Mechanisms, polymerization rate scaling, and oxygen inhibition with an ultra-rapid monovinyl urethane acrylate

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Certain monovinyl (meth)acrylate monomers with secondary functionalities such as urethanes have been shown to exhibit extremely rapid curing rates. In this work, the polymerization mechanism, polymerization rate scaling, and relative oxygen inhibition are evaluated for an ultra-rapid butyl urethane acrylate and an analogous aliphatic urethane diacrylate. The aliphatic urethane diacrylate was found to have increased polymerization rates at higher initiation rates relative to the butyl urethane acrylate, primarily due to different termination mechanisms. Additionally, due to higher viscosity and crosslinking density, the aliphatic urethane diacrylate was found to exhibit a greater resistance to oxygen inhibition. The flux of oxygen into the aliphatic urethane diacrylate was 1/3 that of butyl urethane acrylate. Suppressed termination likely contributes to the rapid polymerization kinetics of butyl urethane acrylate.

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1. Introduction

Recently, there has been significant interest in a class of novel monovinyl (meth)acrylate monomers whose constituents have exhibited numerous unique properties [1–12]. For example, many of these monomers with certain secondary and tertiary functionalities, such as carbonates, urethanes (carbamates), urea, cyclic carbonates, oxazolidone, cyclic acetals, and aromatic rings, have exhibited cure rates approaching and in many cases exceeding that of acrylates characterized by a higher functionality. The various mechanistic underpinnings leading to this enhanced reactivity vary depending on the chemical nature of the monomer. In certain cases, hydrogen abstraction has been shown as a means for leading to crosslinking and increased polymerization rates [13]. Features such as hydrogen bonding and conjugation of aromatic rings lead to increased viscosity, and subsequently an increase in polymerization rate through suppressed termination [12,14]. Hydrogen bonding may also lead to non-covalent linkages between monomers, causing them to exhibit similar characteristics to multifunctional monomers. In some cases molecular dipole has been shown to correlate to enhanced reactivity [1,2]. Recently, Kilambi et al. [3] have deconvoluted the effects of intermolecular versus intramolecular interactions for a wide variety of monovinyl monomers. It was shown that both bulk intermolecular interactions such as medium polarity, conjugation, and hydrogen bonding, as well as intramolecular interactions contribute to enhanced polymerization rates. Molecular conformations [15] or possible electron rich intermediates [4,16] have been theorized to affect polymerization reactivity through intramolecular interactions.

Another aspect of ultra-rapid monomer systems that has raised interest is a possible reduction in polymerization inhibition by oxygen. Oxygen is well known to strongly inhibit free-radical polymerizations by reacting with initiator, primary, and polymer radicals to form peroxy radicals [17–22]. The peroxy radicals do not efficiently reinitiate polymerization, thus reaction with oxygen effectively terminates radicals in the time-scale of the 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 ($\sim 10^{-3}$ M), particularly during curing under low irradiance conditions. Once the concentration of dissolved oxygen is reduced to a minimal level, the polymerization reaction proceeds. During cure of films exposed to ambient oxygen, particularly for thin films, oxygen diffuses rapidly back into the sample through the air–film interface, inhibiting or severely retarding the polymerization depending on polymerization conditions. In thicker films, the lower depths of the film polymerize, while the top layer remains "tacky" as oxygenation of the resin near the interface leads to decreased conversion and
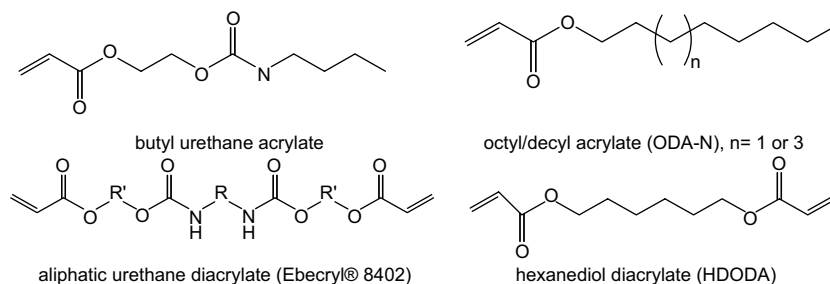
Fig. 1. Chemical structures of monomers.

shorter polymer chain lengths, affecting physical, chemical, and optical properties [17,23].

A free-radical system's susceptibility to oxygen inhibition is a function of the initiation rate, polymerization rate, dissolved oxygen concentration, and the rate of oxygen diffusion into the polymerizing resin. In the case of the ultra-rapid monomer, cyclic carbonate acrylate, it was shown that under high initiation rate conditions, the system was able to overcome oxygen inhibition [5–8,24]. However, the classical termination of radicals by oxygen was just as prevalent as in typical radical polymerizations [24].

In all previous studies, ultra-rapid monovinyl monomers have been evaluated for their surprisingly rapid polymerization kinetics and excellent mechanical properties under a given set of curing conditions. In this study, an ultra-rapid monovinyl monomer has been directly compared to an analogous divinyl monomer over a range of polymerization conditions to evaluate further the unique nature of these systems in regards to polymerization kinetics and polymerization rate scaling. This work has focused on both fundamental and practical questions in further characterizing oxygen inhibition effects among novel monovinyl (meth)acrylate monomers. First, the kinetic effects of oxygen inhibition in novel monomers exhibiting rapid polymerization kinetics are evaluated and compared to those in a typical multifunctional acrylate monomer. Second, to address practical issues of oxygen inhibition, this work studies the correlation between the kinetics of oxygen inhibition under laboratory scale conditions (FTIR and low irradiance) and polymerization results under industrial curing conditions (Fusion brand UV curing line and high irradiance). Results presented herein describe the polymerization kinetics and fundamental mechanistic parameters for one example (butyl urethane acrylate) from the novel monovinyl monomer class in comparison to results for several conventional acrylate resins. Butyl urethane acrylate was chosen as a model monomer because of its relatively simple chemical structure (Fig. 1) and extremely rapid polymerization kinetics (Fig. 2 and Table 1).

2. Experimental

Butyl urethane acrylate (Ebecryl® 1040), an aliphatic urethane diacrylate (Ebecryl® 8402), 1,6-hexanediol diacrylate (HDODA), and octyl/decyl acrylate (ODA-N; a mixture of octyl and decyl acrylate) were donated by Cytec Specialty Chemicals (Smyrna, GA). 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was purchased from Aldrich (Milwaukee, WI) and utilized as the photoinitiator.

Samples were either laminated between NaCl windows or are spread on NaCl windows with Gardco brand wire wound rollers to thicknesses of approximately 50 μm, 25 μm, or 6 μm. A small amount of a polyether modified dimethylpolysiloxane copolymer surfactant, BYK-Chemie's BYK 307, was added to prevent aggregation for non-laminated samples. Samples contained 0.1 wt% photo initiator unless otherwise specified. Viscosity was measured with a TA Instruments ARES rheometer.

2.1. Fusion curing line

Curing line studies were conducted with a Fusion UV Systems Curing Line, Model DRS-10/12, with Variable Power Supply (25–100%) and 13 mm 600 W/inch Fusion D bulb. Samples were irradiated at 25% power with a conveyor belt speed of 100 ft/min (fpm). Samples received approximately 0.5 s of irradiation per pass at 100 fpm.

2.2. Fourier transform infrared spectroscopy (FTIR)

FTIR studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beam-splitter 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. Polymerization rates (dX/dt) were calculated by taking the average polymerization rate from 10 to 40% conversion. All samples were irradiated with an EXFO brand Ultracure light source with a medium pressure Hg bulb and a 320–500 nm filter with an irradiation intensity of 5 mW/cm^2. Principle output for this system was at 365 nm. Irradiation intensity was measured with an International Light, Inc. Model IL1400A radiometer (Newburyport, MA).
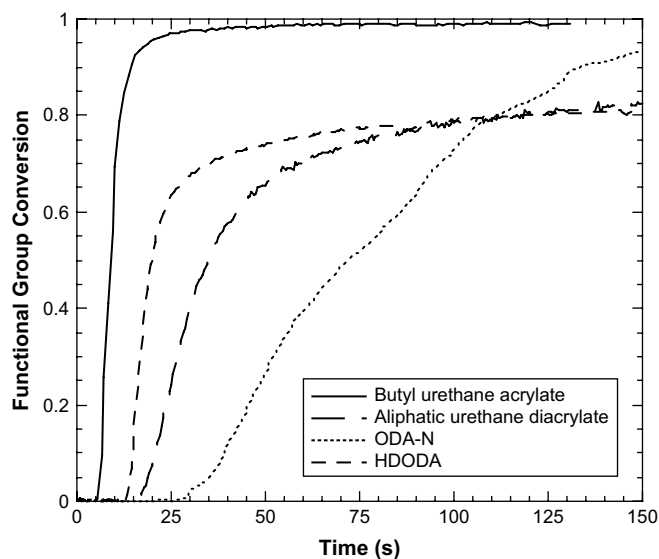

Fig. 2. Conversion versus time results for butyl urethane acrylate, aliphatic urethane diacrylate, HDODA, and ODA-N. Samples contain 0.1 wt% DMPA and are irradiated at 5 mW/cm^2 at ambient temperature.

Table 1
Average polymerization rates from 10% to 40% conversion of butyl urethane acrylate, aliphatic urethane diacrylate, HDODA, and ODA-N. Samples contain 0.1 wt% DMPA and are irradiated at 5 mW/cm^2 at ambient temperature. Standard deviations are represented in parenthesis

	Butyl urethane acrylate	Aliphatic urethane diacrylate	HDODA	ODA-N
$R_{p,max}$ (1/s)	0.16 (0.03)	0.031 (0.002)	0.085 (0.004)	0.014 (0.002)

2.3. Dynamic mechanical analysis (DMA)

DMA studies were conducted using a TA Instruments Q800 Dynamic Mechanical Analyzer. Samples were ramped at a rate of 3 °C/min. Loss tangent and storage modulus were determined as a function of temperature, applying a sinusoidal stress at a frequency of 1 Hz. The T_g was taken to be the maximum of the loss tangent–temperature curve.

3. Results and discussion

Butyl urethane acrylate was studied as a model novel monomer system with secondary functionalities. Results from this study can be extended to additional monovinyl systems with rapid polymerization kinetics due to secondary functionalities. To evaluate the polymerization mechanism of butyl urethane acrylate the polymerization rate was compared to several typical monomers. Unsteady-state polymerizations and polymerization in the presence of acetic acid were also evaluated. Unsteady-state polymerizations give insight into the termination mechanism and whether a reduction in termination rate may be leading to enhanced polymerization kinetics via intermolecular affects. Polymerizations with acetic acid evaluate whether the presence of an anionic intermediate may be enhancing the polymerization rate via intramolecular affects. Finally, by comparing aliphatic butyl urethane acrylate to an analogous aliphatic urethane diacrylate, the effects of monomer functionality and resin viscosity on polymerization kinetics are examined.

3.1. Polymerization mechanisms

In Fig. 2 and Table 1, baseline kinetic screening results are given for butyl urethane acrylate and compared to an analogous aliphatic urethane diacrylate, hexanediol diacrylate (HDODA), and a typical monovinyl acrylate, octyl/decyl acrylate (ODA-N). Chemical structures of these monomers are given in Fig. 1. From Fig. 2 and Table 1 it is seen that for the given conditions, butyl urethane acrylate exhibits a polymerization rate that is 16 times greater than the aliphatic analog ODA-N, twice as rapid as HDODA, and more than five times as rapid as the aliphatic urethane diacrylate.

The rapid polymerization rate of butyl urethane acrylate has been previously observed in other similar monovinyl acrylates and methacrylates with secondary functionalities such as carbonates, urethanes (carbamates), urea, cyclic carbonates, oxazolidone, cyclic acetals, and aromatic rings [3]. The results of this study are in agreement with previous evaluations where butyl urethane acrylate was found to exhibit a polymerization rate 17 times greater than hexyl acrylate [3]. In this previous study, it was found that the reactivity increase of butyl urethane acrylate due to intramolecular interactions accounted for approximately a 2.7-fold rate enhancement while contributions from bulk intermolecular interactions (such as hydrogen bonding) attributed to a 6.3-fold rate enhancement.

The intermolecular polymerization rate enhancement of butyl urethane acrylate is attributed to hydrogen bonding effects from
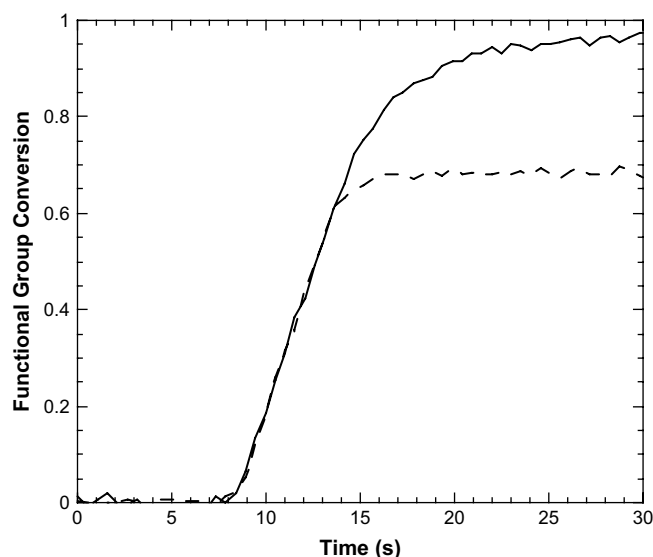
Fig. 3. Polymerization of butyl urethane acrylate with continuous irradiation (—) and with irradiation terminated 12 s into the polymerization (---). Samples are irradiated at 5 mW/cm^2 at ambient temperature.

the urethane functionality. In Fig. 3, unsteady-state kinetics of butyl urethane acrylate are examined. Butyl urethane acrylate was shown to exhibit ∼20% additional conversion after the irradiation source was extinguished. 20% dark reaction is extremely high, for a monoacrylate; however, it is not abnormal for a multiacrylate [25,26]. This result supports the hypothesis that hydrogen bonding contributes to rate enhancement through suppression of termination either by molecular organization or viscosity induced termination suppression.

The polymerization rate enhancement of nearly a factor of 2.7 via intramolecular affects remains largely unexplained. A contribution to rate enhancement from an anionic intermediate has been hypothesized for several types of ultra-rapid monomers, such as phenyl urethane acrylate [3,4,16]. A reaction mechanism that is proceeding through an ionic intermediate will exhibit several distinct (and detectable) kinetic characteristics. First, the termination reaction will be suppressed if the propagating species are ionic in nature. Second, if the ionic contribution is anionic, the polymerization reaction should be quenched or significantly inhibited in the presence of an acidic media. While the dark polymerization kinetics in Fig. 2 show a high level of dark polymerization, the amount of dark polymerization is not enough to indicate an anionic mechanism [4,16,25,26]. To validate this hypothesis, in Fig. 4, polymerizations of butyl urethane acrylate are performed with 300 ppm and 7000 ppm acetic acid. No significant reduction in polymerization rate is observed. A contribution to rate enhancement from an anionic intermediate, therefore, appears unlikely for butyl urethane acrylate. We hypothesize that intramolecular interactions of the acrylate functionality with the urethane functionality are responsible for the intramolecular contribution to rate enhancement. However, a detailed proposal, as of yet, cannot be ascribed to this phenomenon.

3.2. Scale-up and oxygen inhibition

When the initiation rate of the butyl urethane acrylate system is increased to higher levels, as is common under industrial curing processes, the rapid polymerization rate relative to the aliphatic urethane diacrylate is no longer evident. A comparison of polymerization kinetics at two different initiation rates (0.1 wt% DMPA, 5 mW/cm^2 and 2.0 wt% DMPA, 20 mW/cm^2 – an 80-fold increase in
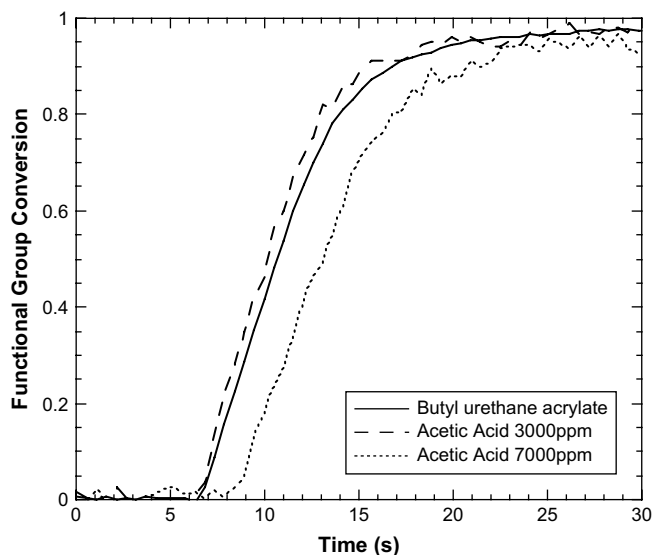
Fig. 4. Polymerizations of butyl urethane acrylate with 300 ppm and 7000 ppm acetic acid. Samples are irradiated at 5 mW/cm² at ambient temperature.

initiation rate) is given in Fig. 5. The results clearly indicate that at higher initiation rates the polymerization rate of the aliphatic urethane diacrylate is equivalent to that of butyl urethane acrylate, representing an approximately 5-fold increase in the relative polymerization rate of the aliphatic urethane diacrylate.

Given in Fig. 6 is a comparison of conversions of butyl urethane acrylate and aliphatic urethane diacrylate on the high intensity Fusion curing line. Initiation rates with the Fusion curing line (600 W/inch bulb) are several orders of magnitude greater than in the FTIR (5–20 mW/cm²). Under the high intensity irradiation conditions of Fig. 6, the aliphatic urethane diacrylate reaches a higher conversion than butyl urethane acrylate in a single exposure, indicating a more rapid polymerization rate for the aliphatic urethane diacrylate. This result is consistent with the polymerization rate trends observed in Fig. 5.

3.3. Polymerization rate scaling

Classical photopolymerization systems exhibit bimolecular radical–radical termination and observe the relationship where the polymerization rate (R_p) is proportional to the initiation rate (R_i) to the 1/2 power [27]; $R_p \propto R_i^{1/2}$. The initiation rate is directly proportional to the irradiation or light intensity (LI) for equivalent initiator concentrations, and the relationship can also be expressed as $R_p \propto LI^{1/2}$. In cases where chain length dependent termination (CLDT) is prevalent, a scaling exponent less than 1/2 is observed [28–34]. For systems exhibiting unimolecular termination, a scaling exponent greater than 1/2 is observed [35,36].

The calculated average polymerization rate for butyl urethane acrylate with 0.1 wt% DMPA and 5 mW/cm² is 0.16 (1/s) versus ~0.8 (1/s) with 2.0 wt% DMPA and 20 mW/cm². This indicates a scaling exponent, $\alpha \approx 0.4$. For the aliphatic urethane diacrylate, the polymerization rate increases from 0.03 to ~0.8 (1/s) for the same range of initiation conditions, indicating an $\alpha \approx 0.8$. If ideal polymerization kinetics held ($R_p \propto R_i^{1/2}$) throughout this initiation rate regime and CLDT (or unimolecular termination) were not important, butyl urethane acrylate would be expected to exhibit a polymerization rate, $R_p \approx 1.4$ (1/s) and aliphatic urethane diacrylate a polymerization rate, $R_p \approx 0.3$ (1/s). For the conditions in Fig. 5 (samples laminated between NaCl plates have a thickness of ~10 µm) near isothermal polymerization results. When cured under the Fusion line, additional factors such as the polymerization temperature, due to heating from the Fusion lamp, and differences in spectral output (affecting initiation efficiency) also affect the polymerization rate scaling. Thus, the enhanced rate scaling under the high intensity irradiation conditions in Fig. 6 is not attributed solely to termination kinetics. However, the dramatic difference in scaling of the two systems under lower intensity thin film laminate conditions indicates that the termination mechanism differences likely account for a significant portion of the observed kinetic differences. When cured with 0.1 wt% DMPA and 5 mW/cm², the T_g of butyl urethane acrylate is 14 °C while the T_g of the aliphatic urethane diacrylate is 53 °C. Given this difference in T_g between the two systems and the increased crosslinking density of the diacrylate system, two different termination mechanisms are highly likely with radical trapping, a unimolecular reaction, more likely in the diacrylate and CLDT more likely in the monoacrylate. This type of result has been previously observed when comparing monovinyl systems or systems with low T_g [28–34] to divinyl systems with high T_g [26,35–37]. The termination mechanism in the butyl urethane acrylate system is dominated by classical and chain length dependent termination whereas the termination mechanism in the aliphatic urethane diacrylate system is dominated by classical and unimolecular termination.
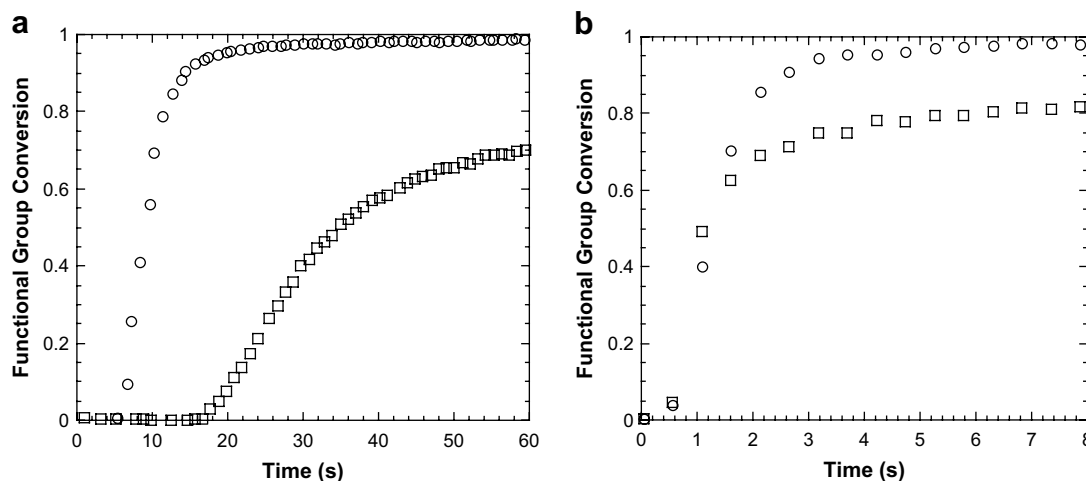

Fig. 5. Conversion versus time for polymerization of butyl urethane acrylate (○) and the aliphatic urethane diacrylate (□) with (a) 0.1 wt% DMPA and 5 mW/cm² irradiation intensity and (b) 2.0 wt% DMPA and 20 mW/cm² irradiation intensity.
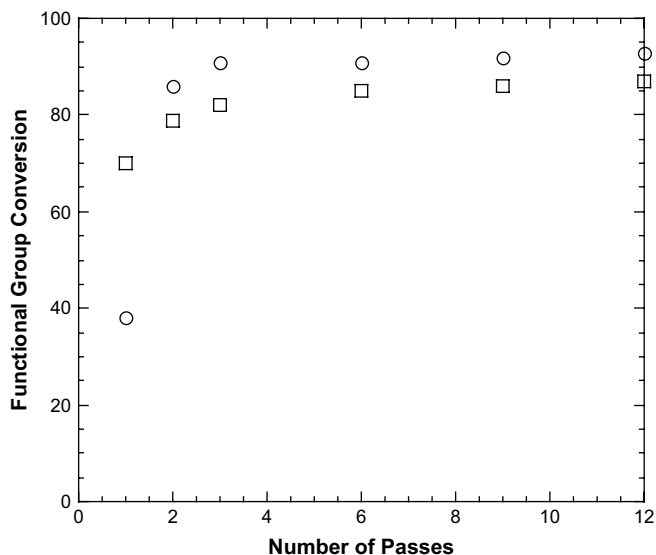
Fig. 6. Conversion versus number of passes under the Fusion curing line for butyl urethane acrylate (○) and the aliphatic urethane diacrylate (□). Samples contain 0.1 wt% DMPA and are laminated between NaCl windows. Samples were irradiated at 25% power with a conveyor belt speed of 100 ft/min (fpm).

3.4. Oxygen inhibition

In Fig. 7, the polymerization kinetics are examined for butyl urethane acrylate and the aliphatic urethane diacrylate as thin films (50 μm, 25 μm, and 6 μm) exposed to 5% ambient oxygen and compared to samples polymerized with a nitrogen blanket. Under a nitrogen blanket, butyl urethane acrylate achieved full cure (100% conversion) in approximately 3–5 s while the aliphatic urethane diacrylate achieved full cure (∼85% conversion) in approximately 5–10 s. When exposed to 5% oxygen, the initial polymerization rate of the aliphatic urethane diacrylate was not significantly affected, whereas at higher conversions, the reaction is more strongly inhibited. The polymerization rate and overall conversion of butyl urethane acrylate were much more strongly impacted by the presence of oxygen than the aliphatic urethane diacrylate.

The variation in polymerization rates with sample thickness is due to a higher flux of oxygen from the environment into the butyl urethane acrylate sample. Butyl urethane acrylate is a low viscosity monomer (60 cP at 25 °C) compared to the higher viscosity

Table 2
Unpolymerized tacky layer (δ) thicknesses for butyl urethane acrylate and aliphatic urethane diacrylate as calculated from Eq. (1) and the results of Fig. 7

Monomer	δ (μm)
Butyl urethane acrylate	9 ± 6
Aliphatic urethane diacrylate	3 ± 1

aliphatic urethane diacrylate (9000 cP at 25 °C). Additionally, the diacrylate (aliphatic urethane diacrylate) will have significant crosslinking and hence, the viscosity increases more rapidly during the initial stages of conversion than for the monoacrylate (butyl urethane acrylate). Both of these factors contribute to a greater flux of oxygen into the butyl urethane acrylate samples.

In systems that are polymerized in the presence of oxygen, the top layer (with a nearly infinite supply of oxygen from the environment) is more strongly affected by oxygen inhibition than the lower layers where oxygen must diffuse through the resin before affecting the polymerization. If this top layer is assumed to be an unpolymerized "tacky" surface layer, the following equation may be applied to calculate its thickness [38]:

$$\delta = y\left(1 - \frac{X_{\mathrm{avg}}}{X_{\mathrm{max}}}\right) \tag{1}$$

where δ is the thickness of the unpolymerized tacky layer, y is the total thickness, X_{avg} is the average conversion of the unpolymerized tacky layer and the underlying layer, and X_{max} is the ultimate conversion of the sample without exposure to oxygen. From this equation and the results of Fig. 7, the thickness of the unpolymerized tacky layer (δ) is calculated and the results are given in Table 2. From these results, the flux of oxygen into the polymerizing resin can also be approximated. The thickness of the unpolymerized tacky layer (δ) will be directly proportional to the flux of oxygen into the resin and inversely proportional to the initiation rate.

$$\delta \approx \frac{\mathrm{Flux\ O_2}}{R_{\mathrm{i}}}$$

Since the initiation rates are equal for both systems, the relative flux of oxygen into each resin is directly proportional to the ratio δ in the two systems. Hence, the flux of oxygen into a film of butyl urethane acrylate is approximately three times greater than the flux of oxygen into a film of aliphatic urethane diacrylate. This result is
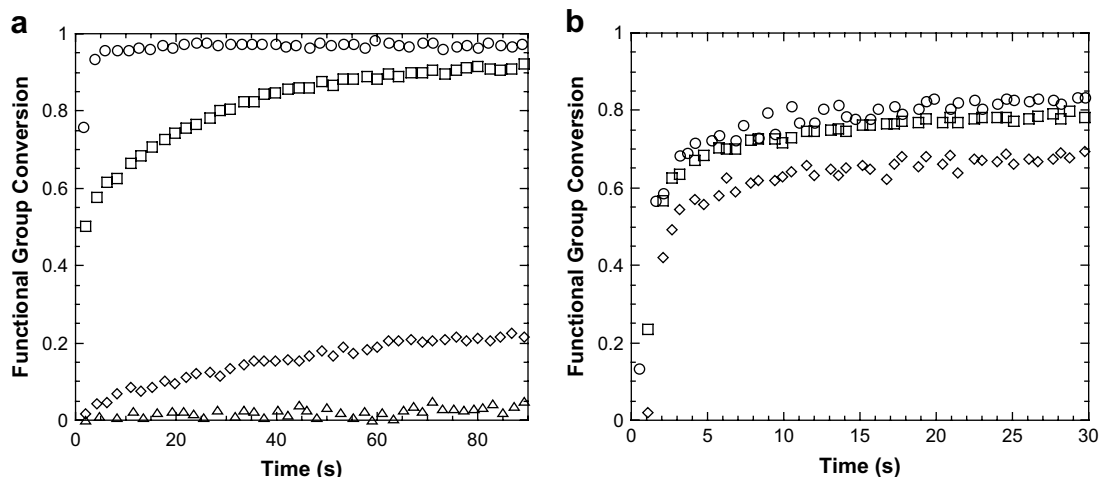

Fig. 7. Functional group conversion versus time for (a) butyl urethane acrylate and (b) aliphatic urethane diacrylate samples that are laminated (○) or exposed to a 5% oxygen environment with thicknesses of 50 μm (□), 25 μm (◇), and 6 μm (△). Samples contain 2.0 wt% DMPA and are irradiated at 20 mW/cm². The aliphatic urethane diacrylate could not be uniformly dispersed to a thickness of 6 μm.

consistent with the observed greater effect of oxygen inhibition on butyl urethane acrylate than the aliphatic urethane diacrylate.

4. Conclusion

Two analogous monomers, butyl urethane acrylate and an aliphatic urethane diacrylate were evaluated for polymerization rate scaling and the effect of oxygen inhibition. Butyl urethane acrylate is a model monoacrylate with secondary functionalities that exhibits extremely high polymerization rates (approximately 16 times greater than the corresponding aliphatic acrylate ODA-N) and low rates of termination as evidenced by significant dark cure. Rate enhancement is a result of contributions from both intermolecular and intramolecular contributions. The aliphatic urethane diacrylate is a difunctional analog to butyl urethane acrylate. Both fundamental polymerization kinetics and practical oxygen inhibition studies were performed to understand better the utilization of these types of monomers. The aliphatic urethane diacrylate was found to have increased polymerization rates at higher initiation rates relative to butyl urethane acrylate. Differences in polymerization rates with varying initiation rate conditions were primarily attributed to differences in the termination mechanisms due to crosslinking density and glass transition temperatures. Butyl urethane acrylate and aliphatic urethane diacrylate were also evaluated under varying oxygen exposure conditions. Due to its higher viscosity and cross-linking density, aliphatic urethane diacrylate was shown to exhibit a greater resistance to oxygen inhibition. The flux of oxygen into the aliphatic urethane diacrylate was 1/3 that of the lower viscosity and crosslink density butyl urethane acrylate system.

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