the acrylate monomers were carried out at room temperature in 1-mm short-path quartz cuvettes, which were selected due to the high extinction coefficient of the DMA. For each monomer, the appropriate concentrations of the SG (Zn-ttp) and ST (DMA) were established based upon solubility, reactivity, and absorption criteria, a more detailed discussion on the method has been reported in a related paper in press. The UV-visible absorption spectra were recorded using an Agilent 8453 Spectrophotometer. For each sample, the absorbance spectrum was recorded prior to illumination (time  $t=0$ ), then a series of spectra were collected at ten second intervals until the intensity of the DMA peaks no longer decreased. All the measurements were made at an ambient temperature of 21°C. Results for the dissolved oxygen concentration in seven acrylate monomers are shown in Table 1.

Table 1 illustrates that the experimental values for the dissolved oxygen depend significantly on the structure of the acrylate monomers, and range from a low of  $0.59 \times 10^{-3}$  moles/liter for the ethoxylated (2)-hydroxyethylmethacrylate to a high of  $2.07 \times 10^{-3}$  moles/liter for butyl acrylate. In addition, the experimental results shown in Table 1 illustrate some interesting correlations between the monomer structure and the DO concentration. For example, the relatively low DO concentration observed for HEMA suggests that the presence of the hydroxyl group lowers the oxygen solubility (this is consistent with oxygen solubility trends in organic solvents). The E-HEMA results illustrate that the additional presence of the ether linkage further decreases the oxygen solubility. The relationship between the monomer structure and the oxygen solubility will be more systematically investigated in future work.

**Table 1:** Dissolved oxygen concentration in air-saturated monomers

Monomer	Zntpp conc. ( $10^{-4}$ mol/l)	DMA conc. ( $10^{-3}$ mol/l)	Measured DO conc. ( $10^{-3}$ mol/l)	Std. Dev. ( $10^{-3}$ mol/l)
HEMA <sup>1</sup>	1.00	2.00	0.83	0.002
HDDA <sup>2</sup>	1.00	2.00	1.17	0.004
Butyl Acrylate	1.00	2.50	2.07	0.019
E-HEMA <sup>3</sup>	1.00	2.00	0.59	0.005
TPGDA <sup>4</sup>	1.00	2.00	1.43	0.014
TEGDMA <sup>5</sup>	1.00	2.00	0.98	0.002
TMPTA <sup>6</sup>	0.1	2.00	1.05	0.012

<sup>1</sup>2-hydroxyethyl methacrylate; <sup>2</sup>1,6-hexanediol diacrylate; <sup>3</sup>ethoxylated (2)-hydroxyethyl methacrylate; <sup>4</sup>tripropylene glycol diacrylate; <sup>5</sup>triethyleneglycoldimethacrylate; <sup>6</sup>trimethylolpropanetriacrylate

**Enhancement of the free radical polymerization rate due to oxygen consumption.**

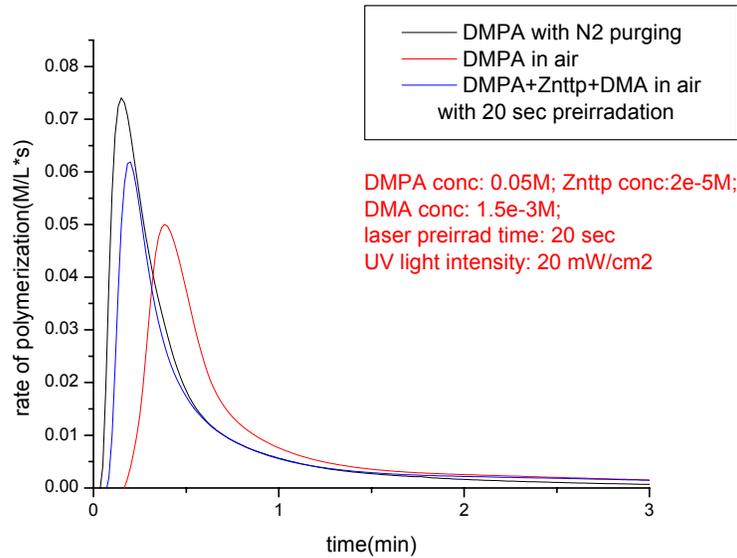
The DSC studies were carried out using Zn-ttp as the singlet oxygen generator, DMA as the singlet oxygen trapper, pentaerythritol triacrylate (PETA) as the free radically polymerizable

monomer, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the free radical photoinitiator. The polymerization reaction rate as a function of time was determined using in situ differential scanning calorimetry (DSC) to measure the rate at which heat is released from the sample as a function of time. The rate at which heat is released from the sample is directly proportional to the polymerization rate since the polymerization reaction is exothermic.

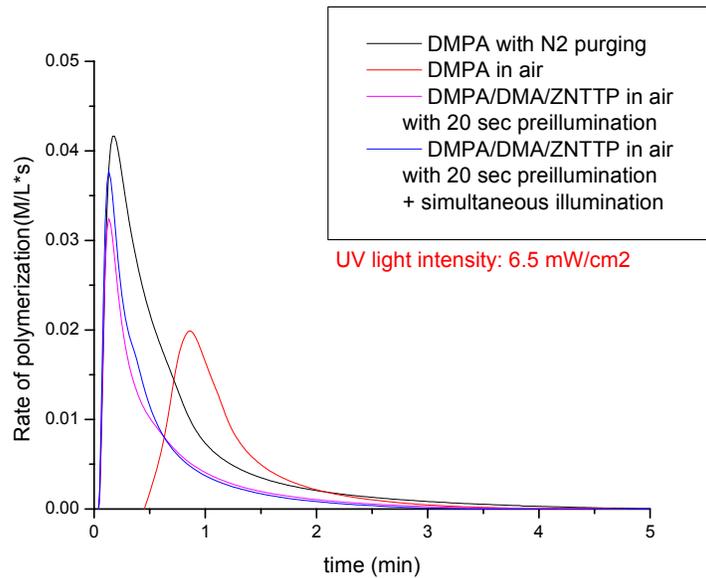
The photopolymerization rate profile of the PTA/DMPA system was obtained through DSC experiments performed under two conditions: Nitrogen purging and air saturation. To demonstrate the effect of the photochemical consumption of the oxygen on the polymerization kinetics, the sample containing Zn-ttp and DMA were subject to illumination with 670 nm light from a diode laser prior to illumination with UV light. The probe of the laser was adjusted to approximate 10 cm above the DSC sample chamber, and the distributed spot of laser was positioned so that the reference and sample cell will be radiated by equal amount of the laser light. A 200 watts Xe-Hg lamp was used as UV light source, and the intensity of the light was adjusted by adding neutral density filters and changing the height of the lamp. The amount of sample injected into the DSC pan ranges from 13.2 to 13.7 mg. Before the photo-curing process, sample was kept in the DSC chamber and purged with ambient atmosphere for 10 minutes to achieve the saturation.

Figure 6 illustrates the effect of the 670 nm illumination on the reaction kinetics of the PTA/DMPA system. Compared with nitrogen purging condition, there is a pronounced decrease of the maximum rate and prolongation of the time required to reach this rate in the case of air-saturated condition. However, even in an air environment, the inhibitory effect was significantly reduced after addition of the Zn-ttp and DMA and the pre-illumination with the 670 nm diode laser for the polymerization. (The maximum rate was increased from 0.49 M/(l•s) to 0.62 M/(l•s), and the time to reach the reaction peak rate was decreased from 0.4 min to 0.2 min.) The rate profile of the pre-illuminated sample in the air is close to the one of the Nitrogen purged sample in which almost no molecular oxygen is present. These results indicate that the observed enhancement in the polymerization rate and reduction in the inhibition time result from the photochemical consumption of the oxygen in the reaction system. Under the conditions of this experiment (light intensity, species concentrations, etc) the optimum pre-illumination time is 20 seconds; additional lengthening of the illumination time did not lead to the further enhancement in the rate. This optimum time may vary for different monomers and is related to the concentration and photochemical properties of SG and ST. Previous studies showed that the increase of SG concentration will lead to the reduction of the optimum pre-illumination time.

Lower UV light intensity has been applied to the same sample and the result was shown in Figure 7 and Figure 8. For the 6.5 mW/cm<sup>2</sup> UV light source, pre-illumination again notably improved the peak rate in air environment. More importantly, the inhibition periods has been completely eliminated according to the rate profile showed in Figure 7, which suggest a fully consumption of dissolved oxygen before the photopolymerization. However, the reaction rate dropped rapidly compared with the nitrogen purged sample after reaching the peak. A possible explanation for this observation is the effect of diffused oxygen becomes more significant in the case of low UV light intensity. The rate profile of the polymerization with simultaneous laser illumination shows some evidence of the enhanced monomer conversion, which indicates that the combination of DMA/Zn-ttp and laser is capable of consuming the molecular oxygen during the process of polymerization.



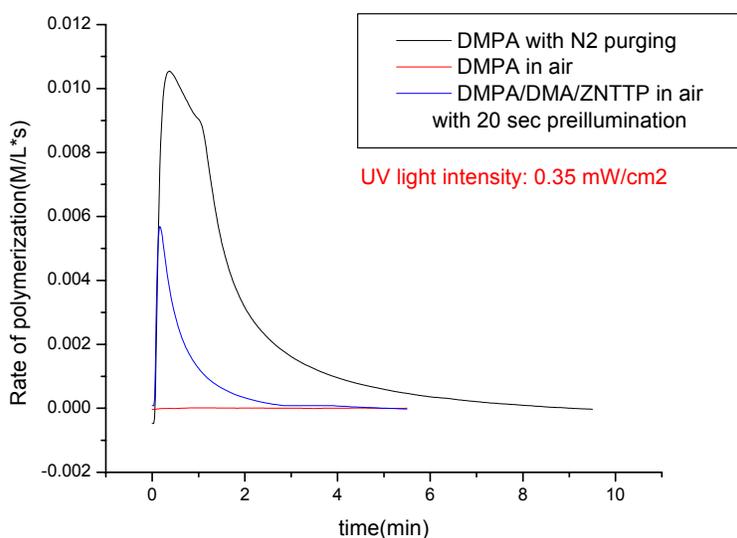
**Figure 6:** Rate of polymerization for PTA as a function of time. Photoinitiator: 0.05 M DMPA, SG:  $2.0 \times 10^{-5}$  M Zn-ttp, ST:  $1.5 \times 10^{-3}$  M DMA. UV light intensity: 20 mW/cm<sup>2</sup>.



**Figure 7:** Rate of polymerization for PTA as a function of time. Photoinitiator: 0.05 M DMPA, SG:  $2.0 \times 10^{-5}$  M Zn-ttp, ST:  $1.8 \times 10^{-3}$  M DMA. UV light intensity: 6.5 mW/cm<sup>2</sup>.

Figure 8 illustrates that, for the 0.35 mW/cm<sup>2</sup> UV light source, no polymerization was observed for sample containing 0.05 M DMPA in air environment, suggesting that the propagation of the active center was completely inhibited by the dissolved oxygen under this low-intensity UV radiation. However, the addition of the DMA/Zn-ttp system and the pre-illumination successfully induce the photo-curing of the samples in the air under the same

condition of UV light source. This result again proved that our oxygen consumption system (Znttp/DMA) can effectively consume the dissolved oxygen upon the illumination of 670 nm laser and start the polymerization for a system completely inhibited by molecular oxygen.



**Figure 8:** Rate of polymerization for PTA as a function of time. Photoinitiator: 0.05 M DMPA, SG:  $2.0 \times 10^{-5}$  M Zn-ttp, ST:  $1.4 \times 10^{-3}$  M DMA. UV light intensity: 0.35 mW/cm<sup>2</sup>.

These studies on the polymerization of the DMPA/PETA system demonstrate that Zn-ttp as a SG can efficiently generate singlet oxygen upon the pre-illumination without producing radicals, and DMA as a trapper can rapidly react with the singlet oxygen while remain relatively stable in the acrylate monomers. Also the DSC result is consistent with our hypothesis that the combination of Zn-ttp/DMA and pre-illumination can effectively consume the molecular oxygen dissolved in the system. As a result, the inhibition period was significantly reduced and the rate of polymerization increased dramatically.

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