Novel Monovinyl Methacrylic Monomers Containing Secondary Functionality for Ultrarapid Polymerization: Steady-State Evaluation

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ABSTRACT: Experimental investigations were made into the effects of monomer structure and functionality on free-radical polymerization kinetics. A more comprehensive understanding of how structural characteristics, monomer traits, and polymerization conditions influence the polymerization mechanisms and network evolution was desired. Variations in the nature of the monomers' secondary functionality and the terminal substitution were the primary variables examined. The three factors hypothesized as important to the advantageous polymerization characteristics observed are hydrogen bonding, hydrogen abstraction, and the electronic characteristics of the monomer. The experimental evaluations presented clearly demonstrate that each of these mechanisms contributes to the reactivity of these monomers and the networks that they form. The combination of these factors leads to cross-linked network formation and enhanced polymerization kinetics, i.e., monovinyl monomers with reactivities that rival those of commonly used divinyl monomers.

Background/Introduction

The quality and performance of polymers are critically linked to the cure characteristics of the polymerization system. Improvements in monomer curing efficiency allow optimal polymer properties to be achieved with minimal irradiation times, intensities, or initiator concentrations, which has significant industrial relevance. The development of monomers that exhibit high reactivities, superior mechanical properties, and enhanced aging characteristics is the ultimate goal. In part, this task entails the use of monomers that react rapidly to very high conversions and result in the formation of a mechanically and chemically stable three-dimensional network. Their development and eventual use require, above all, a detailed understanding of the polymerization kinetics and the underlying mechanisms that define those kinetics. Additionally, it is essential to understand how the kinetics and corresponding mechanisms are affected by changes in factors such as monomer structure and functionality.

Recent studies by Decker et al. were aimed at the development of monovinyl acrylates (Table 1) that exhibit rates of cure equivalent to that of multivinyl acrylate monomers but with higher extents of cure and equivalent if not superior mechanical properties. It was shown that by including certain chemical groups such as carbonates (structures **1** and **5**),[1−5] carbamates (structure **2**),[3,4,6] cyclic carbonates (structures **3** and **5**),[2,7−10] and oxazolidones (structure **4**)[3−5] into the structural unit of a monovinyl acrylate, the reactivity of the resulting monomer is well in excess of that of more commonly used monovinyl systems. Although there are many other functional groups that have been explored, and surrounding structures examined, there are four monomers (structures **2**−**5**) that were shown to polymerize most rapidly and completely, leading to polymers with a hardness comparable to that which can be achieved with a trivinyl monomer, e.g., trimethylolpropane triacrylate (TMPTA), while simultaneously maintaining the flexibility of a standard polymeric monovinyl material, e.g., ethyldi(ethylene glycol) acrylate (EDGA).[4,11]

Table 1. Molecular Structures of Several Previously Studied Novel Acrylic Monomers

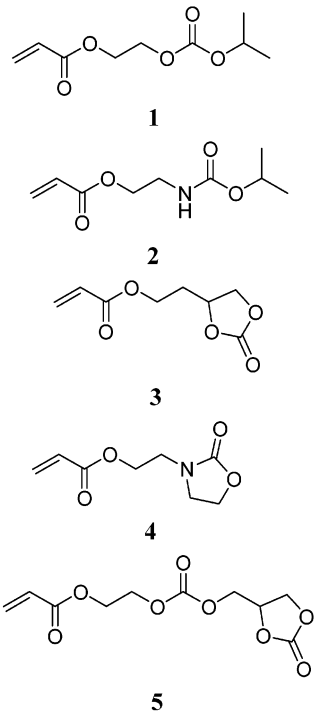

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Table 2. Performance Analysis of Novel vs Typical UV-Curable Acrylic Monomers[a]

monomer	$R_{p,max}$ (1/s)[c]	$R_{p,max}$ (1/s)[c,d]	RU[e] (%)	gel fraction (%)[f]	hardness (s)[g]	flexibility (mm)[d,h]
carbonate (**1**)	2	12	5		−/30	0
carbamate (**2**)	7	90	2	90	−/70	0
cyclic carbonate (**3**)	40	100	4	15[i]	360/260	0
oxazolidone (**4**)	6	120	3	96	−/90	0
linear and cyclic carbonate (**5**)	200	165	5	80[i]	200/100	0
EDGA[b]	1	8	2	10	50/40	0
TPGDA[b]	4	27	10	100	−/120	1
HDDA[b]	3	20	18	100	250/130	2
TMPTA[b]	10	100	55	100	340/270	5

[a] The data presented in this table are a compilation from the references noted above in the text next to each monomer type. Polymerization conditions: initiator, 5 wt % DMPA; light intensity, 500 mW/cm^2; film thickness, 25 μm. [b] Key: ethyldi(ethylene glycol) acrylate (EDGA); tripropylene glycol diacrylate (TPGDA); hexanediol diacrylate (HDDA); trimethylolpropane triacrylate (TMPTA). [c] Normalized measure of the maximum polymerization rate: $R_{p,max}$ (mol/L·s)/initial double bond concentration (mol/L). [d] Copolymerization with an equivalent amount of a polyurethane-diacrylate oligomer (Actilane 20 from SNPE). [e] Residual unsaturation of the tack-free film. [f] Fraction of insoluble polymer after an extended irradiation time. [g] Persoz hardness of the tack-free film (homopolymerization/copolymerization[d]). [h] Mandrel flexibility of the tack-free film−mandrel diameter at which cracks first appear. [i] Insoluble fraction at 60% conversion.

Overall, the reactivity of these monomers was found to increase in the following order for polymerizations in air: carbonate (structure **1**) < carbamate (structure **2**) < oxazolidone (structure **4**) < cyclic carbonate (structure **3**) ≪ linear and cyclic carbonate (structure **5**), where reactivity is defined as the maximum polymerization rate normalized by the initial acrylate concentration. The reactivity and properties of these monomers have been compared to several commonly used acrylates in Table 2. Gel fractions have been measured for the polymer product in several of these systems. Interestingly, several of these monomers are, for the most part, insoluble in organic solvents, indicative of the formation of a cross-linked network. In addition, these monomers are capable of forming very hard and yet very flexible polymers (Table 2). This behavior has significant advantages over standard multifunctional, i.e., multivinyl, polymerization systems chosen for their rapid cure and hard polymer products. Specifically, as vinyl functionality is increased, the polymerization rate also increases, but only at the cost of a greater degree of residual unsaturation and the formation of a hard, but typically brittle polymer.[6,12,13]

The reason for the enhanced reactivity and gelation behavior of these monoacrylates is not fully understood.[5] One hypothesis of Decker et al. is that the reactivity is a result of an efficient chain transfer reaction that involves labile hydrogens from the newly introduced functional group.[5,8] This hypothesis is supported by the gelation results as well as results where an initiator dependent on the hydrogen donor characteristics of the system, i.e., benzophenone, was used. Benzophenone was very successful in rapidly polymerizing the new monomers, but no polymer was formed when polymerizations of HDDA and TMPTA were initiated by benzophenone.[5] Additionally, the high rates have been attributed to the presence of an inefficient termination process in the polymerization of these new materials. This hypothesis is supported by kinetic data, which show a dramatic decrease in the termination kinetic constant during the polymerization, while the propagation kinetics closely follow those of standard acrylic systems.[14,15] More recent work hypothesizes that many of these results are explained by hydrogen bonding[16,17] and monomer polarity.[17,18] Specifically, Jansen et al. assert that hydrogen bonding affects preorganization in the polymerization system, which, in turn, enhances the polymerization rate. Evidence of preorganization is presented via tacticity data for undecyl amide *N*-ethyl methacrylate.[16,17] Additionally, polarity, as defined by the calculated molecular dipole, was correlated with monomer reactivity, quantified by a nonnormalized measure of the maximum polymerization rate.[17,18] These investigations provide insight into factors that are potentially important to the reactivity observed in these materials; however, many unanswered questions remain.

This class of monomers has great promise for leading to advancements in the design of new materials. The rapid and complete polymerization of these systems directly translates to minimal required exposure times and intensities. This decrease in required exposure and initiation intensity has significance for a wide range of curing applications. Examples include applications that require cure through a secondary layer and cure of systems containing fillers, which absorb a fraction of the initiating light. Additionally, the potential exists for reducing initiator concentrations without compromising the rate or extent of cure. This reduction would certainly have an impact on the long-term color stability of some polymer products, as initiators are a leading cause of polymer discoloration and long-term degradation reactions.

A complete understanding of the mechanisms that contribute to these desirable cure characteristics is important to the continued development of this class of materials and photopolymers in general. The knowledge of such polymer evolution intricacies will have a pronounced effect on the ability to design materials rationally. Correspondingly, a more detailed kinetic analysis of such monovinyl systems is imperative to the comprehension of those underlying mechanisms. The aim of this work is to begin to understand the interactions that exist between monomer structure and functionality and the polymerization kinetics and corresponding network formation. Specifically, a series of model monomers that have been designed for the purpose of mechanism elucidation has been synthesized and evaluated. There are three primary factors hypothesized as important to the advantageous polymerization characteristics observed in these systems.[19] Those factors, hydrogen bonding, hydrogen abstraction, and electronic effects, are introduced via changes in monomer structure and functionality, and experimental findings in support or opposition to their prevalence are presented.

Experimental Section

Materials. The commercially available monomers used for the experimental studies are 2-ethoxyethyl methacrylate (EEMA), 2-(methacryloyloxy)ethyl acetoacetate (acetoacetoxy

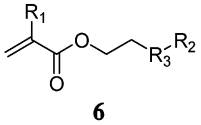
MA), *n*-butyl methacrylate (*n*-BuMA), tetrahydrofurfuryl methacrylate (THFFMA), 1,6-hexanediol dimethacrylate (HDDMA), 1,6-hexanediol diacrylate (HDDA) [Aldrich, Milwaukee, WI], di(ethylene glycol) dimethacrylate (DEGDMA, Sartomer Co., Exton, PA), and tri(ethylene glycol) dimethacrylate (TEGDMA, Polysciences Inc., Warrington, PA). 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. 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. An UV light source (Ultracure 100SS 100 W high-pressure Mercury vapor short-arc lamp, EXFO, Mississaugua, Ontario, Canada) equipped with a liquid light guide and band-pass filter (320−390 nm, peak 365 nm, EXFO, Mississaugua, 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 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 to enable mounting of samples in a horizontal orientation for FTIR measurements.[20,21] 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[20,22] and analyses[20,22,23] 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

Experimental investigations were made into the effects of monomer structure and functionality on free-radical polymerization kinetics. A more comprehensive understanding of how structural characteristics, monomer traits, and polymerization conditions influence the polymerization mechanisms and corresponding network evolution was desired. Thus, a series of model monomers whose structure and functionality were systematically varied was designed, synthesized, and characterized to provide insight into the effects of those parameters and polymerization conditions on their polymerization characteristics and corresponding network development. Monomer attributes were varied systematically via synthesis of a number of monomers corresponding to the general structure (structure **6**):



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where R_1 is CH_3 or H for methacrylates and acrylates, respectively. R_3 is a secondary functionality typically bearing electron withdrawing characteristics, and R_2 is the terminal non-(meth)acrylate side substituent. Variations in the nature of the monomers' secondary functionality (R_3), end group substitution (R_2), and vinyl functionality (R_1) are examined. Results of initial studies surrounding systematic variations in both R_3 and R_2 are presented, and they are followed by a discussion of those data in the context of the three factors hypothesized as important to the polymerization characteristics observed: hydrogen bonding, hydrogen abstraction, and electronic characteristics.

Secondary Functionality, R_3. In examining the relationship between monomer structure and reactivity, the characteristics of the secondary functionality impact numerous aspects of the polymerization system and the subsequently observed reactivity. For example, the secondary functionality plays a significant role in each monomer's hydrogen bonding and other lower strength inter- and intramolecular interactions (e.g., dipole−dipole interactions and London dispersion force induced interactions), the susceptibility of the molecule to radical attack at sites other than the point of unsaturation, and the monomer's ability to form radical stabilizing intermediates. These traits are all defining factors with respect to the polymerization environment and potential polymerization mechanisms and should thus be accounted for in generating an understanding of the relationships that will enable successful, rational materials design.

Synthesis of monovinyl monomers with varied secondary functionality is used to elucidate the functionality characteristics most important to monomer reactivity. The ability of the functionality to induce local dipoles within the molecule potentially affects both double bond reactivity and lability of abstractable hydrogens. Molecular dipoles affect intermolecular organization and conformational preferences. The monomer's hydrogen bond donor character affects monomer organization and polymerization environment mobility. Thus, secondary functionality, through its ability to impart a wide range of electronic character and hydrogen-bonding capabilities to a monomer, significantly impacts both the chemical and physical attributes of the polymerization system and correspondingly, monomer reactivity. The aforementioned monomer attributes were varied systematically via synthesis of a number of model monomers corresponding to structure **6**. The R_2 group is held constant in these studies for a range of R_3 substituents to isolate effects associated with the secondary functionality. The intent is not to imply that the effects of the R_2 and R_3 groups are mutually exclusive, but rather to assert that maintaining the same R_2 substituent while varying the secondary functionality, R_3, provides a systematic means for gathering basic information regarding the contribution of the secondary functionality. Subsequently, additional studies that examine a series of functionalities with a different R_2 substituent are presented in the next section to assess the synergistic effect.

Variations in Secondary Functionality with an Aliphatic R_2 Substituent. Initial kinetic studies on the effect of secondary functionality were performed on a series of ethyl methacrylate, $R_1 = CH_3$, monomers with straight chain aliphatic R_2 substituents, primarily ethyl groups. A variety of R_3 groups are evaluated to

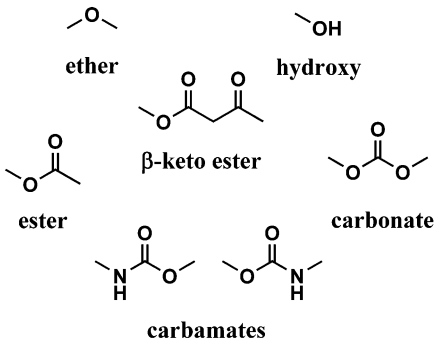


Figure 1. Structures of the secondary, R_3, functionalities evaluated.

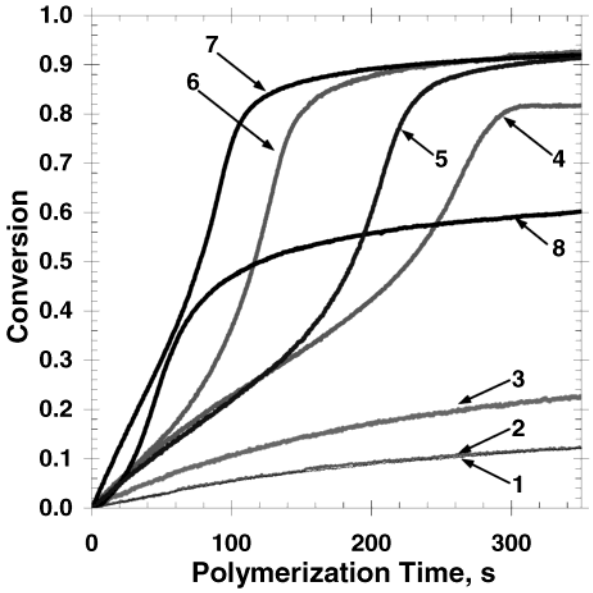


Figure 2. Effect of the secondary functionality in a series of methacrylate monomers. Ethoxy ethyl MA (**1**), *n*-butyl MA (**2**), propyl ester MA (**3**), acetoacetoxy MA (**4**), hydroxypropyl MA (**5**), ethyl OCO MA (**6**), and ethyl NCO MA (**7**) are presented. HDDMA (**8**) is also shown for reference. Polymerizations were conducted at 25 °C. Polymerization conditions: initiator concentration, 0.1 wt %; light intensity, 5 mW/cm^2.

elucidate the qualities that have the largest impact on monomer reactivity. Specifically, the functionalities studied here are: ethers, esters, β-keto esters, hydroxys, carbonates, and carbamates (both structural isomers) (Figure 1).

The steady-state polymerization kinetics of these systems and their comparison to standard mono- and divinyl polymerization systems are presented in Figure 2. The monomer structures and a quantification of their polymerization characteristics are presented in Table 3. The reactivity of these model systems was examined from several perspectives. Rate information at different conversions is used to evaluate the aspects of the polymerization that have the greatest impact on the overall cure behavior. Thus, trends in polymerization rate at low conversion, e.g., 10%, have been compared with those at later stages using the maximum polymerization rate. Additionally, an effective combination of these two rates, the cure time, was evaluated using the representative quantification of the time necessary to achieve 60% conversion.

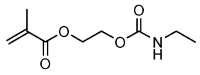
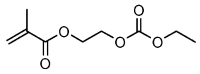
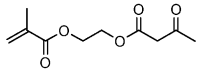
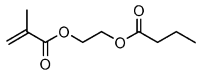
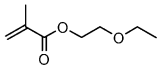
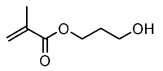
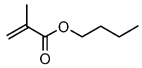
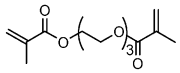
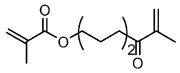
These results indicate the following trend in monomer reactivity: carbamate > carbonate > hydroxy > β-keto ester $\gg$ ester > ether and pure alkyl monomethacrylate. This trend is most visible in the overall polymerization rate as represented by the polymerization time required to achieve 60% conversion. Interestingly the β-keto ester, hydroxy, carbonate, and carbamate polymerizations behave in a nearly classical manner in which a distinct autoacceleration region is observed in the mid to high conversion range of the polymerization.[24] The β-keto ester, hydroxy, and carbonate monomers all exhibit very similar polymerization profiles at low conversions; however, the onset, duration, and magnitude of autoacceleration are affected significantly by the monomer type. The change in conversion where autoacceleration occurs, accompanied by a decrease in duration and an increase in magnitude, are also observed in linearly polymerizing systems where an increasing amount of cross-linking agent is added. This similarity, although perhaps coincidental, may be an indication of a mechanism or mechanisms that lead to cross-link formation or the formation of a termination inhibiting reactive intermediate, either of which would contribute to accelerated polymerization kinetics. The effectiveness of such a mechanism is certainly a function of monomer structure and functionality. Thus, changes in functionality traits that follow the measured reactivity trends provide evidence for mechanistic hypotheses.

The overall reaction rates of the carbamate and carbonate containing monomers are significantly higher than those of the other functional groups. Interestingly, the primary difference between these two systems is their polymerization rate prior to the onset of autoacceleration. Their kinetics following autoacceleration are quite similar, including the conversion where the maximum polymerization rate is realized.

Decker et al. evaluated a similar series of acrylate monomers (structure **6**, R_1 = H) in a 50/50 copolymerization with a polyurethane acrylate oligomer.[4] The monomers contained a branched aliphatic, isopropyl end group (R_2 = CH[CH_3]$_2$) and ether, ester, carbonate (structure **1**), and carbamate (structure **2**) secondary functionalities. Copolymerizations were conducted with 5 wt % DMPA and 500 mW/cm^2 of broadband UV illumination. Their work also indicated the high reactivity of the carbamate functionalized monomer (structure **2**) compared with the other functionalities. However, the relative reactivities, as defined by $R_{p,max}$ (s^{-1}), were substantially different from those of the methacrylate homopolymerizations of this work. Their results indicate a trend of carbamate $\gg$ ether > carbonate > ester, where $R_{p,max}$(carbamate) = $5R_{p,max}$(ether) = $7.5R_{p,max}$(carbonate) = $10R_{p,max}$(ester). The differences between the two studies may be indicative of the change in vinyl functionality, or of the strong interrelationship between R_2 and R_3, i.e., changing from an ethyl to an isopropyl end group impacts the kinetics and potentially the mechanisms through which the polymerization proceeds. Unfortunately, this acrylate monomer series was only evaluated in copolymerization.[4] Thus, the system's chemical, physical, and electronic properties and correspondingly the polymerization kinetics and mechanisms are further convoluted by the comonomer's presence, making it impossible to draw any firm conclusions without further investigation.

Carbamate Isomers and Temperature Effects. Given the high reactivity of the carbamate methacrylate, and the asymmetric nature of the carbamate, the effect of changing the orientation of the carbamate was also evaluated. Thus, the ethyl isocyanate based mono-

Table 3. Performance Analysis of Non-Aromatic Methacrylate Monomers at 25 °C[a]

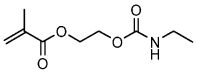
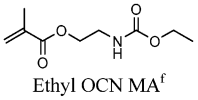
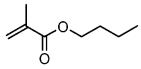
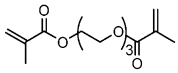
Monomer	$[DB]_0$[a] (mol/L)	T_m (°C)	$R_{p,10\%Conv}$[b] (1/s)	$R_{p,Max}$[c] (1/s)	X at $R_{p,Max}$ (%)	X_{Max}[d] (%)	Time to X=60 % (s)
 Ethyl NCO MA	5.5	28	0.006	0.012	64	94	87
 Ethyl OCO MA	5.3	< 25	0.003	0.0114	65	95	130
 Acetoacetoxy MA	4.9	< 25	0.0023	0.006	68	82	250
 Propyl Ester MA	5.3	< 25	0.0007	0.001[e]	—[e]	27	N/A
 Ethoxy Ethyl MA	6.1	< 25	0.0002	0.0005[e]	—[e]	15	N/A
 Hydroxy Propyl MA	7.4	< 25	0.002	0.010	67	94	200
 n-Butyl MA	6.3	< 25	0.0002	0.0006[e]	—[e]	16	N/A
 TEGDMA	7.4	< 25	0.0056	0.014	29	72	119
 HDDMA	7.8	< 25	0.006	0.0084	21	58	N/A

[a] Polymerization conditions: initiator, 0.1 wt % DMPA; light intensity, 5 mW/cm^2; film thickness, 15−20 μm. Key: (a) initial double bond concentration; (b) normalized measure of "initial" polymerization rate: R_p/double bond concentration at 10% conversion; (c) normalized measure of the maximum polymerization rate, $R_{p,max}$/double bond concentration at $R_{p,max}$; (d) maximum conversion reached after 600 s of irradiation at ambient conditions; (e) constant R_p over the initial 100 s of polymerization time, with no observed autoacceleration.

mer from above, ethyl NCO MA, and its structural isomer formed from isocyanatoethyl methacrylate and ethanol, ethyl OCN MA, were synthesized and evaluated. These monomers differ significantly in melting point ($T_{m,EtNCO\ MA} \approx 28$ °C, $T_{m,EtOCN\ MA} \approx 43$ °C, Table 4). This melting point difference is likely a consequence of differences in their hydrogen-bonding interactions. One method for preliminarily evaluating the extent of hydrogen bonding is to examine changes in the monomer's vibrational spectra as a function of monomer structure. The vibrational transitions of primary interest are those associated with the strong hydrogen bond donor and acceptors, specifically, the NH stretching mode (3200−3500 cm^{-1}), the C═O stretching mode (1620−1760 cm^{-1}), and the NH in-plane bending mode, often referred to as the amide II mode (1530−1570 cm^{-1}). These transitions, especially the NH stretch, are known to be highly sensitive to changes in hydrogen bonding. As a result, information regarding the effect of the carbamate orientation on hydrogen-bonding characteristics is obtained from the relative vibrational frequencies of the moieties involved in the hydrogen bonding. The role of the urethane and ester alkoxyl oxygens (1100−1300 cm^{-1}) in the hydrogen-bonding process should also be acknowledged; however, their efficacy in this preliminary evaluation of hydrogen bonding is limited in comparison to that of the aforementioned regions.

It is important to note that each of these regions does not contain a single peak that expresses only the vibrational transition of interest. For example, the NH stretching region contains separate contributions from non-hydrogen-bonded or monomeric NH groups, singly hydrogen-bonded or dimer NH groups, and multiply hydrogen-bonded or chainlike bonded NH groups, as well as the nonbonded species present on chain ends.[25,26] These various contributions complicate any attempt at quantification, as molar absorptivities are a strong function of the extent and strength of the hydrogen bond, with an increase in hydrogen bonding accompanied by a decrease in frequency and an increase in absorptivity. To complicate the analysis further, combination or two-phonon bands and overtones also appear in this region. Thus, no attempt to quantify the concentrations of free and hydrogen bonded NH species will be made here, although such evaluation is certainly worthwhile for future exploration. Alternatively, qualitative variations in the strength and/or extent of hydrogen-bonding interactions are explored via second derivative analysis of each monomer's infrared spec-

Table 4. Performance Analysis of Non-aromatic Methacrylate Monomers as a Function of Temperature (25/50/67/80 °C)[a]

Monomer	$[DB]_0$ (mol/L)	T_m (°C)	T_p[g] (°C)	$R_{p,10\%Conv}$ (1/s)	$R_{p,Max}$ (1/s)	X at $R_{p,Max}$ (%)	X_{Max} (%)	Time to X=60 % (s)
 Ethyl NCO MA	5.5	28	25	0.006	0.012	64	94	87
			50	0.007	0.017	77	100	83
			67	0.007	0.015	67	100	79
 Ethyl OCN MA[f]	5.5	43	50	0.009	0.024	61	100	56
			67	0.009	0.025	76	100	58
			80	0.009	0.028	79	100	60
 n-Butyl MA	6.3	< 25	25	0.0002	0.0006[e,h]	—[e]	16	N/A
			67	0.0005	0.0005[e]	—[e]	37	N/A
 TEGDMA	7.4	< 25	25	0.0056	0.014	29	72	119
			67	0.012	0.028	35	78	43

[a] Polymerization conditions: initiator, 0.1 wt % DMPA; light intensity, 5 mW/cm^2; film thickness, 15−20 μm. Key: (e) constant R_p over the initial 100 s of polymerization time, no observed autoacceleration; (f) ethyl OCN MA was not polymerized at 25 °C due to its high melting point, 43 °C, and rapid recrystallization behavior; (g) polymerization temperature; (h) the maximum polymerization rate for *n*-butyl MA was achieved at <5% double bond conversion.

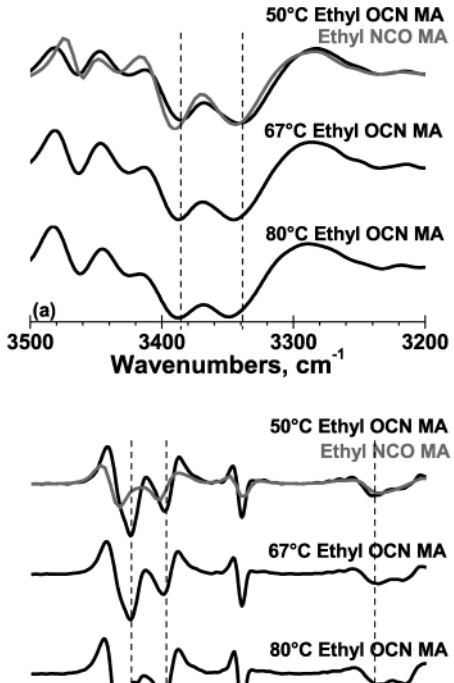


Figure 3. Effect of carbamate orientation and temperature on the hydrogen-bonding characteristics of two ethyl carbamate ethyl methacrylate structural isomers as determined by second derivative analysis of their infrared absorption spectra. Comparative spectra of ethyl OCN MA (black line) and ethyl NCO MA (gray line) at 50 °C and of ethyl OCN MA at 50, 67, and 80 °C are presented. The NH (3200−3500 cm^{-1}) stretching region is presented in part a. The C═O (1620−1760 cm^{-1}) stretching and NH in-plane bending (1530−1570 cm^{-1}) regions are presented in part b.

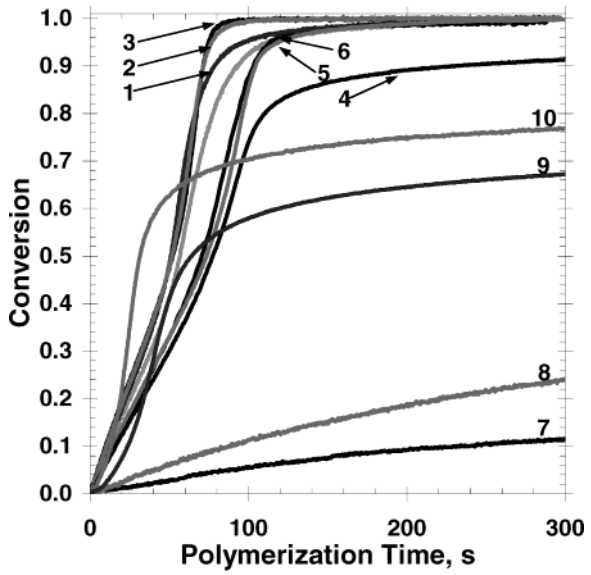
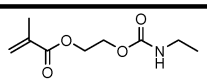
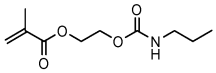
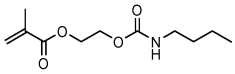
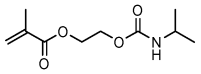
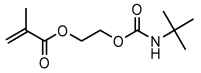
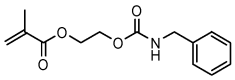
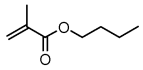
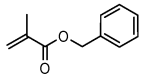
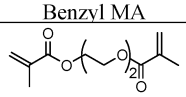
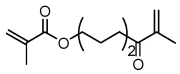
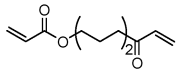


Figure 4. Effect of carbamate orientation on the polymerization kinetics of two ethyl carbamate ethyl methacrylate monomers: ethyl OCN MA at 50 (**1**), 67 (**2**), and 80 (**3**) °C and ethyl NCO MA at 25 (**4**), 50 (**5**), and 67 (**6**) °C. Conversion vs time information has also been presented for the polymerization of *n*-butyl MA at 25 (**7**) and 67 (**8**) °C and TEGDMA at 25 °C (**9**) and 50 °C (**10**). Polymerization conditions: initiator concentration, 0.1 wt %; light intensity, 5 mW/cm^2.

trum. Second derivative spectra are useful for determining locations of convoluted peaks such as those in the NH and C═O stretching regions. Comparative spectra at 50 °C, a temperature above the T_m of both monomers, are presented in Figure 3. Absorbance bands in both the NH and C═O stretching regions are shifted to a higher frequency when the carbamate orientation is changed from ethyl OCN to ethyl NCO. These relative NH and C═O stretching absorbance band locations confirm a greater extent or higher strength of hydrogen bonding in the higher melting, ethyl OCN MA, monomer. Additional confirmation is found in the relative location of the NH in-plane bending absorbance peak (Figure 3b). In this region, a shift to higher frequency indicates an increase in either the strength or extent of hydrogen bonding.

Kinetic studies of these monomers were performed at various temperatures above each isomer's T_m (Figure 4). Tri(ethylene glycol) dimethacrylate (TEGDMA) and

Table 5. Performance Analysis of Carbamate Ethyl Methacrylate Monomers at 25/67 °C[a]

Monomer	$[DB]_0$ (mol/L)	T_m (°C)	$R_{p,10\%Conv}$ (1/s)	$R_{p,Max}$ (1/s)	X at $R_{p,Max}$ (%)	X_{Max} (%)	Time to X=60 % (s)
 Ethyl NCO MA	5.5	28	0.006/ 0.007	0.012/ 0.017	64/77	94/100	87/83
 n-Propyl NCO MA	5.1	< 25[h]	0.005/ 0.005	0.015/ 0.024	64/71	95/99	91/90
 n-Butyl NCO MA	4.8	< 25[h]	0.009/ 0.011	0.014/ 0.019	64/78	95/100	65/68
 i-Propyl NCO MA	5.1	65	N/A[j]/ 0.010	N/A[j]/ 0.022	N/A[j]/61	N/A[j]/100	N/A[j]/54
 t-Butyl NCO MA	4.8	27	0.014/ 0.011	0.024/ 0.034	45/70	80/97	36/49
 Benzyl NCO MA	4.2	59	0.033/ 0.022	0.045/ 0.049	55/74	97/100	17/25
 n-Butyl MA	6.3	< 25	0.0002/ 0.0005	0.0006[e]/ 0.0005[e]	—[e]/—[e]	16/37	N/A/N/A
 Benzyl MA	5.9	< 25	0.0009/ —[i]	0.0014[e]/ —[i]	—[e]/—[i]	24/—[i]	N/A/—[i]
 DEGDMA	8.7	< 25	0.008/ 0.0175	0.012/ 0.034	22/30	61/78	487/37
 HDDMA	7.8	< 25	0.006/ 0.016	0.0084/ 0.025	21/26	58/76	N/A/53
 HDDA	8.9	< 25	0.089/ 0.114	0.126/ 0.172	28/28	82/90	9/5

[a] Polymerization conditions: initiator, 0.1 wt % DMPA; light intensity, 5 mW/cm^2; film thickness, 15−20 μm; R = CH_3. Data are presented as polymerization at 25 °C/polymerization at 67 °C. Key: (e) constant R_p over the initial 100 s of polymerization time, no observed autoacceleration; (h) melting point is between 0 and 25 °C; (i) not polymerized at this temperature; (j) isopropyl NCO MA was not polymerized at 25 °C due to its high melting points and rapid recrystallization below its melting point.

n-butyl methacrylate (*n*-butyl MA) were also polymerized at multiple temperatures for comparison. It is apparent from these results that the orientation of the carbamate functional group is an important factor in dictating the homopolymerization kinetics, as the polymerization kinetics of the structural isomers differ significantly. The 50 °C polymerization of ethyl OCN MA achieves cure rates essentially equivalent to the commonly used divinyl TEGDMA system (Table 4). Compared to TEGDMA, the onset of autoacceleration is delayed in the monovinyl carbamate system which is accompanied by essentially quantitative conversion. In contrast, the TEGDMA polymerization reaches a conversion of less than 80% after 600 s of irradiation. Also of interest are the nearly temperature independent polymerization kinetics of ethyl OCN MA and ethyl NCO MA (Figure 4). The higher reaction rate of the higher melting isomer seems to imply the importance of hydrogen bonding. Thus, one might hypothesize that a change in the hydrogen bond character of the polymerization system would lead to a corresponding change in polymerization rate. Temperature was utilized to examine this effect. As polymerization temperature is increased from 50 to 80 °C, significant changes in hydrogen bonding are observed via frequency shifts in the infrared spectra (Figure 3). This disruption of the monomer's hydrogen bonding is accompanied by minimal polymerization rate changes. One might hypothesize that the activation that typically occurs with increasing temperature counteracts the negative activation associated with decreased strength and/or extent of hydrogen bonding. However, many of the other carbamate methacrylate materials examined over the course of this work, also exhibit minimal temperature dependence. Thus, it is doubtful that these two competing effects would be that closely matched for multiple

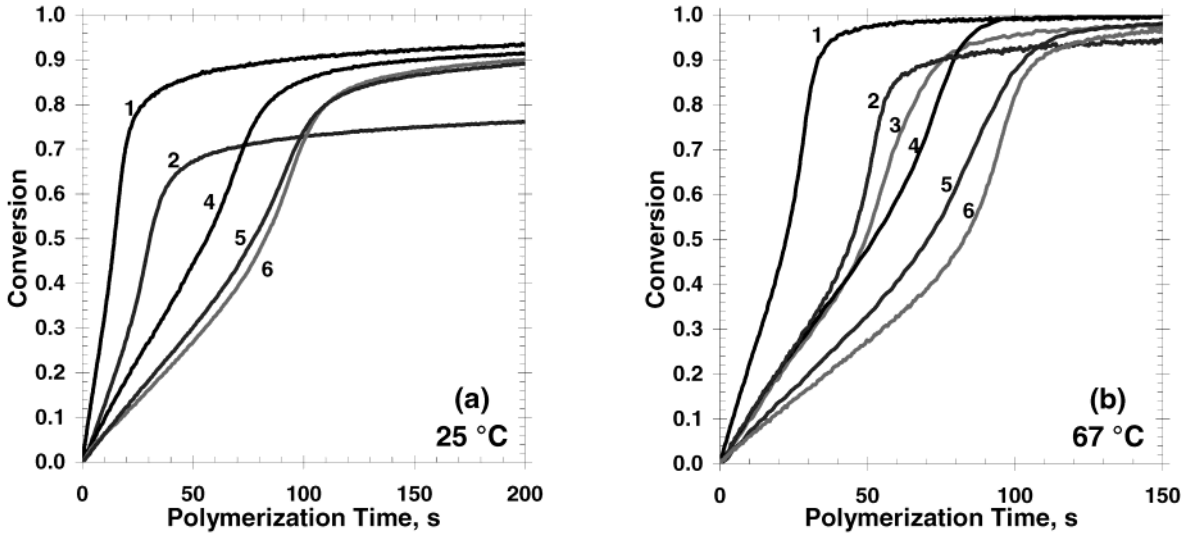


Figure 5. Effect of the structure and characteristics of the substituents adjacent to the secondary functional group. Monomers of general formula R_2 NCO MA (structure **6**, $R_1 = CH_3$, R_2 = NCO (carbamate)), where R_2 = benzyl (**1**), *tert*-butyl (**2**), isopropyl (**3**), and $-(CH_2)_nCH_3$ where $n = 3$ (**4**), 1 (**5**), and 2 (**6**) are presented. Polymerizations were conducted at (a) 25 and (b) 67 °C. Polymerization conditions: initiator concentration, 0.1 wt %; light intensity, 5 mW/cm^2.

materials, indicating that hydrogen bonding is not the sole rate enhancing factor.

End Group, R_2. The chemical, physical, and electronic characteristics of this class of monomers are also dependent on the nature of the substituent on the nonmethacrylate side of the secondary functionality, R_2. Monomer reactivity is also potentially a function of R_2. It is conceivable that characteristics such as the size, number and lability of abstractable hydrogens adjacent to the secondary functionality, and conjugation or lack thereof and its impact on radical stabilization will dramatically affect monomer reactivity. Thus, model monomers with the general structure **6**, bearing carbamate secondary functionalities, R_3, with the R_2 NCO Et MA orientation and a range of R_2 groups aimed at variations in the aforementioned traits were synthesized and evaluated. The R_2 groups examined are both aliphatic and aromatic in nature. Specifically, straight chain alkyl groups (ethyl, *n*-propyl, and *n*-butyl), two of their structural isomers (isopropyl and *tert*-butyl), and an aromatic (benzyl) were evaluated. The synthesized monomers were compared to each other and to several commercially available monovinyl and divinyl monomers. Experiments were conducted at both 25 and 67 °C. The higher temperature was chosen to perform experiments above the melting points of all of the monomers. Additionally, these studies are used to gain insight into the impact of the hydrogen-bonding extent and character on the polymerization kinetics. It should be noted that 25 °C polymerization information has been presented for several monomers with $T_m > 25$ °C, i.e., polymerized below their melting points. These materials are temporarily stable in the liquid state after heating above their melting points and cooling back to ambient conditions. The introduction of a shear force or substantial cooling below 25 °C was typically required to induce recrystallization.

The steady-state polymerization kinetics for the R_2 NCO MA monomers were evaluated. Their cure kinetics at 25 and 67 °C are presented in Figure 5, parts a and b, respectively. Additional comparisons of those polymerizations are explored via quantitative comparisons of monomer and polymerization features in Table 5. It is apparent from these results that the R_2 group plays a significant role with respect to monomer reactivity, as represented by the polymerization kinetics. Differences in polymerization rate are not inherently surprising, as changes in the R_2 group potentially affect the physical properties of a monomer significantly and, in turn, the kinetics. For example, as the R_2 group is varied, substantial differences in melting points result (Table 5); however, the trends of such physical characteristics are not intuitively obvious. Branched chain hydrocarbons tend to have lower melting points than their linear counterparts since branching tends to interfere with packing. Trends such as this, however, do not translate directly to the materials in question. In the case of the isopropyl carbamate ethyl methacrylate, the melting point is significantly higher than its linear chain analogue, *n*-propyl carbamate ethyl methacrylate, indicating more efficient packing and/or hydrogen bonding when the branched substituent is present. The bulkiness of the *tert*-butyl group is sufficient to suppress the melting point below the 65 °C observed in the isopropyl, but it also exceeds that of its linear *n*-butyl counterpart.

With ethyl methacrylate as the core and a carbamate as the secondary functional group, the polymerization time increased as the end-substituent was changed from: benzyl < *tert*-butyl < isopropyl < *n*-butyl < ethyl and *n*-propyl (Figure 5). Interestingly, this trend held at both 67 and 25 °C, where several of the monomers were polymerized below their melting points in their supercooled liquid form.

In general terms, the results seem to suggest a higher reactivity for aromatic-containing monomers over those containing branched hydrocarbons over those containing linear alkyl groups. This result is reflected in the initial rate behavior as characterized by the polymerization rate at 10% conversion, the maximum rate, and correspondingly, an appropriate combination of the two, the time to 60% conversion. These monomers have also been compared to several commercially available methacrylates (Table 5). The rapidly polymerizing aromatic carbamate is presented in Figure 6 for such a comparison. The monovinyl *tert*-butyl methacrylate, *n*-butyl

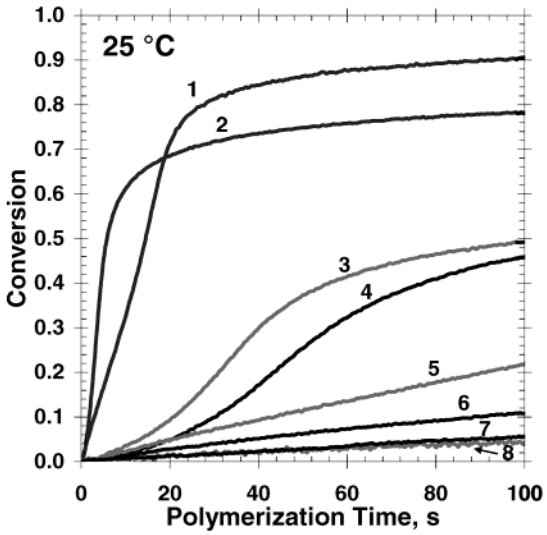


Figure 6. Comparison of benzyl (**1**) carbamate ethyl methacrylate (benzyl NCO MA) with other mono and divinyl (meth)acrylates. The other monovinyl polymerizations presented are *tert*-butyl methacrylate (**8**), *n*-butyl methacrylate (**7**), benzyl methacrylate (**6**), and hydroxypropyl methacrylate (**5**). Divinyl HDDA (**2**), HDDMA (**4**) and DEGDMA (**3**) polymerizations are also presented for reference. Polymerization conditions: temperature, 25 °C; light intensity, 5 mW/cm^2; initiator concentration, 0.1 wt %.

methacrylate, benzyl methacrylate, and hydroxypropyl methacrylate are significantly slower than all of the carbamates over the time frame of the carbamate polymerization. The presence of an aromatic moiety alone, as in benzyl methacrylate, is not sufficient to increase the polymerization rate dramatically, nor is the presence of a substituent capable of hydrogen bonding such as in the hydroxy functionalized hydroxypropyl MA.

These monomers were also compared to several commonly used divinyl (meth)acrylates. Both dimethacrylate materials presented polymerize on much longer time scales than the benzyl carbamate monomethacrylate. In fact, $R_{p,max}$ of the monovinyl benzyl NCO MA is more than five times higher than that of the divinyl HDDMA at 25 °C! Perhaps the most interesting comparison is that of the monomethacrylate performance with the diacrylate HDDA. Also worthy of note are the similarities in the initial polymerization rates, $R_{p,10\%\,conv}$, of HDDMA and the nonbranched aliphatic carbamate methacrylates and their contrast with that of benzyl NCO MA.

Variations in Hydrogen Bonding. Again, an important question to address is the impact of hydrogen bonding on apparent monomer reactivity. In fashion similar to the structural isomer evaluation in the previous section, vibrational spectroscopy is used to probe hydrogen bonding qualitatively as a function of structure in these carbamate materials, both as a function of temperature and physical state, i.e., monomer vs polymer. It is important to reiterate that the absorbances in the regions of interest are typically not represented by a single peak related to the vibrational transition of interest. Instead, each region is often comprised of a series of convoluted peaks, primarily related to the moiety of interest. As an initial assessment of the system environment across these carbamate materials, the NH stretching mode was examined. This evaluation utilized the frequency of maximum absorbance, i.e., the frequency of maximum peak height of the NH stretch, $\nu^{NH}_{peak\ max}$, as a measure of the average extent of hydrogen bonding, with lower frequencies attributed to a larger extent of hydrogen bonding.[25,26] The results for polymerizations conducted at 25 and 67 °C are presented in Table 6.

No absolute correlations of $\nu^{NH}_{peak\ max}$ with polymerization rate were obtained via this method. In general, higher rate polymerizations were skewed toward lower frequency and perhaps a larger hydrogen bonding extent. However, these results alone are not sufficient to draw any firm conclusions regarding the importance of hydrogen bonding in these polymerizations. Interestingly, there does seem to be a correlation in the direction of the peak shift during polymerization with the carbamate orientation at both 25 and 67 °C. In each case, the polymerization of the monomers synthesized from isocyanato ethyl methacrylate (R_2 OCN MA) induced a shift in the overall peak position toward lower frequencies. A shift in the opposite direction was observed in the R_2 NCO MAs. The details of the benzyl OCN MA polymerization will be presented in the next section.

Variations in Secondary Functionality, R_3, with an Aromatic R_2 Substituent. As mentioned previously, examination of how trends observed in the systems with aliphatic end (R_2) groups apply to systems with other end groups is also important to the understanding of these materials. It is clear from the results in the previous section that the end group has a significant impact on monomer reactivity in systems where all other structural characteristics remain identical. The influence of that end group on the reactivity

Table 6. Variations in $\nu^{NH}_{peak\ max}$ as a Function of R_2 and Carbamate Orientation for Polymerizations at 25 and 67 °C[a]

	25 °C			67 °C		
	$\nu^{NH}_{peak\ max}$[b]			$\nu^{NH}_{peak\ max}$[b]		
	prepolymerization, cm^{-1}	postpolymerization, cm^{-1}	$\Delta\nu$, cm^{-1}	prepolymerization, cm^{-1}	postpolymerization, cm^{-1}	$\Delta\nu$, cm^{-1}
benzyl NCO	3352	3371	19	3363	3377	14
ethyl NCO	3352	3381	29	3371	3386	15
n-propyl NCO	3377	3383	6	3386	3386	0
n-butyl NCO	3350	3385	35	3371	3390	19
isopropyl NCO	*c*	*c*	*c*	3359	3383	24
tert-butyl NCO	3371	3381	10	3379	3386	7
ethyl OCN	*c*	*c*	*c*	3364	3359	−5
benzyl OCN	3352	3344	−8	3363	3356	−7

[a] Spectra were taken and evaluated at the polymerization temperature; i.e., $\nu^{NH}_{peak\ nax}$ for polymerization conducted at 67 °C was evaluated on both monomer and polymer at 67 °C. [b] $\nu^{NH}_{peak\ max}$ is the frequency in the NH stretching region (3200−3500 cm^{-1}) where the maximum absorption is observed. [c] Isopropyl NCO MA and ethyl OCN MA were not polymerized at 25 °C due to their high melting points and their rapid recrystallization below their melting points.

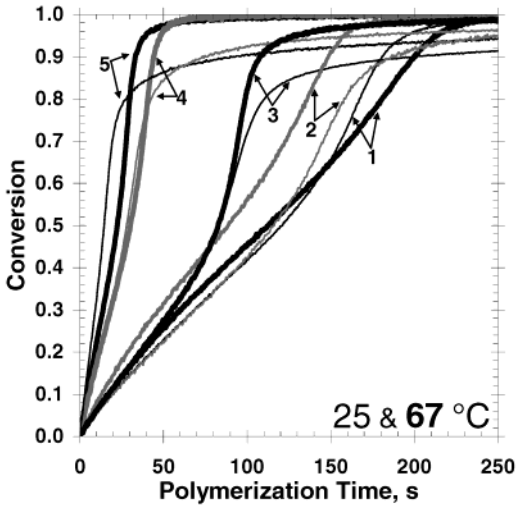


Figure 7. Effect of the secondary functionality, R_3, in a series of methacrylate monomers containing a benzyl end group. Benzyl ester MA (**1**), benzyl OCO MA (**2**), benzyl OCN MA (**4**), and benzyl NCO MA (**5**) are presented. *n*-Propyl NCO MA (**3**) is also shown to aid comparisons with systems presented previously. Polymerizations were conducted at 25 °C (thin lines) and 67 °C (thick lines). Polymerization conditions: initiator concentration, 0.1 wt %; light intensity, 5 mW/cm^2.

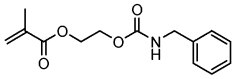
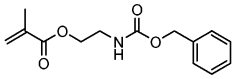
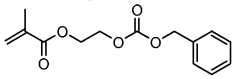
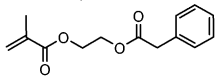
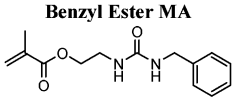
trends associated with secondary functionality changes is the focus of this line of experimentation. Given the significant kinetic differences between carbamate ethyl methacrylates with an aromatic (benzyl) vs aliphatic end groups, benzyl end groups have been chosen for further investigation.

The series of benzyl methacrylates produced similar results to those of the aliphatic systems, with reactivities of the order carbamate ≫ carbonate ≈ ester (Figure 7, Table 7). The most notable difference between this series and the aliphatics involves the carbamate structural isomers. Once again, they differ in melting points, this time with the NCO MA species having the higher of the two, an unexpected result given the bulkiness of the benzyl substituent. Like the ethyl carbamate isomers, the monomer with the higher melting point was also the one to polymerize at a higher rate. Additionally, the benzyl NCO MA and benzyl OCO MA monomers exhibit a significant difference in polymerization rate with a temperature increase from 25 to 67 °C (Figure 7). The temperature increase in the benzyl NCO MA polymerization results in a polymerization rate decrease at low conversion, whereas the same temperature increase in the benzyl OCO MA polymerization results in an increased polymerization rate at low conversion, indicating an increased hydrogen-bonding influence in the aromatic, benzyl-substituted materials. In the remainder of the polymerizations, including that of *n*-propyl NCO MA presented for reference, the primary effect of the temperature increase is an increase of the final conversion. Polymerization rates of the commercially available mono- and dimethacrylate monomers evaluated, *n*-butyl MA, *tert*-butyl MA, benzyl MA, HDDMA, and DEGDMA, are all significantly activated by a polymerization temperature increase though they are not shown here.

The high polymerization rates achieved by the carbamates certainly indicate that the quality of the hydrogen bond donor is important. If this is a key factor, a urea-functionalized material, i.e., a material with greater hydrogen-bonding potential, would also exhibit high reactivity. The melting point of the urea compound that fits into the benzyl R_3 ethyl methacrylate series, benzyl NCN MA, exceeds our "standard" high-temperature polymerization of 67 °C, an initial testament to the increase in hydrogen bonding resulting from urea functionalization. The polymerization of this monomer was conducted at 75 °C, a temperature above T_m (Figure 8). As expected, the urea functionality produced an increase in polymerization rate over the carbamates studied.

Copolymerization Behavior. Kinetic evaluations were also conducted on copolymerizations of the urea and carbamate systems with a commercially available

Table 7. Performance Analysis of Aromatic Methacrylate Monomers at 25 °C/67 °C[a]

Monomer	$[DB]_0$ (mol/L)	T_m (°C)	$R_{p,10\%Conv}$ (1/s)	$R_{p,Max}$ (1/s)	X at $R_{p,Max}$ (%)	X_{Max} (%)	Time to X=60 % (s)
 **Benzyl NCO MA**	4.2	59	0.033/ 0.022	0.045/ 0.049	55/74	97/100	17/25
 **Benzyl OCN MA**	4.2	< 25[e]	0.017/ 0.016	0.028/ 0.036	63/77	97/100	32/35
 **Benzyl OCO MA**	4.0	< 25	0.004/ 0.007	0.009/ 0.009	70/81	100/100	133/107
 **Benzyl Ester MA**	4.2	< 25	0.005/ 0.005	0.009/ 0.006	76/82	100/100	141/139
 **Benzyl NCN MA[‡]**	4.2	70	—[‡]/ 0.061[m]	—[‡]/ 0.082[m]	—[‡]/40[m]	—[‡]/93[m]	—[‡]/10[m]

[a] Polymerization conditions: initiator, 0.1 wt % DMPA; light intensity, 5 mW/cm^2; film thickness, 15−20 μm. Key: (‡) not evaluated at this temperature; (m) polymerization at 75 °C. Benzyl NCN MA was not polymerized at 25 or 67 °C due to its high melting point, 70 °C, and rapid recrystallization behavior.

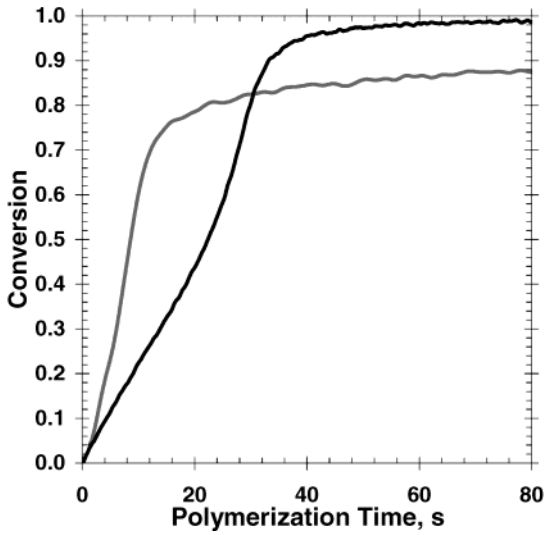


Figure 8. Comparison of a urea, benzyl NCN MA (gray line), and a similar carbamate, benzyl NCO MA (black line), functionalized methacrylate. Benzyl NCN MA and benzyl NCO MA were polymerized at 75 and 67 °C, respectively. Polymerization conditions: initiator concentration, 0.1 wt %; light intensity, 5 mW/cm^2.

monovinyl monomer, THFFMA, and divinyl monomer, HDDMA, at 25 °C. Copolymerization mixtures comprised of 50 wt % commercial monomer and 50 wt % of the synthesized species were prepared. In both scenarios, i.e., monovinyl and divinyl comonomers, the polymerization kinetics of the commercial comonomer were significantly enhanced by the addition of the carbamates and urea compounds (Figure 9). As was the case in homopolymerization, the urea-functionalized systems were superior on all fronts except for their ultimate conversions, which were less than 85% and 70% for the THFFMA and HDDMA copolymer systems, respectively.

The relationship between the carbamate structural isomers was evaluated further with copolymerization. Interestingly, in both copolymer systems, the relationship between structural isomer and maximum polymerization rate was reversed from the homopolymerization observations, i.e., $R_{p,max}$(benzyl OCN copolymerization) > $R_{p,max}$(benzyl NCO copolymerization), although their initial polymerization rates were very similar. Thus, hydrogen-bonding-induced organization is certainly affected by the introduction of a comonomer without hydrogen bond donor character. If long-range self-association via hydrogen bonding is important to the benzyl NCO MA reactivity, then copolymerization, through its ability to disrupt such organization, will affect the polymerization rate.

Discussion

Monovinyl methacrylate monomers with reactivities that surpass those of commonly used dimethacrylate monomers have been developed via systematic evaluation of a generic monomer template (structure **6**) and adaptation of desirable monomer traits based on experimental findings. A more comprehensive understanding of how structural characteristics and monomer traits influence polymerization mechanisms and network evolution was achieved by systematic structural variation. Three primary factors hypothesized as important to the advantageous polymerization characteristics observed in these systems are evaluated. Those factors, hydrogen bonding, hydrogen abstraction, and electronic effects, are introduced, and experimental findings in support or opposition to their prevalence are presented.

Hydrogen Bonding. Hydrogen bonding is important from a number of perspectives. Inter- and intramolecular hydrogen bonding affect system mobility, organization, and monomer conformation. These factors, in turn, affect polymerization rate. The impact of hydrogen bonding is evaluated via several avenues: varying the hydrogen bond donor characteristics while minimally changing other aspects of monomer composition, changing the length of the alkyl chain between the (meth)acrylate and the hydrogen bond donor, and introducing bulky end group substituents aimed at sterically disrupting hydrogen bonding.

Extensive intermolecular hydrogen bonding between a strong donor and acceptor will, at a minimum, reduce the mobility of the monomer mixture. Previous work has demonstrated the combined importance of monomer

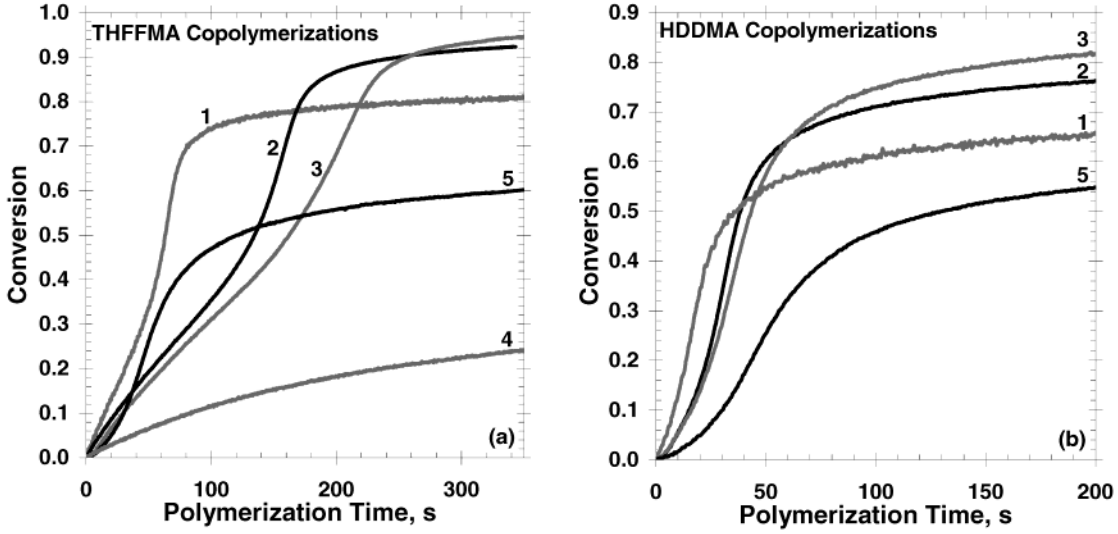


Figure 9. Copolymerization characteristics of benzyl urea and benzyl carbamate methacrylates. Copolymerizations with (a) monovinyl (THFFMA) and (b) divinyl (HDDMA) monomers were conducted. All comonomer mixtures were comprised of 50 wt % commercial monomer and 50 wt % of the synthesized species (benzyl NCN MA (**1**), benzyl OCN MA (**2**), and benzyl NCO MA (**3**)). Homopolymerizations of the commercial monomers, THFFMA (**4**) and HDDMA (**5**), are also presented for reference.

viscosity and reactivity[27] in the copolymerization of two multimethacrylate monomers with very different viscosities. Hydrogenation of each monomer and copolymerization with its reactive comonomer at varied compositions demonstrate the significant influence of monomer viscosity on the polymerization kinetics. An increase in initial viscosity restricts termination, leading to a buildup in radical concentration and to a higher polymerization rate than is achieved in a lower viscosity medium. Hydrogen bonding also affects the organization of monomer molecules. It is feasible that hydrogen bonding induces double bond alignment, thereby having a positive impact on propagation.[16]

Carbamates vs Carbonates. The comparison of carbamates to carbonates with the same end group, R_2, substitution and vinyl functionality is a starting point for hydrogen-bonding evaluation. The carbamate functional group provides strong hydrogen bond donor/acceptor character to the monomer, whereas the carbonate removes the hydrogen bond donor with minimal perturbation of the remainder of the structure. Each comparison of carbamates and carbonates with methacrylate vinyl group substitution indicated the superior reactivity of the linear carbamate containing monomers. Methacrylates with ethyl and benzyl end group substitution polymerized at 25 °C illustrate this relationship ($R_{p,max(ethyl\ NCO)} = 0.012\ s^{-1}$, $R_{p,max(ethyl\ OCO)} = 0.011\ s^{-1}$; $R_{p,max(benzyl\ NCO)} = 0.045\ s^{-1}$, $R_{p,max(benzyl\ OCO)} = 0.009\ s^{-1}$). Melting point differences are also an indication of the presence and extent of hydrogen bonding, and correspondingly, the impact of functionality on system mobility. In each carbamate/carbonate pair, the carbamate functionalized monomer has a higher melting point than its carbonate analogue (R_2 = ethyl, $T_{m,NCO}$ = 28 °C, $T_{m,OCO}$ = <25 °C; R_2 = benzyl, $T_{m,NCO}$ = 59 °C, $T_{m,OCO}$ = <25 °C).

Carbamate Orientation. The carbamate orientation is another variable used to manipulate hydrogen-bonding characteristics, and thus evaluate their effect on the polymerization kinetics. In each structural isomer pair evaluated, the hydrogen-bonding characteristics were impacted by carbamate orientation. This influence is characterized by melting point differences ($T_{m,ethyl\ NCO}$ = 28 °C, $T_{m,ethyl\ OCN}$ = 43 °C; $T_{m,benzyl\ NCO}$ = 59 °C, $T_{m,benzyl\ OCN}$ = <25 °C) and via analysis of the relative infrared absorption frequencies of the substituents known to participate in hydrogen bonding. The end group substituent also contributes to determining the isomer with the higher T_m. Much like the carbamate/carbonate methacrylate comparison, the carbamate methacrylate isomer with the higher melting point and likely the greater hydrogen-bonding strength polymerized more rapidly. This result demonstrates that it is not merely the presence of a hydrogen bond donor and acceptor pair that results in rate enhancement but the participation of that pair in hydrogen-bonding interactions that is important to monomer reactivity.

The presence of hydrogen-bonding interactions affects molecular organization via the same mechanisms that impact monomer mobility. For example, if every hydrogen bond interaction in benzyl NCO MA occurred between the NH of one monomer molecule and the carbamate carbonyl of its neighbor, then potential templating of the double bonds is envisioned. Such an alignment is advantageous with respect to radical propagation, whereas, the depressed monomer mobility will restrict termination, both of which result in a rate elevation. In contrast, organization may also be detrimental to the polymerization rate. If every carbamate NH hydrogen bonds to the methacrylic ester carbonyl, then long-range double bond alignment is not obtained.

Urea Functionality. The impact of hydrogen bonding is illustrated further via the comparison of urea and carbamate functionalized monomers. Introducing another hydrogen bond donor into the monomer structure increases the hydrogen-bonding potential further, as demonstrated by the melting point increase from 59 °C for benzyl NCO MA to 70 °C for benzyl NCN MA. The urea containing monomer polymerizes significantly faster than its carbamate analogue, another indication of the importance of hydrogen bonding.

Temperature. The minimal impact of temperature on the methacrylate polymerization rate is surprising if hydrogen bonding is *the* important factor in polymerization rate determination. Polymerizations of several carbamate methacrylate monomers with varied end group substitution were examined. Polymerization at 67 °C yields polymerization rates that mimic those at 25 °C, although polymerization at 67 °C consistently leads to higher double bond conversions. Hydrogen bonding in urethanes is highly temperature dependent, with higher temperatures resulting in a decreased extent or strength of hydrogen bonding. The temperature change from 25 to 67 °C is sufficient to affect hydrogen bonding as evidenced by FTIR evaluation of frequency shifts in the NH stretching region with increased temperature. Shifts in the overall NH stretching peak maximum of up to 20 cm^{-1} (Table 6) were obtained over the 42 °C temperature change. However, polymerization over this temperature range and varied hydrogen-bonding environment only minimally affects polymerization rate. These results illustrate that, although the impact of hydrogen bonding on system mobility and organization may lead to methacrylate polymerization rate enhancements, it is not the only feature of significant import.

Copolymerization. The effect of system mobility change was examined further via copolymerization experiments. Copolymerizations of the two benzyl carbamate structural isomers with two monomers without hydrogen bond donor character (HDDMA and THFFMA) were examined. Such comonomer mixtures disrupt hydrogen bonding, and thus provide insight into the contribution of mobility to apparent monomer reactivity. The relative polymerization rates of the two benzyl carbamate structural isomers are reversed from those observed during homopolymerization both at 26 and 67 °C. This result illustrates the significant impact of hydrogen bond induced mobility restrictions or templating on polymerization rate.

Summary: Hydrogen Bonding. These results demonstrate that hydrogen bonding has a pronounced effect on the polymerization kinetics of monovinyl monomers. However, results including the minimal temperature dependence of the carbamate methacrylate illustrate that, although important, hydrogen bonding is not the only factor critical to polymerization rate and network structure determination in these monomers.

Hydrogen Abstraction. Hydrogen abstraction is another mechanism hypothesized to be responsible for the advantageous polymerization characteristics exhibited by many of the monovinyl monomers examined in this work, although it was not directly evaluated here. Many of the monovinyl monomers evaluated by our

group,[19,28,29] as well as those examined by Decker et al.,[2−5,8,11] produce cross-linked polymer networks despite their monovinyl nature. It is difficult to imagine any possible mechanism for cross-link formation that does not involve abstraction. For example, abstraction from the monomer or polymer side chain results in branching. Subsequent termination of those branched segments via combination results in cross-link formation. Thus, the mechanism of cross-link formation, as well as the characteristics that lead to high polymerization rates, are of interest, be they mutually exclusive or complementary effects, and should be explored further.

Electronic Effects. The electronic characteristics of these monovinyl monomers are thought to play a significant role in determining reactivity. Monomer dipole−dipole interactions affect organization and system mobility as addressed in the discussion of the strong dipole−dipole interactions of hydrogen-bonded species. Additionally, intra- and intermolecular interactions potentially affect factors such as double bond reactivity and hydrogen lability and, correspondingly, the reactivity and stability of the active species formed after reaction at those sites.

Every aspect of the monomer structure contributes to the electronic structure of the monomer and thus, to the reactivity and network evolution. Specifically, features of importance include: the nature of the double bond, characteristics of the secondary functionality, and the characteristics of the end group substituent. It is difficult to separate the impact of these aspects of monomer structure due to the extent of their interdependence. Thus, their impact on the polymerization characteristics are discussed both individually and in combination.

Functional Group, R_2, Contributions: Methacrylates with Ethyl End Group, R_3, Substitution. The incorporation of secondary, nonvinyl functionality into the monomer structure is the primary variable for manipulation of the monomer's electronic character. The electron withdrawing characteristics of the secondary functional group are thought to facilitate abstraction from the carbons adjacent to the functionality. Thus, monomers with varied secondary functionality were designed, synthesized, and evaluated to test the importance of electron withdrawing character and to ascertain those factors most important to the polymerization characteristics.

It is worthwhile to begin the discussion with the examination of various functionalities introduced onto an ethyl methacrylate core with straight chain alkyl end group substitution. Holding the vinyl type and end group substitution constant enables evaluation of the impact of the secondary functionality. Additionally, the use of a straight chain alkyl end group facilitates functional group characterization with minimal interference due to end group contributions.

As a baseline, *n*-butyl methacrylate, a monomer that forms linear polymers, was used as an example of a polymerization in the absence of a secondary functionality. Incorporation of an ether substituent, Ethoxy ethyl MA, had little effect on the polymerization behavior at low conversions (Figure 2), and the polymer formed is still linear. Several other functional groups with greater electron withdrawing capabilities were also examined. The results for this series of ethyl methacrylate based monomers indicate secondary functionality reactivity in the following order: carbamate > carbonate > hydroxy > β-keto ester ≫ ester > ether and pure alkyl substitution.

The observed trend does not specifically confirm the importance of an abstraction mechanism that is dependent on secondary functionality characteristics. It does indicate that the characteristics of the secondary functionality impact polymerization rate dramatically. Interestingly, the hydrogens in the α position of a β-keto ester are known to be very acidic compared to those adjacent to the other functional groups evaluated. It was anticipated that this structure would also contribute to a very abstractable hydrogen at the α position, due to the available resonance stabilization for a radical at that position. However, the β-keto ester containing monomer, acetoacetoxy ethyl MA, is not among the most reactive.

Among the ethyl-substituted methacrylate monomers evaluated, the carbamate and carbonate monomers were the most impressive in terms of reactivity. The maximum polymerization rates of ethyl NCO MA and ethyl OCO MA are very similar, but the initial polymerization rate of the carbamate monomer is a factor of 2 higher, possibly a result of its hydrogen-bonding character.

These results demonstrate the impact of functionality on monomethacrylate polymerization. The use of the ethyl end group substituent provides the clearest evaluation of effects primarily due to the functional group. The introduction of secondary functionality, in addition to changing the electronic characteristics of the monomer, also affects monomer rigidity, which affects mobility, and thus potentially polymerization rate.

Effect of End Group, R_3, Substitution: Carbamate Methacrylates with Varied End Group Substitution. If hydrogen abstraction facilitated by the electron-withdrawing characteristics is important, then end group substitution is also crucial to monomer reactivity. The type of hydrogens present on the carbon adjacent to the secondary functionality, one possible site for abstraction, is a critical factor. For example, in general, tertiary hydrogens are more abstractable than secondary, and secondary are more abstractable than primary, which are more abstractable than a methyl hydrogen. Thus, holding the secondary functional group constant while varying the end group functionality provides a means for evaluation of rate enhancing end groups and, correspondingly, the importance of synergism between the end group and secondary functionality. Exploration of these effects was accomplished via evaluation of a series of carbamate methacrylates, R_2 NCO MA, with varied end group substitution, R_2, including both aliphatic and aromatic end groups.

Aliphatic End Group Substitution. Aliphatic groups were examined acknowledging the differences in abstractability between primary, secondary, and tertiary hydrogens. Thus, a minimal impact of alkyl chain length on abstractability was anticipated, since in each case the hydrogens on the carbon adjacent to the functionality are secondary. As expected, the difference between the ethyl and *n*-propyl-substituted monomers was minimal. However, the *n*-butyl-substituted monomer exhibited higher reactivity during the initial stage of polymerization, prior to autoacceleration, in comparison to the ethyl and *n*-propyl monomers, perhaps a result of the longer chain end and its effect on mobility. An isopropyl group was also evaluated, as it has the potential for tertiary hydrogen abstraction. This monomer has an early polymerization rate similar to the *n*-butyl-substituted monomer but with an earlier

onset of autoacceleration. The maximum polymerization rate is similar to that of its *n*-propyl counterpart. Decker et al. also report no significant difference in reactivity for a similar series of aliphatic R_2 OCN acrylates,[4] although the isopropyl-substituted system was identified as the most reactive of the systems studied containing only linear, i.e., noncyclic, functional groups.[9,11]

The last alkyl substituent evaluated in this work was the *tert*-butyl group. It was hypothesized that if hydrogen abstraction was important, that the polymerization rate of a monomer with *tert*-butyl substitution, i.e., without abstractable hydrogens on the carbon adjacent to the nonmethacrylate side of the secondary functionality, would be significantly lower than the isopropyl-substituted monomer. This hypothesis did not hold for *tert*-butyl NCO MA. The initial polymerization rate was similar to that of the isopropyl and *n*-butyl monomers while exhibiting an earlier autoacceleration onset and a higher maximum rate. Thus, the importance of abstraction from the nonmethacrylate side of the secondary functionality is not clear. It is possible, however, that the presence of the *tert*-butyl substituent would assist stabilization of a radical formed via abstraction on the other side of the functionality, thus, increasing the lability of those hydrogens.

Aromatic End Group Substitution. Benzylic hydrogens are known to be extremely labile as a result of resonance stabilization of the resulting radical by the aromatic ring. A benzyl group attached to the electron-withdrawing carbamate functionality increases the likelihood of benzylic hydrogen abstraction further. Thus, excluding steric considerations, the benzyl end group provides an ideal environment for abstraction from the monomer backbone.

As hypothesized from an abstraction perspective, the polymerization rate of the benzyl-substituted carbamate methacrylate exceeded that of all of the aliphatic carbamate methacrylates studied (Figure 5), with a maximum polymerization rate that is a factor of 1.9 times higher than the *tert*-butyl-substituted monomer at 25 °C and 2.2 times higher than the isopropyl monomer at 67 °C. Additionally, benzyl NCO MA achieves a higher extent of conversion than all of the carbamates studied with aliphatic end group substitution at 25 °C.

Functional Group, R_2, Contributions: Methacrylates with Aromatic End Group, R_3, Substitution. Aryl end group substitution has a substantial effect on the carbamate methacrylate polymerization kinetics. The combination of the carbonate and aromatic substitution increased monomer reactivity by almost an order of magnitude over comparable aliphatic polymerizations. The synergistic effect also impacts the functional group reactivity trends obtained from monomethacrylates with aliphatic substitution. Thus, the effect of functional group characteristics was also examined in a series of monomethacrylates with benzyl substitution.

Benzyl substitution affects the magnitude of the difference between the polymerization rates of the various secondary functionalities, but not the order of reactivity, i.e., carbamate $\gg$ carbonate $>$ ester. It should be noted that the relative reactivity of the carbamate isomers is reversed from the ethyl-substituted scenario, but the melting point differences are also reversed. Interestingly, the benzyl carbonate and benzyl ester are very similar in reactivity, with their main difference involving the conversion at which autoacceleration is initiated. This comparison is very different than that observed for the ethyl-substituted methacrylates. A benzyl-substituted urea functionality was also evaluated. This monomer exhibited the highest reactivity of any monomer with benzyl substitution and correspondingly the highest reactivity of any monomer presented here.

Conclusions

A number of monovinyl monomers that incorporate a secondary, nonvinyl functionality into the monomer structure have demonstrated high reactivity and unique material properties. A more comprehensive understanding of how structural characteristics and monomer traits influence the polymerization mechanisms and network evolution in these monomers was obtained. The three factors hypothesized to be important to the advantageous polymerization characteristics observed in these systems are hydrogen bonding, hydrogen abstraction, and the electronic characteristics of the monomer. A discussion of the mechanisms hypothesized as important in these systems and the experimental findings that support or introduce doubt into the basic principles on which those hypotheses are based was presented. Variations in the nature of the aforementioned characteristics were achieved primarily via changes in monomer secondary functionality and end group substitution.

The experimental evaluations presented demonstrate that each of these mechanisms contributes to monomer reactivity. The monomer reactivity is impacted significantly by the electron-withdrawing and resonance stabilization capabilities of both the secondary functionality and the end group substituent and the ability of the monomer to participate in hydrogen-bonding interactions. These factors also potentially affect the propensity for hydrogen abstraction, the reactivity of a radical formed via abstraction, and the mobility characteristics of the polymerization environment. The combination of these leads to enhanced polymerization kinetics, rivaling those of multivinyl systems.

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Supporting Information Available: Text giving monomer synthesis and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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