Evaluation of a Potential Ionic Contribution to the Polymerization of Highly Reactive (Meth)acrylate Monomers

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ABSTRACT: Monovinyl methacrylic and acrylic monomers that exhibit enhanced photopolymerization reactivities were studied to discern a possible secondary polymerization mechanism that involves an anionic contribution to the polymerization. To test for this possible anionic contribution, a strong acid, methanesulfonic acid, was added in small quantities to each of the (meth)acrylic monomers, and the steady-state photopolymerization rate was monitored. Initial control studies with conventional free-radical polymerizing monomers showed that the polymerization rate of these conventional (meth)acrylic monomers are not affected by small amounts of acid. Acid studies of secondary functionalized (meth)acrylate monomers, which typically exhibit rapid polymerization kinetics, demonstrated that the polymerization rate is decreased in these monomers by the addition of the strong acid. More specifically, the acid addition had a greater inhibitory effect on the monomers with faster bulk polymerization rates. The acid addition had a much more profound effect on the polymerization rate of the acrylate monomers compared to analogous methacrylate monomers. More specifically, addition of 250 ppm of the strong acid to the phenyl carbamate acrylate monomer showed that both the steady-state and unsteady-state polymerization profiles were similar to that of a traditional free-radical acrylate monomer. All experiments indicate that an anionic contribution to the polymerization is probable and has a profound impact on the polymerization rate.

Introduction

The photopolymerization process is widely used in today's industrial market to convert liquid monomer rapidly to solid polymer for a variety of applications that include inks, coatings, adhesives, stereolithography,[1−3] dental restoratives,[4−6] and contact lenses.[7,8] The photopolymerization curing mode is widely utilized for numerous reasons, which include solvent-free polymerizations, energy efficiency, and spatial and temporal control of the polymerization process. However, there are several limitations to the photopolymerization process that restrict the industrial viability of these materials. These limitations include residual unsaturation,[9,10] oxygen inhibition,[11−14] limited polymerization speed, and polymer properties.[15] These polymer properties include such aspects as polymer hardness, flexibility, and modulus, as each is influenced by monomer chemistry and functionality.

A typical method to increase the polymerization rate of acrylic systems is to utilize monomers with more than one vinyl group. By increasing the monomer functionality, diffusional limitations are encountered earlier in the polymerization, and thus, termination is more restricted. The reduction in termination leads to more profound autoacceleration and increased polymerization rates.[16] Additionally, in this case, cross-linked materials are formed, which leads to increased modulus and hardness. Unfortunately, increasing the cross-linking density typically leads to brittleness and residual unsaturation,[17] allowing for polymer property variations with age and possible biocompatibility issues. These tradeoffs between polymerization rate, polymer properties, and residual unsaturation are a key constituent in the development and selection of monomers for use in polymerization applications. There has been a longstanding desire to counteract these limitations and develop monomers that polymerize to a higher extent of reaction with greater polymerization rates.

Decker et al. formulated a novel class of monoacrylate monomers that react extremely rapidly despite having only one vinyl group and still form cross-linked, insoluble polymer early in the polymerization.[3,18−22] These polymers are characterized by a unique combination of excellent hardness and flexibility in the same material. These novel acrylates include secondary functionalities such as carbonate, cyclic carbonate, carbamate, and oxazolidone moieties,[18,19] and the polymerization rate was most rapid for a monoacrylate containing both cyclic carbonate and linear carbonate secondary functionalities.[18] Additional monoacrylate monomers that exhibit similar enhanced polymerization characteristics were developed and analyzed in our laboratory[23−25] as well as others.[26−28] The exact mechanism or mechanisms by which these unique polymerization kinetics and polymer properties develop are yet to be fully understood.

Three distinct mechanistic theories to account for the enhanced reactivity of these monoacrylates have been advanced: (1) hydrogen abstraction/chain transfer, (2) hydrogen bonding, and (3) electronic and resonance effects. Decker et al. first proposed a highly efficient hydrogen abstraction mechanism to account for the increased reactivity and cross-linked polymer formation, implicating the labile hydrogens associated with the secondary functionality as the abstractable species.[2,29]

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Recent studies in our laboratory have additionally supported the theory that hydrogen abstraction is a key component to the enhanced reactivity. However, this work has indicated that the hydrogen abstraction location appears to be centered about the carbons directly adjacent to the (meth)acrylic moiety.[30]

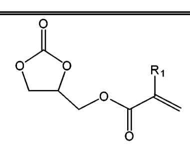
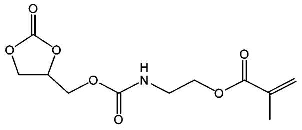
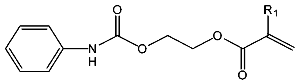
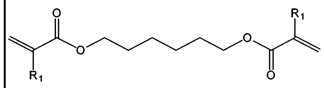
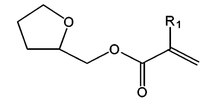
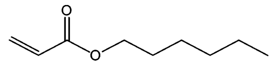
In addition to hydrogen abstraction, hydrogen bonding may also contribute to the increased reactivity by increasing monomer ordering and subsequently increasing the efficiency of radical propagation through prealigned double bonds.[28] Furthermore, hydrogen bonding increases the overall viscosity of the bulk monomer solution, thus hindering radical termination and causing an increase in radical concentration during polymerization. This increased radical concentration directly increases the polymerization rate. Recently, in a systematic study of monomethacrylate monomers with varying secondary functionalities and end groups, Berchtold et al. determined that hydrogen bonding has an impact on the polymerization characteristics of these monovinyl monomers.[31] Nonetheless, by systematically varying the polymerization temperature, it was determined that the polymerization rate was relatively unaffected by temperature. This study demonstrated that hydrogen bonding may be important but is not the primary factor affecting reactivity.

Finally, electronic and resonance effects may also impact the reactivity of these monoacrylate monomers. Specifically, resonance may allow for such mechanisms as an increase in the amount of labile hydrogens or (de)-stabilization of radicals. Recently, Jansen et al. have developed the theory of increasing polymerization rate with increasing dipole moment of the monomer.[26-28] In this dipole moment theory the polymerization rate increases linearly with dipole moment when the overall dipole moment of the solution exceeds a threshold value of 3.5 D. Jansen et al. have indicated that this polymerization rate increase with increasing dipole moment is due to stronger solvent cage effects and a greater charge at the propagating radical.[26-28] Jansen et al. suggested that the aforementioned effects lead to a partial ionic charge on the propagating center, where this charge would lead to a reduction in termination and a subsequent increase in polymerization rate.

Each of the three mechanistic theories has been shown to affect polymerization rates in certain monomer systems. However, no clear explanation for the dramatically enhanced reactivities of these monomers relative to standard monoacrylate momomers has been identified. Hydrogen bonding and electronic and resonance effects appear to contribute to the reactivity of the monomers but do not appear to be the primary contributors. Nonetheless, the partial ionic contribution to the propagating radical may shed some insight into the possible mechanism contributing to the enhanced polymerization characteristics.

In this research, we have hypothesized that an ionic contribution, specifically an anionic contribution, is enabling the enhanced polymerization characteristics that are prevalent in a set of novel (meth)acrylate monomers. This hypothesis builds on the Jansen et al. theory of a partial ionic contribution and expands on it to discern whether an anionic contribution is involved in the overall polymerization mechanism. To explore this phenomenon, small amounts of a strong acid were added to several novel (meth)acrylate monomers, and the steady-state polymerization characteristics were monitored. The acid addition acts to quench any anionic contribution, and a reduction in polymerization rate is expected if this anionic character exists.

Table 1. Molecular Structures of Monomers Studied

Monomer	Structure
Cyclic Carbonate (Meth)Acrylate	 R_1 = H or CH_3
Cyclic Carbonate Carbamate Methacrylate	
Phenyl Carbamate (Meth)Acrylate	 R_1 = H or CH_3
1,6-Hexanediol Di(meth)acrylate	 R_1 = H or CH_3
Tetrahydrofurfuryl (Meth)Acrylate	 R_1 = H or CH_3
Hexyl Acrylate	

Experimental Section

Materials. All monomer syntheses are described in the Supporting Information. Methanesulfonic acid (Aldrich Chemical, Milwaukee, WI, ReagentPlus, ≥99.5%) and triethylamine (Aldrich Chemical, ≥99.5%) were used as received. Control experiments were performed using the commercial monomers of 1,6-hexanediol diacrylate (HDDA, Aldrich Chemical, technical grade, ≥80%), tetrahydrofurfuryl acrylate (THFFA, Aldrich Chemical, ≥85%), 1,6-hexanediol dimethacrylate (HDDMA, Aldrich Chemical, ≥90%), and tetrahydrofurfuryl methacrylate (THFFMA, Aldrich Chemical, 97%). Additionally, the traditional free-radical monomer hexyl acrylate (Aldrich Chemical, 98%) was evaluated. THFFA and THFFMA were distilled prior to use, while HDDA and HDDMA were used as received. All monomer samples are shown in Table 1. All samples were initiated with 0.1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba-Geigy, Hawthorne, NY), which was used as received.

FTIR Analysis. Conversion vs time profiles for all monomers were determined via steady-state analysis using real time Fourier transform infrared (RT-FTIR) spectroscopy.[32-34] Conversion data were obtained by monitoring the decay of the acrylate double bond peak, either ~1637 cm^{-1} (C=C stretching vibration) or ~810 cm^{-1} (C=C twisting vibration), using a Nicolet Magna 760 FTIR spectrometer (Madison, WI) with an XT-KBr beam splitter and a MCT/B detector. The temporal resolution of this instrument is ~200 ms. For ease of sample handling, a custom horizontal transmission accessory (HTA) was utilized to allow for the samples to remain in a horizontal configuration during analysis.[5,35] All samples were placed between NaCl crystals to form a laminate and were irradiated with 5 mW/cm^2 ultraviolet (UV) light (filtered and centered at a wavelength of 365 nm) from an EXFO Ultracure 100ss

(Mississauga, Ontario, Canada) light source; steady-state irradiation duration was 5 min. Additionally, specific samples were heated to a temperature of 67 °C for analysis using a custom temperature cell,[31] since these monomer samples are solids or highly viscous liquids at room temperature.

Unsteady-state analyses were performed for specific samples to discern the overall effects of acid addition on the polymerization characteristics. Unsteady-state analysis is equivalent to the steady-state analysis, except the UV irradiation is extinguished prior to complete conversion and the dark polymerization is monitored. The extent of dark polymerization will give insight into the possible polymerization mechanism with and without the influence of acid on the system.

Control Studies. Approximately 500 ppm of methanesulfonic acid was added to each of the control monomers, including HDDMA, HDDA, THFFMA, and THFFA. Each sample was mixed via a magnetic stir bar for at least 0.5 h after the addition of the acid to ensure a homogeneous mixture. For comparison, a 500 ppm concentration of acid corresponds to $\sim 5 \times 10^{-3}$ mol/L, while the 0.1 wt % concentration of initiator is equivalent to $\sim 4 \times 10^{-3}$ mol/L.

Novel Monomer Studies. Methanesulfonic acid was added to each of the research monomers, varying from approximately 100 to 500 ppm. Each sample was mixed via a magnetic stir bar for at least 0.5 h to ensure homogeneous mixtures. Monomers that were solids at room temperature required gentle heating to melt the monomer in order to facilitate mixing.

Cationic Study. Approximately 1000 ppm of triethylamine was added to phenyl carbamate acrylate. The sample was mixed via a magnetic stir bar for ~0.5 h to ensure a homogeneous mixture. The sample was gently heated to melt the monomer and facilitate mixing.

NMR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova-400 NMR spectrometer, operating at 400.157 MHz for proton observation and 100.628 MHz for ^{13}C observation. ^{1}H NMR was performed using a 30° excitation pulse, an acquisition time of 3.0 s, and a relaxation delay of 1.5 s. ^{13}C NMR was recorded using a 45° excitation pulse, a 1.5 s relaxation delay, and full broadband ^{1}H decoupling using phase-modulated (WALTZ-16) decoupling. Deuterated chloroform (Cambridge Isotope Laboratories, Inc., Andover, MA, 99.8%) was used as received.

Results

An ionic mechanism may exist in conjunction with the traditional radical mechanism, which factors significantly into the overall polymerization rate. Specifically, we propose a secondary anionic contribution for the novel monomers studied within this research. To test for the possibility of an anionic contribution, a small amount of a strong acid, methanesulfonic acid, was added to several novel monomers, and the steady-state polymerization rate was monitored. The addition of the acid should quench any possible anionic contributions or intermediates in the reaction, so that the extent of their contributions can be monitored.

Control Studies. Prior to addition of acid to the novel monomers studied in this research, control studies were conducted to be certain that small amounts of this strong acid would not affect the polymerization characteristics of traditional methacrylate and acrylate monomers. In each of the control experiments, the level of acid is approximately equivalent to the initiator concentration. Figures 1 and 2 show the results of the methacrylate and acrylate control studies. These control studies demonstrate that with up to 500 ppm of strong acid the polymerization kinetics of conventional free-radical monomers are all unaffected within standard error. Therefore, it is shown that small amounts of strong acid do not affect traditional free-radical polymerizations. More importantly, these control studies illustrate that the addition of strong acid does not affect the photodegradation or efficiency of the photoinitiator. Additionally, these results show that the acid molecule itself is not undergoing any significant photodegradation or other side reactions that would limit the polymerization rate of the reactions.

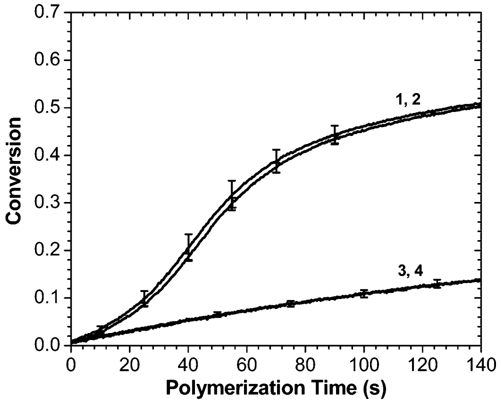


Figure 1. Steady-state polymerization profiles of control methacrylate studies. Unaltered 1,6-hexanediol dimethacrylate (1), 1,6-hexanediol dimethacrylate with 500 ppm methanesulfonic acid (2), unaltered tetrahydrofurfuryl methacrylate (3), and tetrahydrofurfuryl methacrylate with 500 ppm methanesulfonic acid (4) are shown. All polymerizations were initiated at 25 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

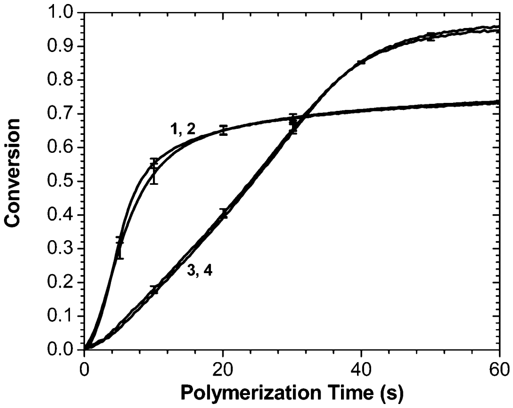


Figure 2. Steady-state polymerization profiles of control acrylate studies. Unaltered 1,6-hexanediol diacrylate (1), 1,6-hexanediol diacrylate with 500 ppm methanesulfonic acid (2), unaltered tetrahydrofurfuryl acrylate (3), and tetrahydrofurfuryl acrylate with 500 ppm methanesulfonic acid (4) are shown. All polymerizations were initiated at 25 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

Methacrylate Monomers. The first set of experiments involved the addition of small amounts of the strong acid to methacrylic versions of several novel monomers. Secondary functionalization of both methacrylate and acrylate monomers has been demonstrated to enhance the reactivity over that of traditional methacrylate or acrylate monomers.[24] Thus, by studying methacrylate and acrylate monomers, greater insight into the possible mechanisms leading to this enhanced reactivity can be deciphered.

The cyclic carbonate secondary functionality is known to increase the reactivity of both acrylic and methacrylic monomers.[2,18,24] Small amounts of methanesulfonic acid (up to 450 ppm) were added to the cyclic carbonate methacrylate (CCMA) monomer, and the steady-state polymerization characteristics were examined. The

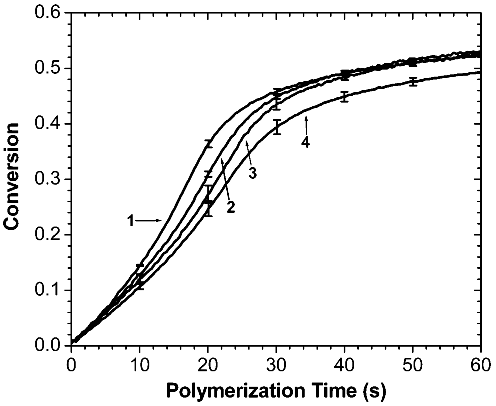


Figure 3. Steady-state polymerization profiles of cyclic carbonate methacrylate acid studies. Unaltered (1), 220 ppm methanesulfonic acid (2), 350 ppm methanesulfonic acid (3), and 450 ppm methanesulfonic acid (4) samples are shown. All polymerizations were initiated at 25 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

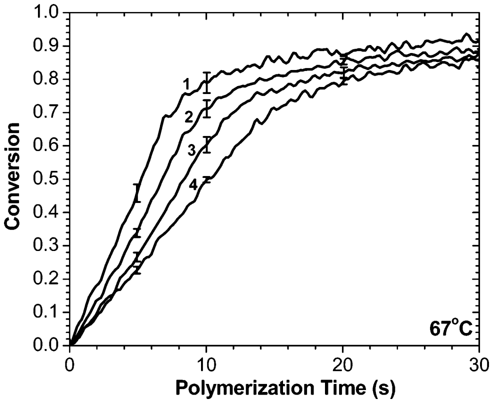


Figure 4. Steady-state polymerization profiles of cyclic carbonate carbamate methacrylate acid studies. Unaltered (1), 150 ppm methanesulfonic acid (2), 250 ppm methanesulfonic acid (3), and 400 ppm methanesulfonic acid (4) samples are shown. All polymerizations were initiated at 67 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

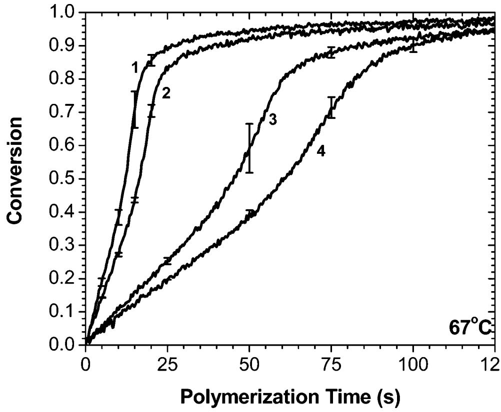


Figure 5. Steady-state polymerization profiles of phenyl carbamate methacrylate acid studies. Unaltered (1), 150 ppm methanesulfonic acid (2), 210 ppm methanesulfonic acid (3), and 350 ppm methanesulfonic acid (4) samples are shown. All polymerizations were initiated at 67 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

steady-state results of these studies are shown in Figure 3. These results show a slight but consistent polymerization decrease with increasing acid concentration. The rate decrease is dramatically greater than that observed for any of the control monomers; however, 450 ppm of the acid decreases the average rate by only 33%. Thus, the addition of a strong acid is mitigating the kinetics, but it does not reduce the rate to the level of a classical monomethacrylate.

Further studies were performed to discern possible trends with respect to other secondary functionalized methacrylate monomers. The cyclic carbonate carbamate methacrylate (CCCMA) monomer is also expected to show acid susceptibility. The effects of acid addition to the CCCMA steady-state polymerizations are shown in Figure 4. As seen with the CCMA studies, the CCCMA studies demonstrated a consistent polymerization reduction with increasing acid concentration. However, the CCCMA demonstrated a greater polymerization rate reduction with increasing acid concentration as compared to the CCMA molecule. Specifically, the CCCMA rate was reduced by 45% with 400 ppm acid as compared to a 33% average rate reduction for the CCMA with 450 ppm acid. It should be noted that there was no significant indication of any ring-opening reactions that could be derived from the FTIR spectra of both the CCMA and the CCCMA, within the limits of the apparatus. Further, the concentration of the acid is ~1000-fold less than the concentration of the monomer.

The cyclic carbonate secondary functionalized monomers had significant but not dramatic polymerization rate reductions with acid addition. A methacrylate monomer with a differing secondary functionality was also analyzed for rate reduction effects. Methacrylic and acrylic monomers with a carbamate secondary functionality and a phenyl end group have been shown to exhibit some of the fastest polymerization rates of the monomers that have been developed in our laboratory.[24] Thus, it is hypothesized that this monomer will additionally show strong polymerization effects due to the introduction of the strong acid. The results of the phenyl carbamate methacrylate (PhNCO MA) acid studies are shown in Figure 5. From these results it is evident that the addition of the phenyl carbamate secondary functionality has a larger impact on the potential anionic contribution to the molecule than the previous two molecules studied. Specifically, the PhNCO MA rate was reduced 81% with 350 ppm acid.

Figure 6 presents the ratio of the average polymerization rates from 10 to 50% conversion for the pure monomers without acid as compared to the monomers with acid for all of the methacrylate monomers studied in these experiments. From this figure the moderate acid effect on the polymerization rate of these monomers can be visualized more effectively. Nonetheless, from Figure 6, it can be observed that the monomers with the fastest bulk polymerization rates, CCCMA and PhNCO MA, are affected by the acid addition to a greater extent than the more slowly bulk polymerizing CCMA monomer. This indicates further that there may be a correlation between monomer reactivity and the extent of an anionic contribution. Moreover, it should be noted that PhNCO MA, which is the methacrylate monomer most affected by the addition of acid, cannot undergo any ring-breaking reactions that may affect the polymerization rate. This PhNCO MA result along with the lack of definitive ring-breaking evidence via FTIR analysis of the CCMA and CCCMA supports further the theory that a ring-opening reaction due to acid addition is not the primary source of the polymerization rate decrease.

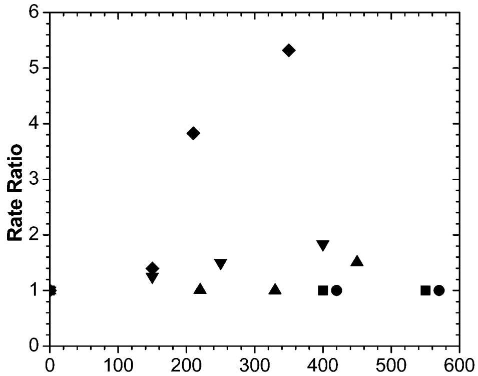


Figure 6. Ratio of polymerization rate averaged from 10 to 50% conversion for unaltered monomer divided by acid containing monomer. Tetrahydrofurfuryl methacrylate (●), 1,6-hexanediol diacrylate (■), cyclic carbonate methacrylate (▲), cyclic carbonate carbamate methacrylate (▼), and phenyl carbamate methacrylate (◆) are shown. Maximum rate reduction due to acid addition is ~5-fold for 350 ppm methanesulfonic acid in phenyl carbamate methacrylate.

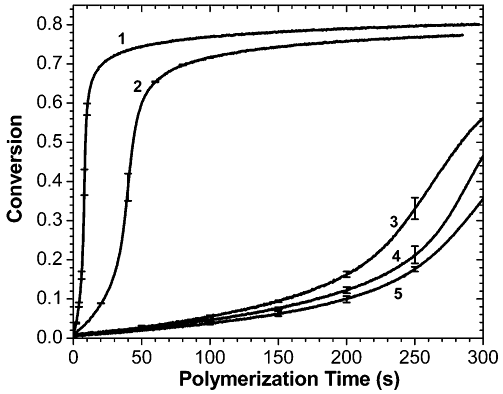


Figure 7. Steady-state polymerization profiles of cyclic carbonate acrylate acid studies. Unaltered (1), 140 ppm methanesulfonic acid (2), 210 ppm methanesulfonic acid (3), 250 ppm methanesulfonic acid (4), and 270 ppm methanesulfonic acid (5) samples are shown. All polymerizations were initiated at 25 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

One key factor that is consistent among all of the novel methacrylic samples studied is that even with the larger quantities of acid added to the monomers, all attained polymerization rates that far exceeded that of the conventional THFFMA monomer. However, each of the monomers still demonstrated a decreasing rate effect with increasing amounts of acid.

Acrylate Monomers. Systematic studies of methacrylate monomers exemplified further the possibility of an anionic contribution in the polymerization mechanism of these novel monomers. Possibly due to the radical stability and steric hindrance of the methacrylic moiety, the rate reductions with acid addition were not extensively pronounced.

The first experiment analyzed the effect of acid on the cyclic carbonate functionalized acrylate monomer. Figure 7 shows the results of acid addition to this cyclic carbonate acrylate (CCA) monomer. Increased susceptibility to acid effects for acrylate monomers appears evident from the steady-state results of the CCA monomer. At ~250 ppm acid, which corresponds to ~2.5 × 10^{-3} mol/L of acid, the reaction shows a very slow initial polymerization rate that autoaccelerates late in the reaction to a relatively slow maximum rate. Specifically, the CCA monomer demonstrated a 97% average rate reduction with 250 ppm acid as compared to the unaltered monomer. As with the CCMA and CCCMA monomers, there was no indication of any ring-opening reactions that could be derived from the FTIR spectra, within the limits of the apparatus.

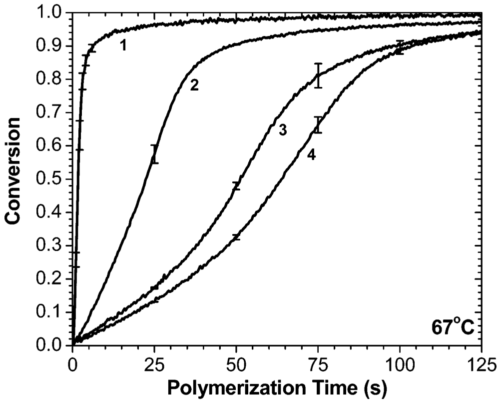


Figure 8. Steady-state polymerization profiles of phenyl carbamate acrylate acid studies. Unaltered (1), 100 ppm methanesulfonic acid (2), 250 ppm methanesulfonic acid (3), and 380 ppm methanesulfonic acid (4) samples are shown. All polymerizations were initiated at 67 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

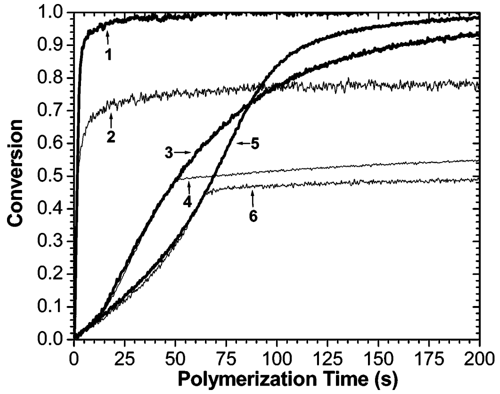


Figure 9. Steady-state (heavy lines) and unsteady-state (light lines) polymerization profiles of acrylate monomers studied. Steady state (1) and unsteady state (2) of the unaltered phenyl carbamate acrylate sample, steady state (3) and unsteady state (4) of the unaltered hexyl acrylate sample, and steady state (5) and unsteady state (6) of the 250 ppm acid phenyl carbamate acrylate sample are shown. The light was extinguished at ~45% conversion in all samples. 250 ppm acid phenyl carbamate acrylate and hexyl acrylate undergo ~5% dark conversion, while the unaltered phenyl carbamate acrylate undergoes ~40% dark conversion.

Continuing with the secondary functionalized acrylate monomers, a carbamate secondary functionalized monomer was additionally evaluated for the effect of acid addition. Figure 8 shows the steady-state polymerization rate profile of the acid studies on the phenyl carbamate acrylate (PhNCO Acr). The PhNCO Acr rate was reduced 98% with 380 ppm acid as compared to the unaltered monomer. More specifically, when the acid-retarded polymerization rate is compared to that of a traditional free-radical monoacrylate, similar polymerization rates are observed. Figure 9 compares the steady-state polymerization profiles of PhNCO Acr with 250 ppm acid to that of the traditional free-radical hexyl acrylate monomer. From this figure it is apparent that

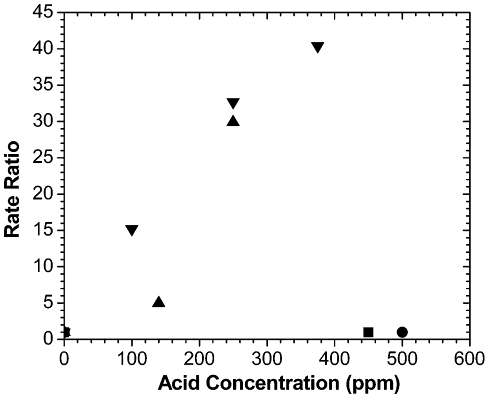


Figure 10. Ratio of polymerization rate averaged from 10 to 50% conversion for unaltered monomer divided by acid containing monomer. Tetrahydrofurfuryl acrylate (●), 1,6-hexanediol diacrylate (■), cyclic carbonate acrylate (▲), and phenyl carbamate acrylate (▼) are shown. The maximum rate reduction due to acid addition is ~40-fold for 380 ppm methanesulfonic acid in phenyl carbamate acrylate.

the overall polymerization kinetics of the PhNCO Acr with 250 ppm acid are slower than that of the hexyl acrylate.

The results of the novel acrylate monomers with acid addition showed a drastic increase in acid susceptibility as compared to the methacrylate monomers. To demonstrate further this increased susceptibility, Figure 10 shows the ratio of the average polymerization rates from 10 to 50% conversion for the pure monomer without acid as compared to the monomer with acid for all of the acrylate monomers studied in these experiments. From Figure 10 it is apparent that the novel acrylate monomers are influenced to a much greater extent by the acid addition than their methacrylate counterparts.

Each of the steady-state methacrylic and acrylic functionalized monomer studies indicates the possibility of an anionic contribution to the overall polymerization. A second analysis was performed to verify this hypothesis. In this analysis an unsteady-state evaluation of PhNCO Acr with 250 ppm methanesulfonic acid was performed. Specifically, the light was extinguished at less than 50% conversion, and the dark polymerization was monitored. Along with this analysis, two control studies were additionally performed. The first control was the unsteady state of the pure PhNCO Acr, and the second was the unsteady state of the traditional free-radical monomer hexyl acrylate. Figure 9 show the unsteady-state analysis of the PhNCO Acr with and without acid and the unsteady-state analysis of the PhNCO Acr with 250 ppm acid as compared to hexyl acrylate, respectively. In this figure, the light was extinguished at ~38% for the unaltered PhNCO Acr, and this monomer continued to react with ~40% additional conversion in the dark. On the contrary, for the 250 ppm solution, the light was extinguished at ~44% conversion, and this system achieved only ~4% additional conversion. This 4% dark conversion is indicative of a more traditional free-radical polymerization once the light source is extinguished. On the contrary, the ~40% dark conversion supports the anionic contribution theory, as termination is clearly limited in this system. The typical free-radical polymerization characteristic is more evident in the figure, where the light is extinguished at ~49% conversion for hexyl acrylate, and this monomer reacted only an additional ~8% in the dark. Figure 9 illustrates that not only are the dark polymerization characteristics approximately equivalent, but the steady-state polymerization rates are additionally similar.

A potential explanation for the decrease in polymerization rate with acid addition relies on hydrogen-bonding reductions due to the presence of the acid. It is theorized that the introduction of acid will block potential hydrogen-bonding sites at the carbonyl of the cyclic carbonate moiety and/or the amine hydrogen of the carbamate moiety, thus allowing for greater mobility leading to lower polymerization rates. To check for possible hydrogen-bonding reductions, the N−H stretch vibration peak (~3300 cm^{-1}), N−H bend vibration peak (~1500 cm^{-1}), and the carbonyl C=O stretch vibration peak (~1750 cm^{-1}) were examined for frequency shifts with and without acid addition. Decreased hydrogen bonding can be identified by a frequency increase in the N−H stretch vibration peak, a frequency increase in the C=O stretch vibration peak, and/or a frequency reduction in the N−H bend vibration peak. Upon frequency analysis of all the monomers with and without acid addition, there did not appear to be any discernible frequency shifts in any of the aforementioned peaks, within the tolerance of the apparatus. Therefore, it is believed that hydrogen bonding is not affected to any significant extent by the addition of small amounts of acid.

The results from these studies conclusively demonstrate that the presence of a strong acid impurity has a dramatic effect on the polymerization kinetics in both acrylate and methacrylate monomers that have inherently high reactivities. These studies do not provide insight into the detailed mechanism, i.e., the chemical identity and reactions of the particular reactive intermediate that is responsible for the rate acceleration. They do, however, indicate that it is highly probable that an intermediate exists which has significant anionic character either as a propagating active center or as a transition compound from the traditional acrylic propagating center to a more reactive active center. The formation of this intermediate anionic species is restricted by the presence of the methanesulfonic acid to such an extent that reductions in polymerization rate of up to 40 times are observed with as little as 400 ppm acid. The control experiments involving multi(meth)acrylates and traditional mono(meth)acrylates demonstrate that this mechanism is unique to this class of monomers. Additionally, the control experiments illustrate that the acid is not affecting the photodegradation or the efficiency of the photoinitiator, and the acid itself is not undergoing photodegradation or other side reactions. Additional experiments are clearly required to ascertain the exact nature of both the reactive intermediate and any mechanisms associated with its formation. It is not at all obvious what the exact nature of either the reactive intermediate or these mechanisms are.

Monomer Degradation Analysis. To be certain that the acid addition does not cause an acid-catalyzed degradation of the monomer leading to the rate reduction, the NMR spectrum of phenyl carbamate acrylate with 25 000 ppm (2.5 wt %) acid was evaluated. The NMR spectrum of this solution is shown in Figure 11. The NMR shows no apparent monomer degradation of the monomer after 1 week at 25 °C. Additionally, FTIR analysis of this sample does not indicate the presence of monomer degradation, within the limits of the ap-

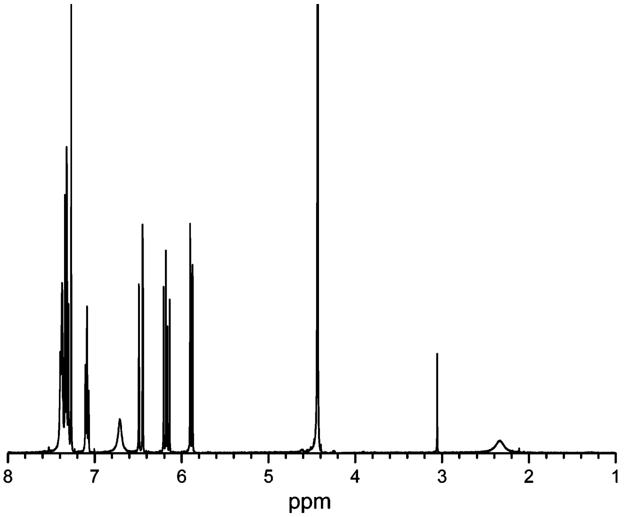


Figure 11. NMR spectrum of the phenyl carbamate acrylate with 25 000 ppm methanesulfonic acid. No monomer degradation is evident. Spectrum shows pure phenyl carbamate acrylate with traces of methanesulfonic acid. Peaks for methanesulfonic acid are at seen at δ 3.1 and δ 2.3.

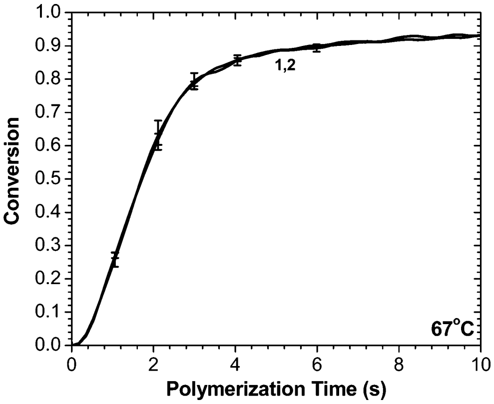


Figure 12. Steady-state polymerization profiles of phenyl carbamate acrylate base studies. Unaltered (1) and 1000 ppm triethylamine (2) samples are shown. No evident change in polymerization rate is evident. All polymerizations were initiated at 25 °C with 0.1 wt % DMPA and irradiation intensity of 5 mW/cm^2.

paratus. Therefore, it is highly unlikely that degradation products or monomer degradation are responsible for the rate deceleration when 2 orders of magnitude less acid is used.

Cationic Contribution. A final control experiment was performed to discern whether any possible cationic contribution is present in the polymerization mechanism. To test this theory, PhNCO Acr was evaluated for possible rate differences when a base was added to this monomer. A base will act to quench any cationic contribution, and thus a rate reduction with the addition of this base will indicate the presence of a cationic contribution. The results of the phenyl carbamate acrylate monomer with and without 1000 ppm of triethylamine are shown in Figure 12. The base results indicate that a cationic contribution is not prevalent in the reaction, as there is no discernible change in the steady-state polymerization rate with the addition of a base.

Conclusions

Novel (meth)acrylate monomers were analyzed for possible anionic contributions to the polymerization mechanism. A strong acid was introduced to several methacrylic and acrylic monomers, and the steady-state photopolymerization rate was monitored. The methacrylate monomers showed weak to moderate polymerization rate reductions with increasing acid concentration. This moderate reduction is hypothesized to be due to the radical stability of the propagating methacrylic radical leading to reduced hydrogen abstraction reactions that contribute to the anionic characteristic. The acrylate monomers showed a much more pronounced polymerization rate decrease with increasing acid concentration than their methacrylate counterparts. This increased acid susceptibility is hypothesized to be due to the less stable acrylic propagating radical, which enhances hydrogen abstraction reactions and other side reactions, leading to the greater anionic contribution by as yet unknown mechanisms. Moreover, unsteady-state analysis demonstrated that with 250 ppm of acid the PhNCO Acr displayed dark polymerization characteristics more closely related to that of a traditional free-radical mechanism. In comparison, the unaltered, pure monomer sample showed much greater dark polymerization than either the acid-containing sample or the traditional free-radical sample. NMR analysis revealed that the addition of the acid does not cause any discernible monomer degradation that could lead to inhibition. Finally, addition of a base demonstrated that there is no discernible cationic contribution to the polymerization mechanism.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bernhard, P.; Hofmann, M.; Schulthess, A.; Steinmann, B. *Chimia* **1994**, *48*, 427−430.
(2) Decker, C. *Nucl. Instrum. Methods Phys. Res. B* **1999**, *151*, 22−28.
(3) Decker, C.; Elzaouk, B. *J. Appl. Polym. Sci.* **1997**, *65*, 833−844.
(4) Elliott, J. E.; Lovell, L. G.; Bowman, C. N. *Dent. Mater.* **2001**, *17*, 221−229.
(5) Lovell, L. G.; Berchtold, K. A.; Elliot, J. E.; Lu, H.; Bowman, C. N. *Polym. Adv. Technol.* **2001**, *12*, 335−345.
(6) Lovell, L. G.; Stansbury, J. W.; Syrpes, D. C.; Bowman, C. N. *Macromolecules* **1999**, *32*, 3913−3921.
(7) Kunzler, J. F.; McGee, J. A. *Chem. Ind. (London)* **1995**, *16*, 651−655.
(8) Martin, S. J.; O'Brien, J. E.; Dowling, J.; McBrierty, V. J. *Eur. Polym. J.* **1998**, *34*, 1817−1828.
(9) Decker, C.; Moussa, K. *Macromolecules* **1989**, *22*, 4455−4462.
(10) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1−61.
(11) Finger, W. J.; Lee, K.; Podszun, W. *Dent. Mater.* **1996**, *12*, 256−261.

(12) Ruiz, C. S. B.; Machado, L. D. B.; Volponi, J. E.; Pino, E. S. *J. Therm. Anal. Calorim.* **2004**, *75*, 507−512.

(13) Studer, K.; Decker, C.; Beck, E.; Schwalm, R. *Prog. Org. Coat.* **2003**, *48*, 92−100.

(14) Lovestead, T. M.; O'Brien, A. K.; Bowman, C. N. *J. Photochem. Photobiol. A* **2003**, *159*, 135−143.

(15) Young, J. S.; Kannurpatti, A. R.; Bowman, C. N. *Macromol. Chem. Phys.* **1998**, *199*, 1043−1049.

(16) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* **1994**, *35*, 3243−3250.

(17) Rodriguez, E. L. *Polym. Eng. Sci.* **1993**, *33*, 115−121.

(18) Decker, C.; Moussa, K. *Macromol. Chem.* **1991**, *192*, 507−522.

(19) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 403−411.

(20) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 881−889.

(21) Decker, C.; Moussa, K. *J. Coat. Technol.* **1993**, *65*, 49−57.

(22) Decker, C.; Elzaouk, B.; Decker, D. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 173−190.

(23) Berchtold, K. A.; Stansbury, J. W.; Bowman, C. N. *J. Dent. Res.* **2000**, *79*, 147.

(24) Berchtold, K. A. Ph.D. Thesis, 2001.

(25) Berchtold, K. A.; Nie, J.; Elliot, J. E.; Hacioglu, B.; Luo, N.; Trotter, A. J. N.; Stansbury, J. W.; Bowman, C. N. *RadTech Europe 2001 Conference Proceedings,* Basel, Switzerland, 2001.

(26) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2002**, *35*, 7529−7531.

(27) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. Patent WO 02/42383, 2002.

(28) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861−3873.

(29) Moussa, K.; Decker, C. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2197−2203.

(30) Beckel, E. R.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2004**, *38*, 3093−3098.

(31) Berchtold, K. A.; Nie, J.; Stansbury, J. W.; Hacioglu, B.; Beckel, E. R.; Bowman, C. N. *Macromolecules* **2004**, *37*, 3165−3179.

(32) Berchtold, K. A.; Hacioglu, B.; Lovell, L. G.; Nie, J.; Bowman, C. N. *Macromolecules* **2001**, *34*, 5103−5111.

(33) Decker, C.; Bendaikha, T. *Eur. Polym. J.* **1984**, *20*, 753−758.

(34) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381−2394.

(35) Berchtold, K. A.; Bowman, C. N. *RadTech Europe 99 Conference Proceedings,* Berlin, Germany; Vincentz: Hannover, Germany 1999, p 767.

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