Novel Photopolymerizable Monomers

Neil B. Cramer¹, Casey O’Brien¹, Chris W. Miller², Jurgen Van Holen³, and Christopher N. Bowman¹,⁴
¹ University of Colorado, Department of Chemical and Biological Engineering, Boulder, CO, USA
² Cytec, Smyrna, GA, USA
³ Cytec, Drogenbos, Belgium
⁴ Biomaterials Research Center, School of Dentistry, University of Colorado Health Sciences Center, Aurora, CO 80045, USA

Introduction

Recently, there have been significant academic and commercial interests in a class of novel monovinyl (meth)acrylate monomers whose constituents have exhibited numerous unique properties¹-⁹. For example, many of these monomers have exhibited rates of cure similar to that of higher functionality acrylates while still polymerizing to very high degrees of conversion. Despite being monofunctional in (meth)acrylate functionality, many of these monomers rapidly polymerize to form crosslinked polymer networks that exhibit improved polymer properties. The mechanistic underpinnings leading to this enhanced reactivity have yet fully to be determined.

Oxygen is well known to strongly inhibit free-radical polymerizations by reacting with initiator, primary, and polymer radicals to form peroxy radicals¹⁰-¹⁵. The peroxy radicals do not efficiently reinitiate polymerization, thus reaction with oxygen effectively terminates radicals in the time-scale of photopolymerization.

While oxygen inhibition is a useful tool in regards to stability during (meth)acrylate resin processing, transportation, and storage, it is generally detrimental during polymerization. An induction or inhibition period is often observed before the onset of polymerization due to dissolved oxygen (~ 10⁻³M), particularly during curing under low irradiance conditions. Once the concentration of dissolved oxygen is reduced to a minimal level (~ 10⁻⁶M), the polymerization reaction proceeds. In films exposed to ambient oxygen, especially thin films, during polymerization oxygen rapidly diffuses into the sample through the air-film interface, inhibiting or severely retarding the polymerization. In thicker films, the lower depths of the film polymerize, while the top layer remains “tacky” as oxygen inhibition causes decreased conversion, shorter polymer chain lengths, and oxygenation of the resin in the surface layers, affecting physical, chemical, and optical properties¹²,¹⁶.

Some of the novel ultra-rapid monomers have shown an apparent resistance to oxygen inhibition, producing thin films with a tack-free surface and reaching full monomer conversion. It has been theorized that these ultra-rapid acrylates, such as cyclic carbonate acrylate, exhibit enhanced resistance to oxygen inhibition potentially due to the faster polymerization rate leading to a shift in the relative rates of the competing reactions, or possibly due to an inherent difference in the polymerization mechanism¹⁴. A free-radical system’s susceptibility to oxygen inhibition is a function of the rate of initiation, polymerization rate, concentration of dissolved oxygen, and rate of oxygen diffusion into the polymerizing resin.
In the case of the novel ultra-rapid monoacrylates, O’Brien showed that the initiation and polymerization rates of cyclic carbonate acrylate were so rapid that the system appeared to be less susceptible to oxygen inhibition. However, the classical termination of radicals by oxygen was just as prevalent as in typical radical polymerizations.

In further characterizing oxygen inhibition effects among the novel monovinyl (meth)acrylate monomers, this work has focused on both fundamental and practical questions. First, this work seeks to evaluate the kinetic effects of oxygen inhibition in novel monomers exhibiting rapid polymerization kinetics, as compared to those in a typical multifunctional acrylate monomer. Second, to address practical issues of oxygen inhibition, this work studies the correlation between kinetics of oxygen inhibition under laboratory scale conditions (FTIR and low irradiance) and polymerization results under industrial curing conditions (Fusion brand UV Processor and high irradiance). Results presented herein describe initial results to-date for one example from the novel mono-functional monomer class in comparison to results for several conventional acrylate resins.

**Experimental Procedures**

Samples of Cytec’s Ebecryl 1040, an aliphatic urethane monoacrylate (UA-1), and Ebecryl 8402, an aliphatic urethane diacrylate (UA-2), 1,6-hexanediol diacrylate (HDODA), and octyl/decyl acrylate (ODA) were obtained from the company and used as received. Polymerization samples were either laminated between NaCl windows or are spread on NaCl windows with Gardco brand wire wound rollers to thicknesses of approximately 50, 25, or 6 μm. A small amount of a polyether modified dimethylpolysiloxane copolymer surfactant, BYK-Chemie’s BYK 307, was added to prevent coagulation. Samples contained the initiator 2,2-dimethoxy-2-phenylacetophenone, Ciba Geigy’s DMPA/Irgacure 651. Viscosity was measured with TA Instruments’ ARES rheometer.

**Fusion Brand UV Processor**

UV processor studies were conducted with Fusion UV Systems’ UV Processor, Model DRS-10/12, with Variable Power Supply (25-100%) and 13mm 600 W/inch Fusion D bulb. Samples were irradiated at 25% or 100% power with a conveyor belt speed of 100 or 150 feet/minute (fpm). Samples received approximately 0.5 seconds of irradiation per pass at 100 fpm and 0.33 seconds of irradiation per pass at 150 fpm.

**FTIR**

FTIR studies were conducted using Nicolet’s 750 Magna FTIR spectrometer with a KBr beamsplitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately two scans per second. The FTIR sample chamber was continuously purged with a nitrogen/oxygen mixture controlled with a mass flow controller. Acrylate conversions were monitored using the carbon-carbon double bond absorption peak at 1636 cm⁻¹. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. Samples were irradiated with an EXFO brand Ultracure light source with a medium pressure Hg bulb and a 320-500 nm filter. Principle output for this system was at 365 nm.
Results and Discussion

Initial polymerization kinetic experiments were conducted under laminate conditions to characterize the basic kinetics of the acrylate resins evaluated in this study. Samples were not sparged to remove dissolved oxygen; however, the laminate conditions prevent oxygen diffusion into the polymerizing resin during cure. In Figure 1, polymerization conversion profiles are given for UA-1, UA-2, HDODA, and ODA cured under identical laboratory low irradiance conditions. Clearly, UA-1 exhibits extremely rapid polymerization kinetics, particularly compared to ODA, which is also a monovinyl acrylate.

![Conversion versus time for UA-1, UA-2, HDODA, and ODA.](image)

In Figure 2, polymerization kinetics are examined for UA-1 and UA-2 systems, both laminated and exposed to 5% ambient oxygen. In laminate samples (no oxygen exposure), bulk UA-1 reached full cure (100% conversion) in approximately 3-5 seconds while bulk UA-2 reached full cure (~85% conversion) in approximately 5-10 seconds.

When exposed to 5% oxygen, the initial polymerization rate of UA-2 was not significantly affected, whereas at higher conversions, the reaction is more strongly inhibited. The polymerization rate and overall conversion of UA-1 was much more strongly impacted by the presence of oxygen than UA-2.

Figure 3 gives results for samples with thicknesses of 50, 25, and 6 μm and were polymerized under 5% ambient oxygen and compared to similar samples polymerized in laminate.

It is readily apparent that the polymerization kinetics of UA-1 are much more strongly affected by sample thickness in the presence of 5% oxygen than UA-2. This variation in polymerization rates with sample thickness is due to diffusion of oxygen from the environment into the sample.

One possible cause for the increased oxygen diffusion is that UA-1 is a low viscosity monomer (60 cP @ 25°C) compared to the higher viscosity UA-2 (9000 cP @ 25°C). Cyclic carbonate acrylate is a waxy solid and thus also is a high viscosity system.
Figure 2. Functional group conversion versus time for (a) UA-1 and (b) UA-2. Samples contain 2 wt% DMPA, are irradiated at 20 mW/cm², and are either laminated or exposed to 5% oxygen.

Figure 3. Conversion versus time for (a) UA-1 and (b) UA-2. Samples contain 2 wt% DMPA and are irradiated at 20 mW/cm². Samples that are unlaminated are exposed to 5% oxygen and are approximately 50, 25, or 6 μm in thickness. Samples with 0% oxygen are laminates.

Polymerization rates of UA-1 and UA-2 were also analyzed under high irradiance conditions. In Figure 4, the formulations contain 0.1 wt% DMPA and are laminated (no oxygen exposure). Both systems are nearly completely cured after only two passes. This result is in contrast to the FTIR results of Figure 1, where UA-1 cures significantly faster than UA-2. When the formulations are exposed to
ambient oxygen (Figure 4b), UA-1 cures more slowly than UA-2, in stark contrast to laminated cures under low irradiance conditions where UA-1 exhibits a much more rapid polymerization rate than UA-2, though in agreement with the kinetic trends observed under 5% oxygen.

Curing profiles were also examined at varying power and conveyor belt speed with the UV processor. Figure 5a shows that UA-2 reaches a higher overall conversion at higher irradiance and a slower belt speed. This may be due to heating affects during polymerization. The sample cured with higher irradiance and lower conveyor belt speed is cured at a higher temperature and thus reaches a greater ultimate conversion and will have a higher glass transition temperature.

A much greater contrast in polymerization rates is seen in Figure 5b with UA-1. In this case, the polymerization rate is not significantly greater than the rate of oxygen diffusion into the system at 25% power and 150 fpm. At 100% power the initiation rate is much greater and the polymerization proceeds more readily.

\[\text{Figure 4. Functional group conversion versus number of passes under the UV Processor for UA-1 and UA-2. Samples contain (a) 0.1 wt\% DMPA and are laminated, (b) 2.0 wt\% DMPA and are exposed to ambient oxygen.}\]
Conclusions

Under low irradiance conditions in laminates UA-1, an aliphatic urethane monoacrylate, exhibits extremely rapid photopolymerization kinetics relative to typical mono and diacrylate resins. However, under both low and high irradiance conditions ambient oxygen retards the rate of polymerization and decreases the ultimate conversion of UA-1 much more significantly than it does those of UA-2, an aliphatic urethane diacrylate, particularly in very thin films. Ambient oxygen concentration as low as 5%, which is much lower than oxygen concentration in air, significantly impacts curing of UA-1 in thin films. The relatively low viscosity of UA-1 likely contributes to higher rates of oxygen diffusion into the film during polymerization; however, this factor alone likely does not explain the significant inhibition effect. Other factors may include oxygen solubility in the resin, glass transition temperature of the polymer film, and crosslink density in the developing network. Additional work is in progress to assess these factors and to characterize oxygen inhibition effects in other novel monomers and mixtures under low and high irradiance curing conditions.

Figure 5. Conversion profiles for (a) UA-1 and (b) UA-2. Samples contain 2.0 wt% DMPA as a photoinitiator, are 25 μm thick, and are open to ambient oxygen.
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References