Reactivity of Monovinyl (Meth)acrylates Containing Cyclic Carbonates

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ABSTRACT: The tremendous diversity of materials properties available with polymers is due in large part to the ability to design structures from the monomeric state. The ease of use of comonomer mixtures only expands this versatility. While final polymer properties are obviously important in the selection or development of a material for a given purpose, for a number of applications, such as optical fiber coatings, photolithography, and microelectronics, the additional requirement of a very rapid polymerization process may be equally critical. A class of unusually reactive mono(meth)acrylate monomers bearing secondary functionality that includes carbonates, carbamates, and oxazolidones, has been demonstrated but not fully explained. Here, the influence of an integral cyclic carbonate functional group on (meth)acrylate photopolymerization kinetics is examined in detail with respect to monomers with a wide variety of alternative secondary functionality structure as well as in comparison to conventional mono- and di(meth)acrylates. The kinetic results from full cure studies of several cyclic carbonate-containing monomers clearly highlight specific structural variations that effectively promote monomer reactivity. Copolymerizations with tetrahydrofurfuryl methacrylate reflect similar dramatic kinetic effects associated with the novel monomers, while partial cure homopolymerization studies reveal exceptional dark cure behavior linked to observations of uncommonly low ratios of termination to propagation rates throughout the conversion profile. Temperature effects on reaction kinetics, including both reaction rate and the individual kinetic parameters, as well as the temperature dependence of hydrogen bonding interactions specifically involving the secondary functional groups, are probed as a means to understand better the fundamentally interesting and practically important behavior of these monomers.

Introduction

Photopolymerization of acrylate and methacrylate monomers is a ubiquitous technology for polymer formation in a range of applications including contact lenses, fiber optic coatings, dental materials, microfluidic devices, integrated circuits, printing plates, and many others.[1−6] The viability of photopolymerization for this range of applications depends on ambient curing, the rapid development and control of appropriate material properties, and the conversion of monomer to polymer upon exposure to limited radiation doses. Frequently, these reactions have been limited by an array of problems associated with residual, unreacted monomer, oxygen inhibition, and polymerization shrinkage and the associated stress that arises from that shrinkage.[4−10] Because the cure characteristics are intimately coupled to the monomer functionality and chemistry,[1,4,8,9,11] the approach with arguably the best hope for overcoming many of these problems relies on the synthesis and implementation of new monomer chemistries and the elucidation of the dependence of polymer properties and polymerization behavior on monomer chemistry.

In the early 1990s, Decker and co-workers[12−19] first developed and evaluated a distinctive class of acrylate monomers that incorporated secondary functional groups such as carbonates, carbamates, cyclic carbonates, and oxazolidones. Though monoacrylates, these monomers exhibited ultrarapid polymerizations and the attainment of unique combinations of mechanical properties such as simultaneously high degrees of hardness and flexibility. More recent work has focused both on expanding the range of monomers that exhibit these unique characteristics[20−23] as well as understanding the nature of their behavior.[23−29]

Several potential explanations have been postulated for the reactivity of these materials. For one group of monomers, Jansen and co-workers[23,28,29] demonstrated a strong correlation between the calculated molecular dipole and the reactivity when the dipole was beyond a critical threshold. This dependence was attributed to several factors, including intramolecular effects that would alter the electron density on the radical and double bond as well as intermolecular effects that would lead to limited extents of molecular organization in the monomeric state. Hoyle and co-workers[27] expanded the range of monomers studied to include various hydroxy-containing compounds and nicely demonstrated the critical relationship in those compounds between hydrogen bonding and reactivity. Other recent work has focused on the potential contributions of partially ionic intermediates to the polymerization rate enhancement.[24−26]

Recent work by Kilambi et al.[26] has focused on deconvoluting the intermolecular and intramolecular interactions that affect different monomers differently. These studies, comparing polymerizations and other reactions at high dilution to those in bulk monomer, demonstrated that certain functional groups primarily lead to intermolecular interactions (e.g., hydrogen bonding, $\pi-\pi$ stacking, etc.) that enhanced the polymerization,

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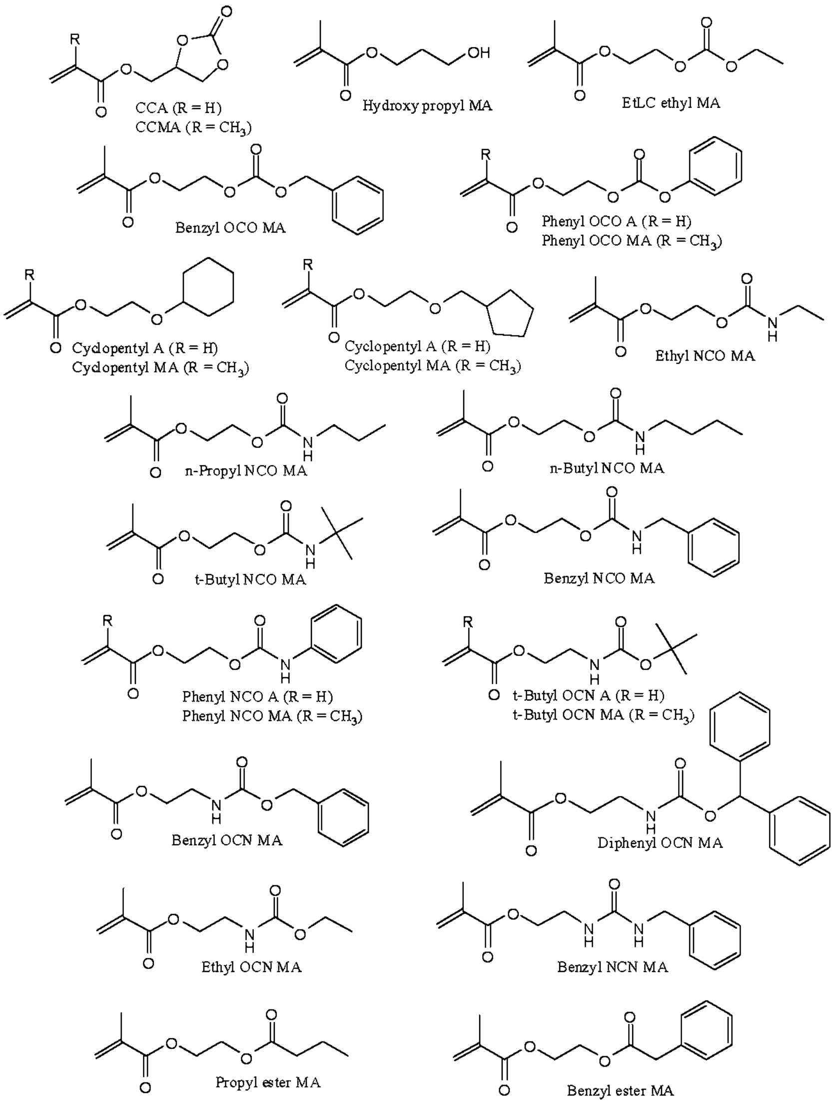


Figure 1. Structures and abbreviations of monomers presented here.

while other substituents lead primarily to intramolecular interactions.

One of the strongest intramolecular contributions arises from the cyclic carbonate moiety.[26] Decker first demonstrated that when this secondary functionality was imbedded in a five-membered cyclic structure, the resulting cyclic carbonate monomer (cyclic carbonate acrylate, CCA) polymerized more rapidly than all of the noncyclic containing monomer studies.[12,13,15−19]

Here, the reactivity of several cyclic carbonate containing monoacrylate and monomethacrylate monomers is detailed in regard to their steady state kinetics, their unsteady state kinetics, and their temperature dependence. Monomers that contain synergistic combinations of multiple nonvinyl functional groups, at least one of which is a cyclic carbonate, are also evaluated. Comparisons to the various other highly reactive systems are presented, as are experiments aimed at discerning the origin of the reactivity.

Experimental Section

Materials. The commercially available monomers used for the experimental studies are tetrahydrofurfuryl methacrylate (THFF-MA), phenyl methacrylate (phenyl MA), cyclohexyl methacrylate (cyclohexyl MA), benzyl methacrylate (benzyl MA), *n*-butyl methacrylate (*n*-BuMA), *t*-butyl methacrylate (*t*-butyl MA), 1,6-hexanediol dimethacrylate (HDDMA), and 1,6-hexanediol diacrylate (HDDA) (Aldrich, Milwaukee, WI). All commercially available materials were purified by column chromatography and/or vacuum distillation prior to use. All other materials evaluated in this work were synthesized in our laboratory and a complete listing of the monomers used is presented along with their abbreviations in Figure 1. Synthesis and purification details can be found in the Supporting Information. Polymerizations were performed using 0.1 wt % of the ultraviolet initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY).

Irradiation. A UV light source (Ultracure 100SS 100 W medium pressure mercury vapor short-arc lamp, EXFO, Mississauga, Ontario, Canada) equipped with a liquid light guide and band-pass filter (320−390 nm, peak 365 nm, EXFO, Mississauga, Ontario, Canada) was used to irradiate the monomer/initiator mixtures. The incident light intensity was controlled using the internal aperture of the UV light source and measured with a UV radiometer with a silicone photoelectric sensor (Cole-Parmer Series 9811 Radiometer, Vernon Hills, IL). All polymerizations were performed using an incident irradiation intensity of 5 mW/cm^2. The molar absorptivity of the photoinitiator, DMPA, at the peak initiating wavelength, 365 nm, is 150 L/(mol·cm).

Fourier Transform Infrared Spectroscopy (FTIR). Real-time FTIR spectroscopy (Nicolet model 760 Magna Series II FTIR, Nicolet, Madison, WI) has been used to monitor the polymerization kinetics. A horizontal transmission accessory (HTA) was designed

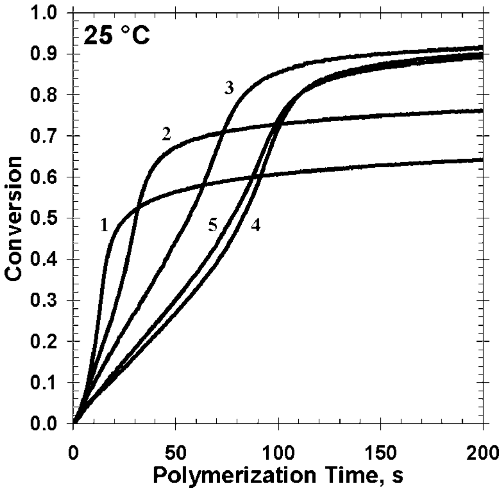


Figure 2. Illustration of the high reactivity of the cyclic carbonate methacrylate in comparison to selected monomethacrylates with secondary functionality and aliphatic end group substitution. Polymerizations of CCMA (curve 1), *t*-butyl NCO MA (2), *n*-butyl NCO MA (3), *n*-propyl NCO MA (4), and ethyl NCO MA (5) are presented. Polymerizations were conducted at 25 °C, 5 mW/cm^2 initiating light, and 0.1 wt % DMPA.

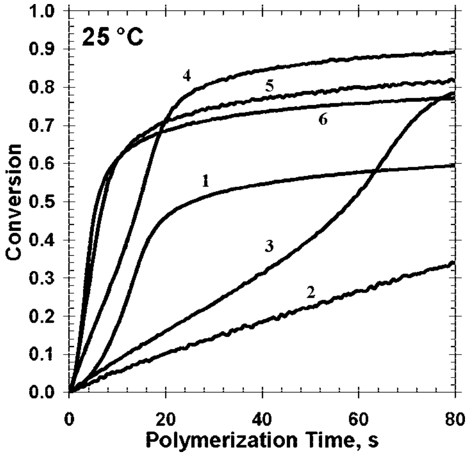


Figure 3. Illustration of the reactivity of the cyclic carbonate methacrylate relative to noncyclic carbamate and carbonate functionalized methacrylates with aromatic end group substitution. Polymerizations of CCMA (curve 1), benzyl OCO MA (2), phenyl OCO MA (3), benzyl NCO MA (4), and phenyl NCO MA (5) are presented. The diacrylate HDDA (6) is also presented for reference. Polymerizations were conducted at 25 °C, 5 mW/cm^2 initiating light, and 0.1 wt % DMPA.

to enable mounting of samples in a horizontal orientation for FTIR measurements.[1,11] A MCT/B-XT KBr detector-beam splitter combination was used in conjunction with the rapid scan feature of the spectrometer to obtain temporal resolutions (~30 ms) sufficient for monitoring these polymerizations. Temperature control was achieved using a temperature control device designed using Peltier technology (Ferro Tec-SuperTEC single stage coolers, Manchester, NH) and constructed for use in conjunction with the HTA. Samples (15−20 μm thick) were prepared by sandwiching a 5 μL drop of monomer/initiator between two NaCl crystals. All experiments[11,30] and analyses[11,30] were conducted as previously described. A minimum of three steady-state polymerizations were conducted on each monomer/comonomer composition at each set of polymerization conditions. The error associated with presented representative measure of conversion as a function of polymerization time is less than 2% conversion for all of the data presented and, in most cases, it is much less than 1%.

Results and Discussion

Cyclic Carbonate-Containing Methacrylate Polymerizations. Decker's studies demonstrated the high reactivity of cyclic carbonate-containing acrylates relative to acrylates containing linear secondary functionalities[12,13,15−17] and these studies were followed up with work by Kilambi et al. that indicated that much of this effect resulted from intramolecular interactions.[26] Here, we focus on observations of a different set of linearly functionalized aliphatic monovinyl monomers. Figure 2 illustrates the polymerization kinetics for the cyclic carbonate methacrylate and aliphatic carbamate methacrylate monomers. Here, only a few representative aliphatic carbamate monomers are presented as comparisons that indicate the dramatic effect of the cyclic carbonate moiety on the methacrylate reactivity. The aliphatic carbamate monomers presented here as comparisons are already significantly more reactive than traditional aliphatic acrylates such as hexyl acrylate due to the carbamate hydrogen bonding and the associated limitations on termination. The characteristics of the cyclic carbonate methacrylate (CCMA) polymerization resemble those of multivinyl polymerizations; most visible here are the early onset of autoacceleration, the high maximum polymerization rate achieved, and the low, limiting conversion.

The addition of an aromatic end group consistently increases reactivity in systems with various secondary functionalities, as presented in Figure 3. In contrast to the aliphatic substituents presented in Figure 2, the presence of an aromatic substituent renders other monomers more reactive than CCMA though the reason for this behavior is the significant extent of intermolecular interactions associated with hydrogen bonding and $\pi-\pi$ stacking.[26] While the cyclic carbonate moiety is also capable of $\pi-\pi$ stacking, a previous analysis has demonstrated that the cyclic carbonate moiety accelerates the polymerization primarily through intramolecular interactions.[26] The aromatic monomethacrylate monomers achieve much higher limiting functional group conversions and, in the case of phenyl NCO MA, exhibit cure rates that closely resemble those of a standard diacrylate polymerization. Despite this repositioning, the cyclic carbonate and perhaps other functionalities imbedded in cyclic structures remain an exciting avenue for exploring the reactivity origins and further improving the performance of these highly reactive monomers.

It is important to verify that the observed reactivity is specifically associated with the cyclic carbonate moiety, and not due simply to the presence of an arbitrary cyclic structure alone, be it aliphatic or aromatic. This dependence was probed by comparing several monomethacrylate polymerizations containing various types of cyclic substitution. The impact of secondary functionality is clearly illustrated in Figure 4. The presence of the cyclic moiety, conjugated or not, does enhance polymerization rates over those observed in purely linear aliphatic monomers, for example, *n*-butyl MA and *t*-butyl MA. When the carbonate is replaced with an ether on the same base structure (THFFMA), the polymerization proceeds very slowly at nearly the same rate as those systems that do not contain any secondary functionality.

Methacrylate Monomers Containing Multiple Secondary Functionalities. Decker's pioneering work focused exclusively on the implementation of secondary functionalities in acrylate-containing monomers while here we first address methacrylates followed by an analysis of acrylates. The fastest monomer studied by Decker et al.[12,13] was one containing multiple secondary functionalities; specifically, the monomer contained both a linear carbonate and a cyclic carbonate moiety. The importance of secondary functionality and end group substitution to polymerization rate has previously been established. For example, changing the secondary functionality from an ester (propyl ester MA) to a carbamate (ethyl NCO MA)

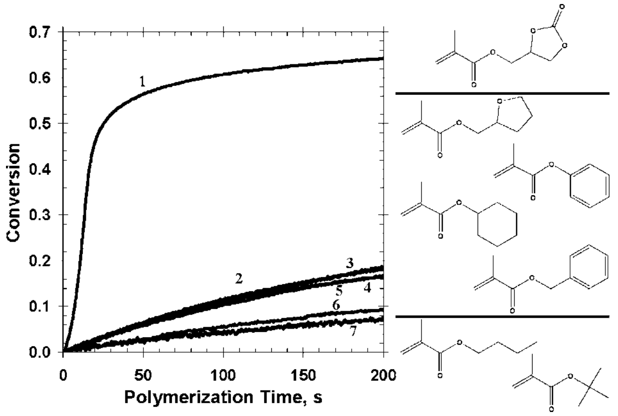


Figure 4. Effect of cyclic substitution on the polymerization kinetics of monovinyl methacrylates. Conversion versus time for the polymerization of monomers containing aliphatic and aromatic cyclic substituents: CCMA (curve 1), THFFMA (2), phenyl MA (3), cyclohexyl MA (4), benzyl MA (5), and monomers without cyclic moieties: *n*-butyl MA (6) and *t*-butyl MA (7). Monomer structures are presented for reference and are drawn from top to bottom in the order they appear in the figure.

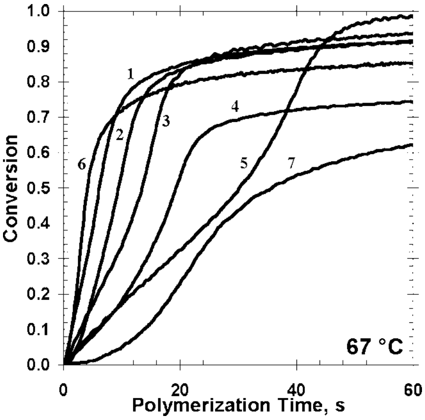


Figure 5. Effect of multiple nonvinyl functionality incorporation. Conversion versus polymerization time for the polymerization of the cyclic carbonate OCN MA (curve 1) compared to monomers with only a carbamate main chain functionality: diphenyl OCN MA (2), phenyl NCO MA (3), cyclic carbonate MA (4), and benzyl OCN MA (5). Two standard divinyl polymerization systems are presented for reference: HDDA (6) and HDDMA (7). All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2. Polymerization temperature: 67 °C.

increases the maximum polymerization rate by a factor of 12 for polymerizations initiated with 0.1 wt % DMPA and 5 mW/cm^2 UV light. Correspondingly, by changing the ethyl end group (ethyl NCO MA) to a phenyl substituent (phenyl NCO MA), an additional factor of 7 increase in polymerization rate is realized, that is, a factor of 84 higher than the initial propyl ester MA polymerization. Decker's rapidly polymerizing monomer replaced the end group substituent with another nonvinyl functionality, namely, a cyclic carbonate. Interestingly, the general structure of this monomer resembles the rapidly polymerizing aromatic substituted materials, for example, phenyl OCN MA. Each of these is based on an ethyl methacrylate core with a cyclic end group substitution. Thus, it is also important to discern the impact of the second carbonate from that of the cyclic structure alone.

A monomer with a cyclic carbonate end group and a main chain carbamate functionality was synthesized (cyclic carbonate OCN MA) to ascertain the effect of the cyclic carbonate relative to the phenyl. The carbamate functionality was chosen as a result of its predisposition toward higher reactivity than the carbonate,[21] as illustrated in Figures 2 and 3. The role of the cyclic carbonate moiety is then evident from comparisons with aromatic end functionalized carbamates.

The melting point of the cyclic carbonate OCN MA is 67 °C, and evaluations of the steady state polymerization kinetics were, therefore, conducted at this temperature. The polymerization of the cyclic carbonate-functionalized carbamate is compared with diphenyl, phenyl, and benzyl-substituted carbamates in Figure 5. The cyclic carbonate OCN MA monomer surpasses all other carbamate systems studied and its rate approaches that of hexanediol diacrylate at 67 °C. The polymerization profile of the diphenyl system strongly resembles that of the cyclic carbonate carbamate with primary differences observed at the polymerization onset. This similarity indicates that perhaps the rigid, nearly planar cyclic structure created by the carbonate and the changes in molecular structure that it induces are of primary importance.

Two nonfunctionalized, nonconjugated cycloaliphatic-substituted carbamate methacrylates were used to explore the impact of the end group's electronic characteristics and rigidity. The effect of the cyclopentyl and cyclohexyl substituents on both factors is minimal in comparison to the carbonate-containing five-membered ring. A comparison of the cyclopentyl and cyclohexyl monomers also provides insight into the importance of the placement of the tertiary abstractable hydrogen with respect to the secondary functionality. The hydrogen at the base of the cyclohexyl ring is expected to be more abstractable due to the six-membered ring and direct attachment to the carbamate.

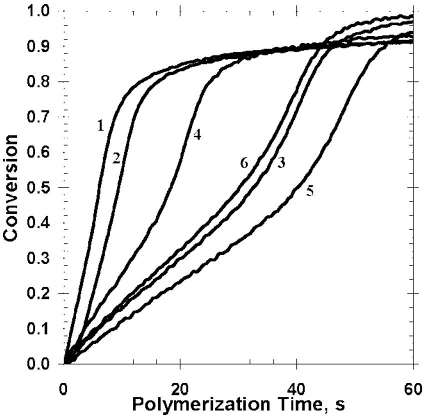


Figure 6. Effect of end group rigidity and electronic characteristics on the polymerization kinetics of several carbamate (OCN) methacrylates. Cyclic carbonate OCN MA (curve 1), diphenyl OCN MA (2), cyclopentyl OCN MA (3), cyclohexyl OCN MA (4), *t*-butyl OCN MA (5), and benzyl OCN MA (6) are presented. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2. Polymerization temperature: 67 °C. The *t*-butyl OCN MA polymerization was conducted at 86 °C.

The rapid polymerization of the cyclic carbonate OCN MA in comparison to all of the other OCN monomers evaluated (Figure 6) is a testament to the advantageous qualities of the cyclic carbonate functionality. The inductive effects and hydrogen bond acceptor character of the carbonate are likely significant contributors to monomer reactivity. If these monomer traits are not important, then a dramatic difference in reactivity between the cyclopentyl and the cyclic carbonate monomers is not expected. Furthermore, the cyclopentyl carbamate methacrylate is significantly less reactive than the cyclohexyl. Thus, the direct attachment of the ring positively influences the polymerization kinetics.

A comparison is also made to a tertiary butyl-substituted system to evaluate the impact of end group rigidity. The melting point of the *t*-butyl system is 81 °C. Thus, the kinetics of this system were evaluated at that temperature. Given previous

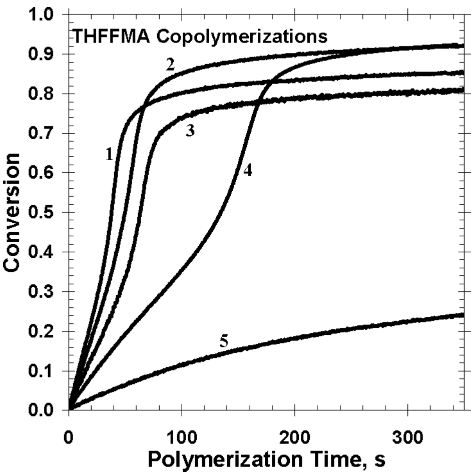


Figure 7. Comparison of several monomethacrylate copolymerizations with THFFMA (50/50 wt/wt). Cyclic carbonate OCN MA (curve 1), *t*-butyl OCN MA (2), benzyl NCN MA (3), and benzyl OCN MA (4) are presented. The homopolymerization of THFFMA (5) is presented for reference. Polymerization conditions: temperature, 25 °C; light intensity, 5 mW/cm^2; initiator concentration, 0.1 wt %.

results that indicate the minimal impact of temperature on polymerization rate in most carbamate-substituted methacrylates, the comparison of this system to others at 67 °C is sufficient. The low polymerization rate of the *t*-butyl OCN MA demonstrates that the rigidity of the end group is not a primary factor of importance. Additionally, it is interesting to note that the cyclopentyl OCN MA monomer polymerization mimics that of the benzyl OCN MA monomer. This result indicates that the influence of the aromatic ring, when separated from the secondary functionality by a single carbon, is minimal.

When considering the polymerization kinetics of each of the cyclic carbonate containing monomers, it is relevant to consider the role of diffusion limited termination as it changes throughout these polymerizations. Such behavior would be significantly dependent on the ultimate glass transition temperature of the polymer that is formed. However, for nearly all of the monomers presented here, dramatic autoacceleration behavior is not observed. While there is an increase in rate with increased conversion, as indicated by the changing slope of the conversion-time plots, the relative increase is small and the autoacceleration behavior mimics that of the initial rates, with the cyclic containing monomers having both faster initial kinetics and overall polymerization kinetics.

Copolymerizations. Several of the carbamate (OCN) methacrylates were evaluated in copolymerization (50/50 wt/wt) with tetrahydrofurfuryl methacrylate (THFFMA) to characterize their polymerizations further as presented in Figure 7. Copolymerizations of the high melting, highly reactive benzyl urea monomer were also examined. The cyclic carbonate OCN MA/THFFMA copolymerization surpasses even the urea copolymerization in regards to its polymerization kinetics. This result confirms the benefit of cyclic carbonate incorporation, as the benzyl NCN MA monomer exhibits nearly the highest maximum homopolymerization rate (s^{-1}) of all of the aromatically substituted methacrylate monomers evaluated, superseded only by the phenyl NCO MA polymerization. The rapid polymerization behavior of *t*-butyl OCN MA in copolymerizations is surprising given its relatively low homopolymerization rate (Figure 6). It is clear from these results that, though these are all methacrylate monomers, because of intermolecular interactions, it is not possible to predict the copolymerization kinetics based simply on the homopolymerization kinetics of each monomer.

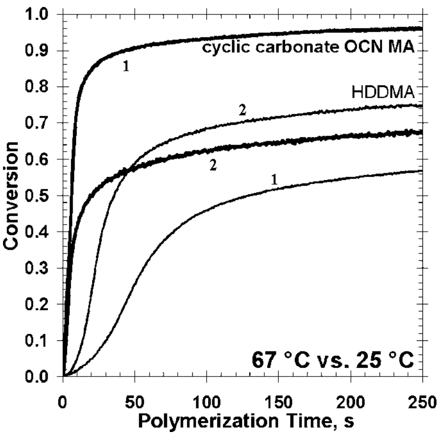


Figure 8. Conversion versus polymerization time for the polymerization of cyclic carbonate OCN MA (thick lines) and HDDMA (thin lines) at 25 °C (curve 1) and 67 °C (curve 2). All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

Temperature Dependence of the Cyclic Carbonate Carbamate Methacrylate Polymerization. The temperature dependence of secondarily functionalized systems has been addressed for a variety of monomers. Results thus far indicate that most methacrylate systems with carbamate or carbonate functionality exhibit minimal differences in polymerization rate when polymerized at various temperatures above the monomer melting point. In these systems, temperature primarily affects the ultimate attainable conversion, and thus, the rate behavior at high conversion. The cyclic carbonate OCN MA polymerization system also appears to follow the trend of minimal temperature impact on low conversion kinetics (Figure 8). This result is particularly interesting as the higher temperature likely reduces the extent of hydrogen bonding associated with the carbamates, thus facilitating termination. To maintain a similar overall initial polymerization rate then, the propagation rate must be significantly enhanced at the elevated temperatures as well. A very different behavior is observed in the classical hexanediol dimethacrylate (HDDMA) polymerization system under the same conditions. The primary effect observed in the cyclic carbonate OCN MA polymerization was again on the ultimate attainable conversion, although the presence of a short inhibition-like period during polymerization at 25 °C was visibly absent in the 67 °C polymerization. It should be noted that the cyclic carbonate OCN MA monomer has a melting point of 67 °C. However, it remains meta-stable in its liquid form for modest intervals upon cooling, as is the case with many of the carbamate monomers. Thus, it is possible to polymerize this material in its noncrystalline state at ambient temperature. However, if the sample is left below its melting point for an extended period, crystallization will occur, and a dramatic suppression in polymerization rate is observed.

Hydrogen Bonding. The high reactivities observed in the carbamate and urea functionalized polymerization systems suggest that hydrogen bonding is important to these polymerization systems. Hydrogen bonding introduces mobility restrictions that contribute to increased monomer viscosity, and affect monomer organization, which potentially leads to templating of monomeric double bonds.[27,31] These factors, in turn, affect polymerization rate. Thus, it is valuable to examine hydrogen bonding changes with temperature and as a function of conversion during polymerization. Although the energies associated with hydrogen bonds are weak (20−50 kJ/mol) in comparison to the energy of a covalent bond (~400 kJ/mol), the hydrogen bonding interaction is substantial enough to produce quantifiable changes in the vibrational absorbance frequencies and peak intensities of the participating species.

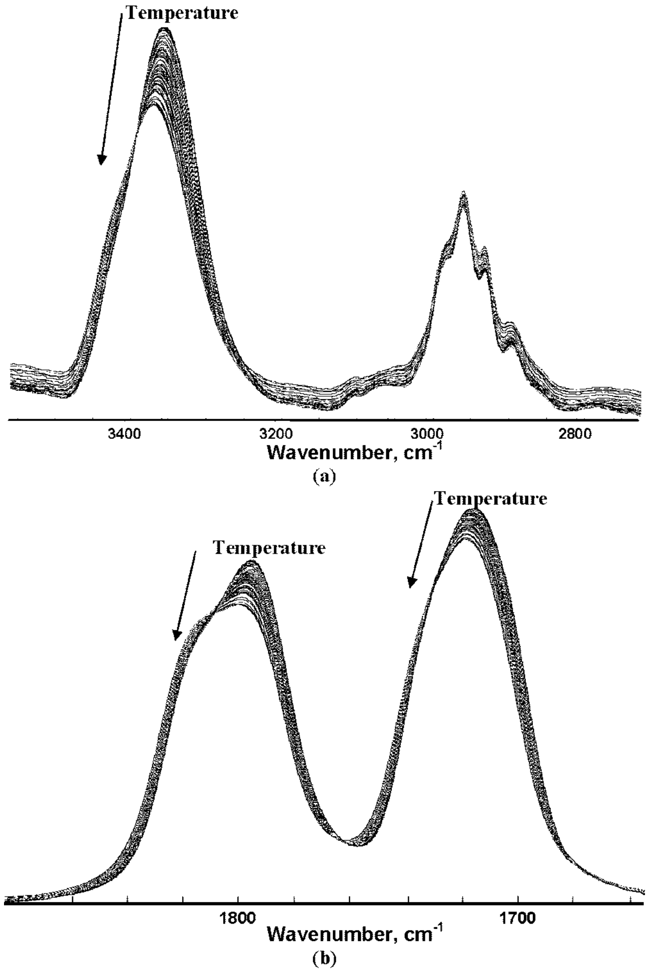


Figure 9. Changes in the vibrational spectrum of the cyclic carbonate OCN MA monomer as a function of temperature. Changes in the NH stretching region (a) and the carbonyl stretching region (b) are visible as the sample is cooled from 80 to 15 °C. The arrows are pointing in the direction of increasing temperature with 15 and 80 °C as the terminus at low and high temperature respectively.

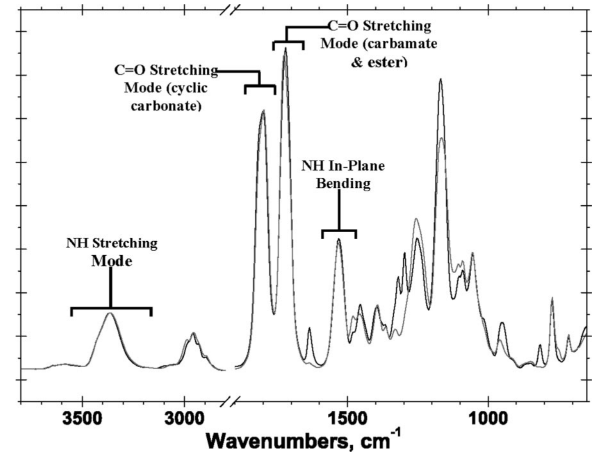


Figure 10. Pre and post polymerization spectra for the polymerization of the cyclic carbonate OCN MA 67 °C. The NH and C═O stretching and NH in-plane bending regions are highlighted.

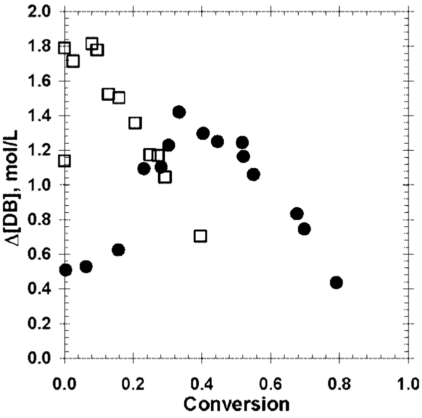
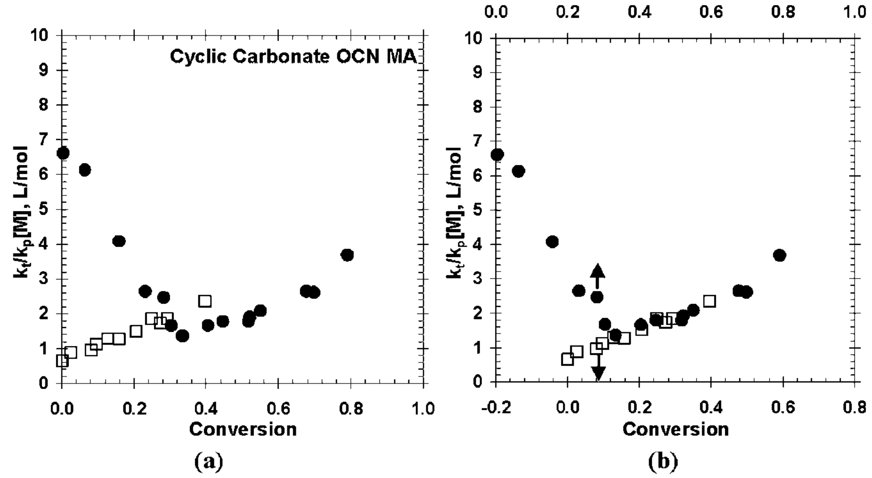


Figure 11. Change in double bond concentration, Δ[DB], in the first 100 s after extinction of the irradiating light source as a function of conversion for the polymerization of the cyclic carbonate OCN MA at 25 (unfilled squares) and 67 °C (filled circles). The initial double bond concentration in the pure monomer, $\Delta[\mathrm{DB}]_0$, is 4.0 mol/L. Polymerization conditions: light intensity, 5 mW/cm^2; initiator concentration, 0.1 wt % DMPA.

Thus, changes in hydrogen bonding are routinely examined with infrared spectroscopy.

The cyclic carbonate carbamate monomer has numerous sites that participate as hydrogen bond acceptors for the carbamate hydrogen. Specifically, every carbamate, carbonate, ester carbonyl and alkoxy oxygen is a possible acceptor site, with the relative hydrogen bond strength decreasing in that order. Figure 9 provides a simplistic overview of the changes in the vibrational spectrum of the cyclic carbonate carbamate over the 15−80 °C temperature range. Because hydrogen bonding is a strong function of temperature,[32] temperature studies are a useful tool for gathering information regarding the extent and strength of hydrogen bonding, both overall and as a function of the acceptor site. Such quantification of hydrogen bonding, however, is not a trivial task. Hydrogen bonded species exhibit multiple absorbances due to various intra- and intermolecular conformations with complications of the infrared spectrum as a result of overtone and combination bands that appear in regions of interest, and absorptivities that are a strong function of hydrogen bond strength.[33] The intent of this discussion is to introduce the wealth of information that is available with such an analysis and to make observations based on the spectral information. Figure 9a presents the NH (3200−3500 cm^{-1}) and CH, aliphatic, and aromatic (2850−3100 cm^{-1}) stretching regions. At elevated temperatures, the contribution due to the stronger intermolecular dimer-type carbamate-carbamate hydrogen bonded interactions is preferentially disrupted with the result being a shift to greater intramolecular interactions. It is difficult to make any quantitative assessment due to a decrease in absorptivity, often by more than a factor of 2.5, as NH hydrogens shift from a strongly bonded to a free state.

Additionally, an increase in hydrogen bond strength and/or a shift from dimer like hydrogen bonds to chain like hydrogen bonded species is observed via a decrease in frequency and an increase in spectral intensity with decreasing temperature. Figure 9b illustrates similar changes in the carbonyl stretching region as a function of temperature. The higher frequency carbonyl mode is attributed to the cyclic carbonate carbonyl, and the lower frequency to a combination of peaks associated with the methacrylic ester carbonyl and the carbamate carbonyl. It is clear from the changes in these absorbances with temperature that the cyclic carbonate carbonyl and at least one (probably both) of the other two are participating in hydrogen bonding. It also seems reasonable to assert that a significant portion of the hydrogen bonding is occurring between the cyclic carbonate and the carbamate NH. The magnitude of change associated with the higher frequency peak appears disproportionately high in comparison to that of the carbamate and ester carbonyls. It is important to stress that without knowledge of the absorptivity change with frequency, this assertion cannot be verified. However, the change in carbonyl absorptivity with frequency



(a)

(b)

Figure 12. Effect of temperature on the cyclic carbonate OCN MA polymerization. The kinetic parameter ratio, $k_t/k_p[M]$, is presented (a) for polymerization at 25 (unfilled squares) and 67 °C (filled circles), and (b) presents the same data with the 25 °C kinetics shifted by 20% conversion (bottom axis). Polymerization conditions: light intensity, 5 mW/cm^2; initiator concentration, 0.1 wt % DMPA.

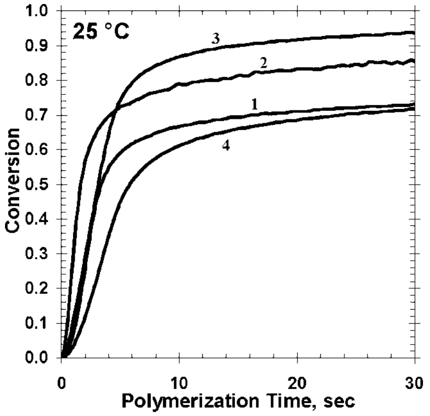


Figure 13. Illustration of the reactivity of the cyclic carbonate acrylate relative to noncyclic carbamate and carbonate functionalized acrylates with aromatic end group substitution. Polymerizations of the cyclic carbonate acrylate (curve 1), phenyl NCO acrylate (2), and phenyl OCO acrylate (3) are presented. The diacrylate HDDA (4) is also presented for reference. Polymerizations were conducted at 25 °C, 5 mW/cm^2 initiating light, and 0.1 wt % DMPA.

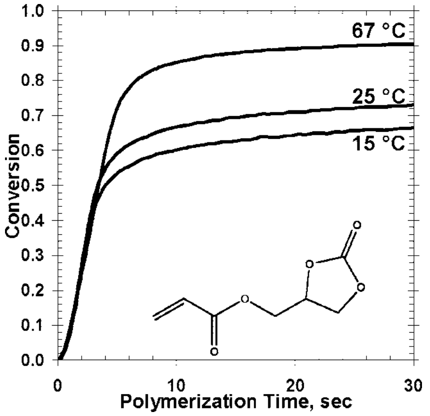


Figure 14. Effect of polymerization temperature on the steady state kinetics of the cyclic carbonate acrylate polymerization. Polymerizations conducted at 15, 25, and 67 °C and initiated with 5 mW/cm^2 initiating light and 0.1 wt % DMPA are presented.

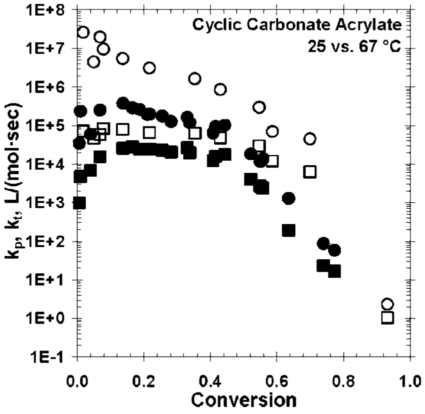


Figure 15. Effect of temperature on cyclic carbonate acrylate polymerization kinetics. Termination, k_t, (circles) and propagation, k_p, (squares) kinetic parameters are presented as a function of conversion for polymerization at 25 (filled symbols) and 67 °C (open symbols). Polymerizations were conducted at either 25 or 67 °C, as noted, 5 mW/cm^2 initiating light and 0.1 wt % DMPA.

is significantly less than that of the NH. Changes are also visible in the NH in-plane bending mode (1530−1570 cm^{-1}) and throughout the fingerprint region at frequencies correlated with the alkoxy oxygens of the carbonate, carbamate, and ester functionalities (1100−1300 cm^{-1}). The absorbances in this region are extremely convoluted, thus, making peak assignments a difficult process.

The changes in the aforementioned vibrational modes with polymerization also contain information useful to mechanistic understanding of these polymerization systems. Figure 10 illustrates the change in the vibrational spectrum of the cyclic carbonate OCN MA as the sample is polymerized. Some important features include the following: (1) The absorbance associated with the cyclic carbonate carbonyl does not undergo a dramatic shift or loss of intensity, indicating that the ring is not broken during polymerization. (2) The small shift that is visible in the cyclic carbonate carbonyl is one to lower frequency indicating an increase in hydrogen bonding to the cyclic carbonate with polymerization. (3) Changes in the ester carbonyl are complex due to changes resulting from the loss of conjugation as the sample polymerizes. Thus, it is difficult to assess changes without second derivative analysis and peak deconvolution. (4) Minimal changes are observed in the NH stretching region. The observed shift to lower frequency indicates an increase in extent or strength of hydrogen bonding during polymerization. These observations provide evidence that prepolymerization organization as a result of hydrogen bonding may orient the polymerizing monomeric system in a way that facilitates propagation and thereby increases the polymerization rate.

Unsteady State Kinetics. Unsteady state evaluation is a useful tool for probing polymerization kinetics and testing mechanistic hypotheses. The kinetics of the cyclic carbonate OCN MA were evaluated at both 25 and 67 °C. Polymerizations were conducted in the liquid state at both temperatures. The dark cure behavior of this system is quite spectacular. When the initiation source is extinguished during the polymerization, before the maximum conversion at those conditions is achieved, an extremely large amount of additional dark cure is frequently observed. At 25 °C as much as 45% conversion has been observed in the absence of continued initiation (Figure 11). This amount of "in the dark" polymerization is dramatically higher than is observed in all of the commercial monomers evaluated and is particularly surprising at such low conversions, where termination is typically quite facile.[34] It is logical to assume that the organization/hydrogen bonding present at 25 °C is sufficient to restrict system mobility and that a partial ionic character of the active center may also lead to such dramatic dark polymerizations.[25,35] However, the effect impacts propagation and termination rates disproportionately. The ratio of kinetic parameters, $k_t/k_p[M]$, which represents the reaction diffusion constant, as a function of conversion at each temperature is presented in Figure 12. This ratio is lower than that of any other system we are aware of in the literature. Additionally, the kinetic constant ratio as a function of conversion is shifted with temperature. Shifting the 25 °C kinetics by ~20% conversion (Figure 12b) produces an overlapping extension of the data obtained at 67 °C.

Cyclic Carbonate-Containing Acrylate Monomers. The acrylate cyclic carbonate system is much like its methacrylate analog. Its reactivity relative to aliphatic-substituted monoacrylates containing secondary carbamate, ether, carbonate, and ester functionality is high.[12,16,17,36,37] However, it is not the most reactive monomer when compared to carbamates and carbonates with aromatic substitution, specifically phenyl NCO acrylate and phenyl OCO acrylate (Figure 13). In particular, the phenyl OCO acrylate is at least as fast as CCA while for the methacrylates the CCMA is significantly faster than the corresponding phenyl OCO methacrylate. The concentration of the phenyl moieties in the acrylate is slightly higher than in the methacrylate which would lead to increased $\pi-\pi$ stacking. Further, the impact of the phenyl and cyclic carbonate structures are likely to be different in regards to their relative effects on the double bond and radical reactivities which would lead to differences in the overall monomer reactivity. With that noted, all of these systems polymerize more rapidly than HDDA, which is a commonly used diacrylate system. Both of the phenyl acrylates, however, achieve final conversions significantly higher than those of HDDA and the cyclic carbonate acrylate systems.

Temperature. Temperature is also a valuable tool for exploring the behavior of the cyclic carbonate acrylate polymerization further. The cyclic carbonate acrylate, like many of the methacrylate systems exhibited little change in polymerization rate with temperature (Figure 14). However, over the 15−67 °C range, the final conversion was increased by more than 20%. Increased conversion is often observed with increasing polymerization temperature in divinyl polymerization. This increase, however, is also typically accompanied by a significant increase in polymerization rate at lower conversions, as observed for the typical methacrylate polymerizations presented in Figure 8 and expected for typical acrylates.

Although the low conversion polymerization rate of the cyclic carbonate acrylate polymerization is minimally affected by temperature changes, the system mobility increase with temperature is clearly observed by the change in the propagation and termination kinetic parameters, k_p and k_t, with temperature (Figure 15). Both k_p and k_t increase upon increasing the polymerization temperature from 25 to 67 °C. While these kinetic paramaters are clearly not measures of a single, idealized propagation or termination reaction, they do provide reasonable indications of the relative rates of termination and propagation in these highly complex systems as well as the conversion dependence of those reactions. Additionally, the conversion where rapid decreases in k_p and k_t are observed is shifted to higher conversion.

This combination of characteristics associated with the cyclic carbonate acrylate polymerization is in contrast to the linear carbonate system represented by phenyl OCO acrylate (Figure 13). For the phenyl OCO acrylate, as the temperature is increased from 25 to 67 °C, the polymerization rate decreases. Accompanying the slowing polymerization rate are relatively unaffected propagation kinetics and increased termination kinetics. This difference in polymerization characteristics with changing temperature indicates that the important mechanisms are a function of both the secondary functionality and how that functionality is incorporated into the monomer structure. While it is typical for such secondary functionality as well as its location to impact the polymerization kinetics, the type and magnitude of effects observed here are unique.

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Supporting Information Available: Synthesis and purification of the monomer systems used. This material is available free of charge via the Internet at http://pubs.acs.org.

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