Deconvoluting the Impact of Intermolecular and Intramolecular Interactions on the Polymerization Kinetics of Ultrarapid Mono(meth)acrylates

Harini Kilambi,[†] Jeffrey W. Stansbury,[†,‡] and Christopher N. Bowman*[,†,‡]

Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309-0424, and University of Colorado School of Dentistry, Aurora, Colorado 80045-0508

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ABSTRACT: Polymerization studies in the presence of extensive amounts of solvent are used here to deconvolute the effects of intermolecular interactions such as bulk medium polarity, $\pi-\pi$ stacking, and hydrogen bonding and characterize the contribution of intramolecular conformational effects to monomer reactivity. For that purpose the solution polymerization kinetics of various monomers in the presence of 95 wt % 1, 4-dioxane were measured and compared to bulk polymerization kinetics. The studies revealed that traditional aliphatic acrylates like hexyl acrylate exhibit approximately 2−3-fold reduction upon dilution. Monomers characterized by only hydrogen-bonding features such as hydroxyethyl acrylate exhibit an 8−12-fold reduction upon dilution. Monomers possessing only aromatic ring stacking interactions such as phenyl acrylate exhibit approximately a 5−10-fold reduction upon dilution under similar conditions. Even at a concentration of 5 wt % monomer in 1,4-dioxane, there were approximately 2−5-fold differences in reactivity observed between various acrylates. These reactivity differences between various acrylates, which exist even upon extensive dilution, were inferred to arise solely from intramolecular interactions. The contribution of intramolecular interactions for various monomers was decoupled from the bulk effects, and the impact of various functionalities upon the reactivity of acrylate monomers was quantitatively estimated.

Introduction

Photopolymerization offers multiple advantages for rapid polymer formation including spatial and temporal control, solventless polymerizations, and energy efficiency. Hence, it is a popular approach for polymer formation in a wide variety of applications including, stereolithography, coatings, dental materials, contact lenses, adhesives, etc.[1−11] Unfortunately, it also suffers from various limitations including residual unsaturation responsible for monomer leaching, discoloration of the cured polymer due to the presence of residual photoinitiator, and oxygen inhibition, which affects the polymerization performance and polymer properties.

Recently, however, certain novel (meth)acrylates have been developed which exhibit enhanced polymerization kinetics rivaling those of traditional multivinylic acrylates while also achieving nearly quantitative double bond conversion.[12−15] These novel (meth)acrylates are characterized by secondary functionalities such as carbonates, carbamates, urea, cyclic carbonates, oxazolidones, cyclic acetals, and aromatic rings. The addition of the secondary functionality leads to dramatic enhancements in photopolymerization kinetics of these monomers. Owing to their enhanced polymerization properties, these materials show excellent promise as reactive diluents. However, the mechanism(s) behind their enhanced polymerization are not well understood.

Several theories have been offered to explain the enhanced kinetics of this class of novel monomers including hydrogen abstraction, hydrogen bonding, and molecular dipole. The hydrogen abstraction theory focuses on hydrogen abstraction as a means for leading to cross-linking and subsequently suppressed termination kinetics, which would lead to increased polymerization rates.[16]

Others have explored the impact of hydrogen bonding on enhanced monomer reactivity.[17−19] Hydrogen bonding causes an increased viscosity of the system, resulting in mobility restrictions inhibiting termination reactions. Suppression of termination reactions leads to a higher radical concentration and, hence, greater polymerization rate. Also, it has been hypothesized that intermolecular hydrogen bonding between monomers forms a noncovalent linkage between monomers, causing them to behave similar to multifunctional monomers and, hence, exhibit increased reactivity.

Alternatively, Jansen and co-workers[20,21] have theorized that for molecules with a high dipole moment the overall medium polarity contributes to the enhanced polymerization kinetics. Recent work has demonstrated that the correlation of molecular dipole to monomer reactivity does not hold universally for all the (meth)acrylate systems, and the molecular dipole moment does not appear to be the primary factor causing enhanced monomer reactivity in at least some of these monomers.[22] In addition to the existing theories, we further hypothesize that the presence of extensive conjugation and aromatic rings in these (meth)acrylic monomers increases the viscosity of the system, suppressing termination and improving the polymerization rate.

The studies described herein focus on deconvoluting bulk, intermolecular effects such as overall medium polarity, hydrogen bonding, and aromatic, cyclic, and heteroatomic stacking interactions from the contribution of intramolecular effects on monomer reactivity. Further, the study also attempts to quantify the relative contributions of bulk intermolecular interactions such as hydrogen bonding and the aromatic and heteroatomic stacking in monomers.

* To whom correspondence should be addressed.
[†] University of Colorado.
[‡] University of Colorado School of Dentistry.

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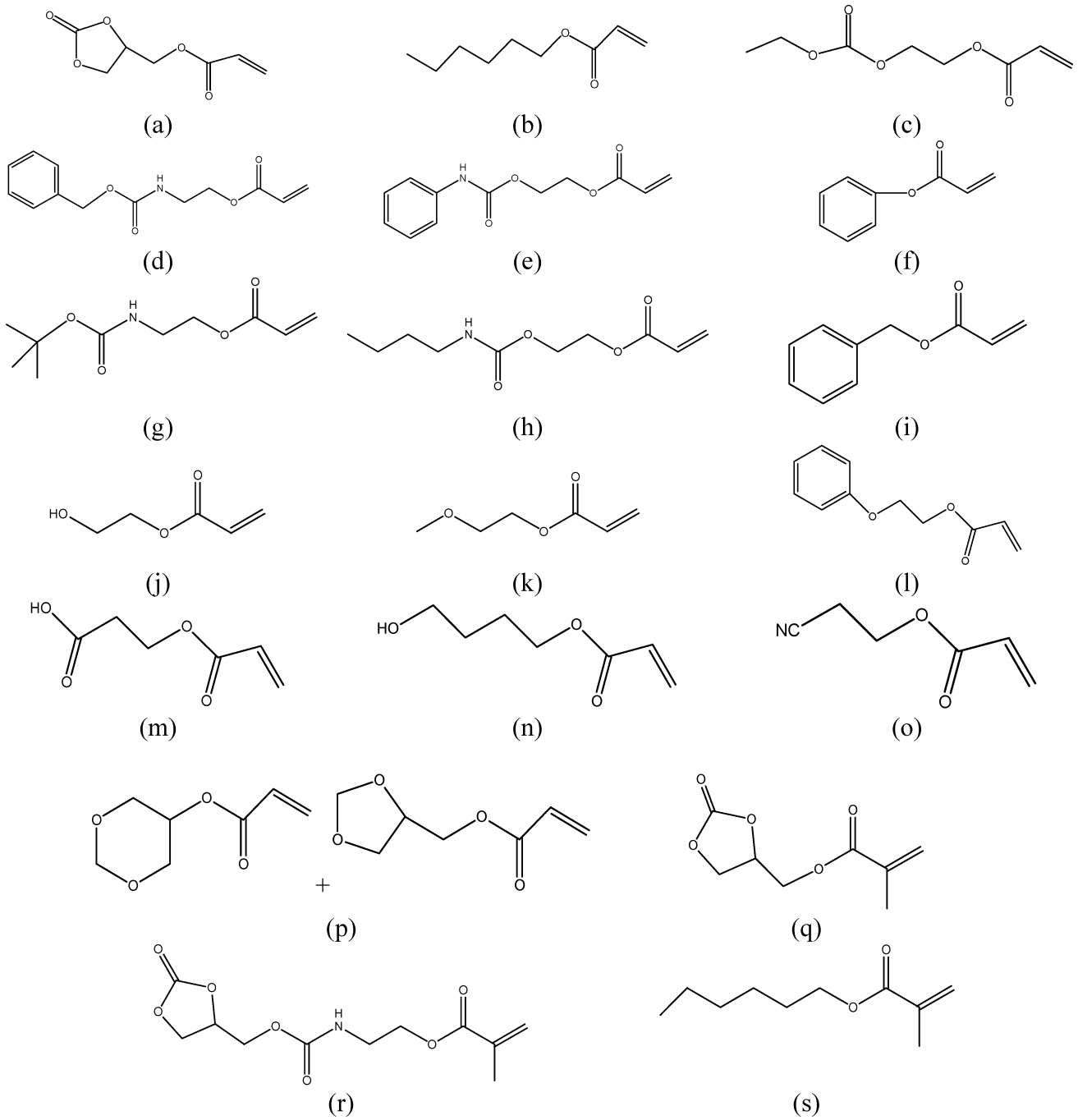

Figure 1. Structures of the monomers used in the study: (a) cyclic carbonate acrylate, (b) hexyl acrylate, (c) ethyl linear carbonate acrylate, (d) benzyl carbamate ethyl acrylate, (e) phenyl carbamate ethyl acrylate, (f) phenyl acrylate, (g) *tert*-butyl OCN acrylate, (h) *n*-butyl carbamate ethyl acrylate, (i) benzyl acrylate, (j) hydroxyethyl acrylate, (k) methoxyethyl acrylate, (l) phenoxyethyl acrylate, (m) carboxyethyl acrylate, (n) hydroxyl butyl acrylate, (o) cyanoethyl acrylate, (p) 1:1 mixture of 5-membered and 6-membered cyclic acetal acrylates, (q) cyclic carbonate methacrylate, (r) cyclic carbamate carbonate methacrylate, and (s) hexyl methacrylate.

Experimental Section

Materials. Cyclic carbonate (meth)acrylate was prepared by the reaction of 4-hydroxymethyl-1,3-dioxolanone (Huntsman, Salt Lake City, UT), with (meth)acryloyl chloride (Aldrich Chemicals, Milwaukee, WI) in the presence of triethylamine.[22] Ethyl linear carbonate acrylate was prepared by reaction of ethyl chloroformate with hydroxylethyl acrylate (Aldrich Chemicals, Milwaukee, WI). Phenyl carbamate ethyl (meth)acrylate was prepared by a reaction of phenyl isocyanate (Aldrich Chemicals, Milwaukee, WI) with hydroxylethyl (meth)acrylate (Aldrich Chemicals, Milwaukee, WI).[14] Similarly, other carbamate acrylates were also prepared by the reaction of the corresponding isocyanates with hydroxyethyl acrylate (Aldrich Chemicals, Milwaukee, WI). Cyclic carbonate carbamate acrylate was prepared by the reaction of 4-hydroxymethyl-1,3-dioxolanone (Huntsman, Salt Lake City, UT), with 2-isocyanatoethyl methacrylate (Aldrich Chemicals, Milwaukee, WI).[23] Cyclic acetal acrylates were synthesized by the reaction of 5-ethyl-1,3-dioxane-5-methanol (Aldrich Chemicals, Milwaukee, WI) with acryloyl chloride in the presence of triethylamine. The monomers, hexyl acrylate, methoxyethyl acrylate, hydroxyethyl acrylate, 4-hydroxybutyl acrylate, carboxyethyl acrylate, phenoxyethyl acrylate, *n*-butylcarbamate acrylate, and lauryl methacrylate, were purchased from Aldrich Chemicals (Milwaukee, WI) and used as received. The monomers, phenyl acrylate, benzyl acrylate, and cyanoethyl acrylate, were purchased from Polysciences (Warrington, PA) and used as received. The structures of all the monomers used in the study are depicted in Figure 1.

Table 1. Comparison of Maximum Rates and Time Taken To React from 10% to 50% Conversion for Various Acrylates Both in Bulk and at High Dilution[a]

monomer	max rate in bulk (s^{-1})	max rate at 5 wt % dilution (s^{-1})	time to react from 10−50% conversion in bulk (s)	time to react from 10−50% conversion in dilution (s)	ratios of av rates from 10% to 50% conversion (bulk/5 wt % dilution)
cyclic carbonate acrylate	0.28 ± 0.03	0.045 ± 0.003	1.46 ± 0.03	9 ± 0.4	6.2 ± 0.3
hexyl acrylate	0.02 ± 0.00	0.014 ± 0.001	18.6 ± 0.3	46.8 ± 3.5	2.5 ± 0.2
phenyl carbamate ethyl acrylate	1.3 ± 0.0	0.027 ± 0.003	0.33 ± 0.03	15.8 ± 0.3	48 ± 4
hydroxyethyl acrylate	0.32 ± 0.02	0.027 ± 0.003	1.8 ± 0.1	16.5 ± 0.5	9.2 ± 0.6
4-hydroxybutyl acrylate	0.19 ± 0.01	0.02 ± 0.00	2.2 ± 0.0	22.1 ± 0.6	10 ± 0.3
methoxyethyl acrylate	0.06 ± 0.01	0.025 ± 0.002	8.3 ± 0.1	21.7 ± 0.6	2.6 ± 0.1
ethyl linear carbonate ethyl acrylate	0.24 ± 0.01	0.028 ± 0.003	1.9 ± 0.0	18.4 ± 0.8	9.7 ± 0.4
tert-butyl carbamate ethyl acrylate	0.28 ± 0.02	0.027 ± 0.002	1.8 ± 0.0	19.5 ± 0.5	10.8 ± 0.3
benzyl carbamate ethyl acrylate	0.45 ± 0.04	0.026 ± 0.004	9.5 ± 0.0	15.8 ± 0.8	16.7 ± 0.9
n-butyl carbamate ethyl acrylate	0.38 ± 0.02	0.027 ± 0.001	1.1 ± 0.0	17.2 ± 0.4	15.6 ± 0.4
benzyl acrylate	0.09 ± 0.01	0.021 ± 0.003	4.7 ± 0.1	28.5 ± 1.4	6.1 ± 0.3
phenyl acrylate	0.23 ± 0.01	0.027 ± 0.004	2.5 ± 0.0	23.4 ± 1.2	9.4 ± 0.5
phenoxyethyl acrylate	0.25 ± 0.02	0.021 ± 0.001	1.8 ± 0.0	24.0 ± 1.2	13.3 ± 0.7
cylic acetal acrylate	0.23 ± 0.01	0.020 ± 0.003	2.0 ± 0.0	26.0 ± 0.8	13.0 ± 0.4
cyanoethyl acrylate	0.24 ± 0.01	0.029 ± 0.002	1.8 ± 0.0	15.0 ± 0.4	8.3 ± 0.2
carboxyethyl acrylate	0.38 ± 0.02	0.028 ± 0.002	1.1 ± 0.0	15.6 ± 0.6	14.2 ± 0.6

[a] Polymerization conditions: light intensity = 10 mW/cm^2, initiator concentration = 0.5 wt % with respect to the overall solution. Solvent is 1,4-dioxane. The polymerization rates are averaged from 10 to 50% as these acrylates all achieve nearly complete conversions, and the acrylate conversion as a function of time is approximately linear in this region for these bulk polymerizations.

Methods. Fourier Transform Infrared Spectroscopy (FTIR). FTIR studies were conducted with a Nicolet 760 Magna FTIR spectrometer (Nicolet, Madison, WI).[7] Samples were laminated by placing monomer solutions between two NaCl crystals with approximate film thicknesses of 15−20 μm in a horizontal transmission apparatus and irradiated with an ultraviolet light source (Ultracure 100SS 100 W medium-pressure mercury vapor short-arc lamp, EXFO, Mississaugua, Ontario, Canada) filtered and centered at 365 nm for a duration of 10 min. Irradiation intensity was monitored using a Cole-Parmer Instruments Co. series 9811 radiometer (Vernon Hills, IL). The initiator used was 0.5 wt % of 2,2-dimethoxy-2-phenylacetophenone (DMPA) for all samples. Acrylate conversion was monitored with the C═C stretching vibration at 1630 cm^{-1} or the C═C twisting vibration at 810 cm^{-1}. The kinetics of most polymerizations were obtained at an ambient temperature of ∼25 °C. The polymerization kinetics of phenyl carbamate ethyl acrylate and benzyl carbamate acrylate in bulk were obtained at 67 °C, as they are solids at ambient temperature. Previously, it has been found that the polymerization kinetics of novel acrylates are fairly independent of temperature[14] in the range of interest. Hence, measuring the bulk kinetics of certain monomers at 67 °C does not significantly affect the conclusions drawn from our study.

Results and Discussion

Experiments were designed to deconvolute the effect of intermolecular interactions such as bulk medium polarity, aromatic and heterocyclic ring stacking, and hydrogen bonding from various intramolecular interactions such as molecular dipole and conformational effects. For this purpose, monomers were polymerized at a dilution of 5 wt % in 1, 4-dioxane as a solvent. Upon dilution, the increased viscosity effects of intermolecular hydrogen bonding and aromatic and heterocyclic ring stacking are removed. At extensive dilution in a solvent the overall medium polarity is determined primarily by the polarity of the solvent, and hence, all solutions should also have similar overall medium polarity. Finally, increased dilution leads to reduced mobility restrictions, which facilitate termination reactions and suppress autoacceleration effects. Thus, an overall reduction in polymerization kinetics is expected with dilution for all monomer systems. However, for those monomeric systems where bulk effects such as overall medium polarity, $\pi-\pi$ stacking, and hydrogen-bonding contribute to monomer reactivity, the reduction in polymerization kinetics upon dilution is expected to be higher. The relative differences in reactivity of different monomeric systems in bulk as compared to dilute solution polymerization reveal the relative contribution of the bulk effects as compared to the intramolecular conformational effects. The solvent chosen for conducting the dilution studies was 1,4-dioxane, as it possesses a low molar extinction coefficient in the region of interest (the 1600 cm^{-1} acrylate peak). Further, it is inert, nonpolar, and nonvolatile so that extent of the dilution remains constant throughout the polymerization. The average polymerization rates of all monomers studied herein, both in the presence of 1,4-dioxane as a solvent and in bulk, are presented in Table 1 and will be discussed in the subsequent sections.

Upon polymerization in the presence of 1,4-dioxane, certain reactivity trends are reversed at 5 wt % dilution relative to the bulk. It can be inferred from Table 1 that phenyl carbamate ethyl acrylate, which polymerized approximately 5-fold faster in bulk relative to cyclic carbonate acrylate, was seen to polymerize almost 2-fold more slowly in dilute solution. The polymerization kinetics of these monomers compared to hexyl acrylate as a control are presented in Figure 2. These results suggest that the faster polymerization kinetics of phenyl carbamate ethyl acrylate in bulk relative to cyclic carbonate acrylate are primarily due to hydrogen bonding and $\pi-\pi$ stacking of the phenyl ring. Through addition of large amounts of solvent, these intermolecular effects are minimized, and phenyl carbamate ethyl acrylate polymerizes more slowly than cyclic carbonate acrylate. It can be inferred from Table 1 that, while hexyl acrylate depicted only a 2.5-fold reduction, cyclic carbonate acrylate, possessing the cyclic carbonate secondary functionality capable of heteroatomic ring stacking interactions, exhibited a 6-fold reduction. Phenyl carbamate ethyl acrylate, capable of both aromatic ring stacking interactions and hydrogen bonding, had almost a 50-fold rate reduction. These results thus emphasize the contribution of bulk intermolecular interactions such as hydrogen bonding and aromatic and heteroatomic ring stacking interactions to monomer reactivity.

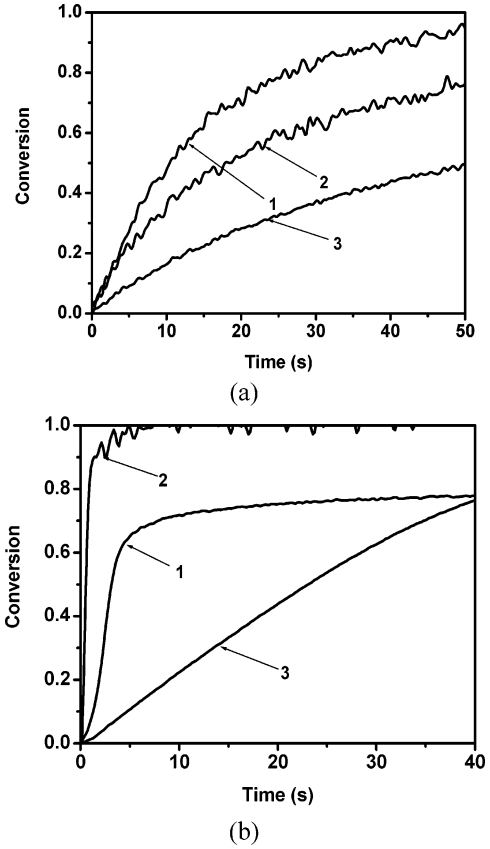

Figure 2. (a) Acrylate conversion as a function of time for monomers polymerized at 5 wt % dilution in 1,4-dioxane and (b) acrylate conversion as a function of time for monomers polymerized in bulk for (1) Cyclic carbonate acrylate, (2) phenyl carbamate ethyl acrylate, and (3) hexyl acrylate. Polymerization Conditions: Initiator Concentration = 0.5 wt % DMPA with respect to overall solution, Light Intensity = 10 mW/cm^2, 95 wt % 1, 4-dioxane as solvent. The bulk kinetics have been presented for the purposes of comparison. Phenyl carbamate ethyl acrylate was polymerized at 67 °C only in bulk. All other polymerizations were conducted at ambient temperature.

However, both of these two monomers, cyclic carbonate acrylate and phenyl carbamate ethyl acrylate, polymerize at a much faster rate relative to traditional acrylates like hexyl acrylate even at very high dilution. For instance, it can be inferred from Table 1 that even at 5 wt % monomer concentration, the average polymerization rates of cyclic carbonate acrylate and phenyl carbamate ethyl acrylate are 5-fold and 3-fold higher as compared to hexyl acrylate, respectively. These results demonstrate that the enhanced polymerization reactivity of the novel (meth)acrylates toward photopolymerization has a distinct contribution from intramolecular interactions.

Impact of Hydrogen Bonding. Hydrogen bonding generally leads to a viscosity increase that results in reduced termination and enhanced polymerization kinetics. Intermolecular hydrogen bonds frequently cause these monovinyl monomers to behave similar to multifunctional monomers and exhibit autoacceleration effects. It has been previously demonstrated by Lee et al. that for the hydroxy-functionalized monomers hydrogen bonding is a significant contribution to monomer reactivity. The experimental results presented in Table 1 also demonstrate that monomers capable of hydrogen-bonding exhibited a much greater reduction in the polymerization kinetics upon dilution as compared to monomers not capable of hydrogen bonding. Specifically, the kinetics of hydroxyethyl acrylate and methoxyethyl acrylate (a monomer similar in structure but without a hydrogen bond donor) were compared both in bulk and in the presence of excess solvent. It was demonstrated that while

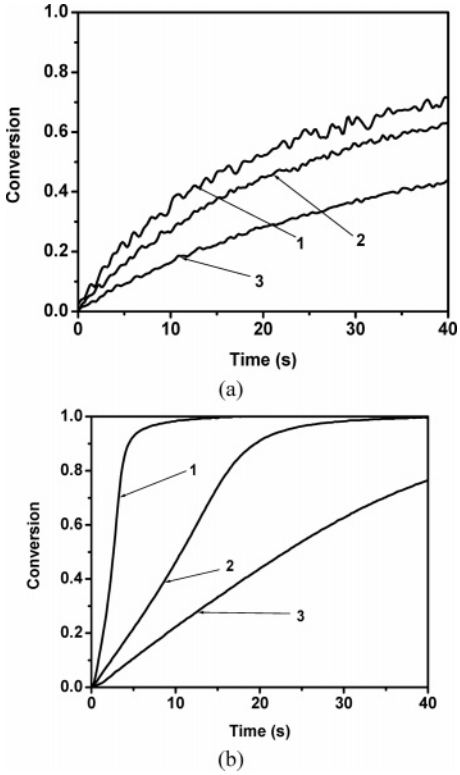

Figure 3. (a) Acrylate conversion as a function of time for monomers polymerized at 5 wt % dilution in 1,4-dioxane and (b) acrylate conversion as a function of time for monomers polymerized in bulk (1) hydroxyethyl acrylate, (2) methoxyethyl acrylate, and (3) hexyl acrylate. Polymerization conditions: initiator concentration = 0.5 wt % DMPA with respect to overall solution, light intensity = 10 mW/cm^2, temperature = 25 °C.

the kinetics of hydroxyethyl acrylate and methoxyethyl acrylate are significantly different in bulk, with hydroxyl ethyl acrylate exhibiting a 5-fold higher polymerization rate, they are very similar at high dilution with hydroxyl ethyl acrylate exhibiting only 1.3-fold increase in the polymerization rate (Figure 3). At high dilution, the effects of increased viscosity due to hydrogen bonding are eliminated, and the two structurally similar monomers, with the exception of the hydrogen-bonding potential, appear to polymerize at the similar rates of 0.027 ± 0.003 and 0.025 ± 0.002.

It can be inferred from Table 1 that the monomers capable of hydrogen bonding such as hydroxyethyl acrylate, 4-hydroxybutyl acrylate, and carboxyethyl acrylate also exhibited a higher rate decrease of approximately 9−15-fold (Table 1) upon dilution, whereas methoxyethyl acrylate exhibited a rate reduction of only 2.6-fold upon dilution, which is very similar to the 2.5-fold reduction exhibited by hexyl acrylate. These experiments thus emphasize the contribution of hydrogen bonding to monomer reactivity and that the effects of hydrogen bonding are eliminated at high dilution.

Impact of Aromatic and Heterocyclic Ring Stacking. Acrylates functionalized by aromatic rings like phenyl acrylate and benzyl acrylate are observed to polymerize much faster than traditional acrylates such as hexyl acrylate. The carbamate acrylates functionalized by aromatic rings also exhibited greatly enhanced reactivity in comparison to aliphatic carbamate acrylates. Hence, it was hypothesized that increased viscosity effects due to $\pi-\pi$ stacking and an increase in molecular rigidity contribute to the monomer reactivity to a significant extent. To study the effect of $\pi-\pi$ stacking on monomer reactivity, monomers containing the carbamate and carbonate functionality

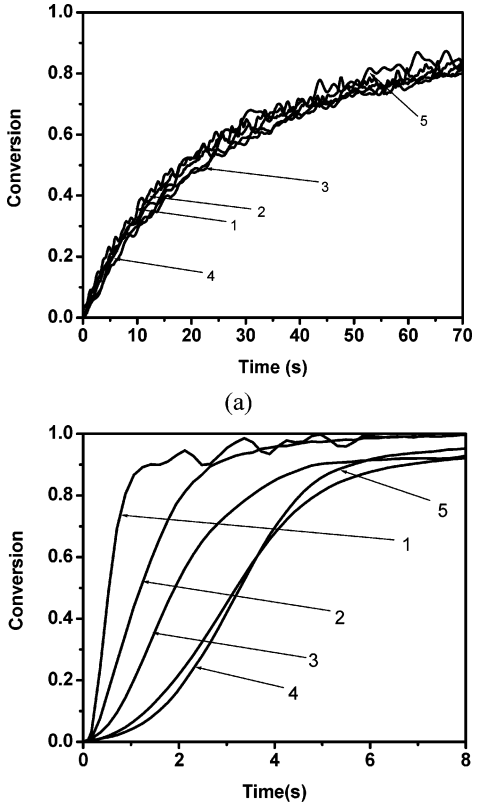

Figure 4. (a) Acrylate conversion as a function of time for monomers polymerized at 5 wt % dilution in 1,4-dioxane and (b) acrylate conversion as a function of time for monomers polymerized in bulk for (1) phenyl carbamate ethyl acrylate, (2) benzyl carbamate acrylate, (3) *n*-butyl carbamate ethyl acrylate, (4) linear carbonate acrylate, and (5) *tert*-butyl carbamate acrylate. Polymerization conditions: initiator concentration = 0.5 wt % DMPA with respect to overall solution, light intensity = 10 mW/cm^2. Phenyl carbamate ethyl acrylate and benzyl carbamate ethyl acrylate were polymerized at 67 °C only in bulk. All other polymerizations were conducted at ambient temperature.

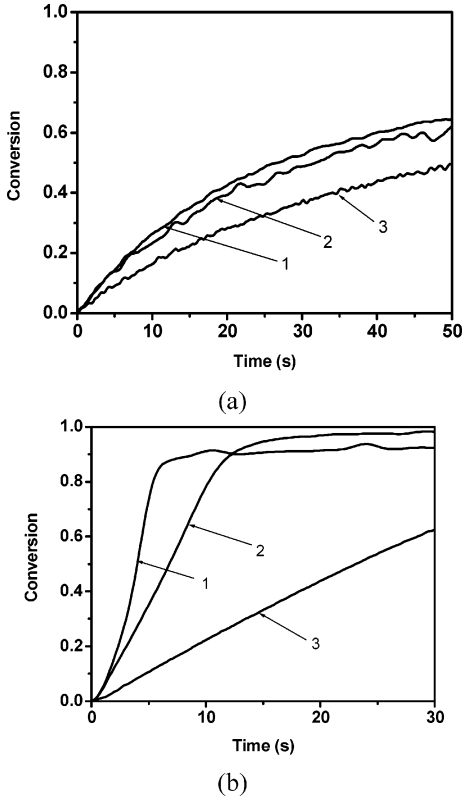

Figure 5. (a) Acrylate conversion as a function of time for monomers polymerized at 5 wt % dilution in 1,4-dioxane and (b) acrylate conversion as a function of time for monomers polymerized in bulk for (1) phenyl acrylate, (2) benzyl acrylate, and (3) hexyl acrylate. Polymerization conditions: initiator concentration = 0.5 wt % DMPA with respect to overall solution, light intensity = 10 mW/cm^2, temperature = 25 °C.

were polymerized both in bulk and at dilution in solvent (Figure 4).

In bulk, phenyl carbamate acrylate is significantly faster than all of the other monomers presented here, including the aliphatic carbamate and carbonate acrylates. However, upon dilution, the kinetics of phenyl carbamate acrylate, benzyl acrylate, and the aliphatic carbamate acrylates are nearly identical, as depicted in Figure 4a. Thus, we hypothesize that the positioning of a phenyl ring adjacent to the carbamate functionality increases the reactivity primarily through increased viscosity and $\pi-\pi$ stacking effects. Further, the conjugation of the phenyl ring with the carbamate secondary functionality increases the molecular rigidity, which increases the bulk monomer reactivity through increased viscosity effects. The reactivity differences between phenyl carbamate ethyl acrylate and benzyl carbamate ethyl acrylate are, thus, also accounted for through increased molecular rigidity due to the conjugation of the phenyl ring and the carbamate functionality.

The results in Table 1 indicate that traditional acrylates which do not possess any rate enhancing features such as $\pi-\pi$ stacking and hydrogen bonding exhibit less reduction in polymerization kinetics upon dilution, approximately 2−3-fold. The rate reduction in these monomers with dilution is attributed to the suppression of autoacceleration effects upon the addition of a solvent through enhanced mobility and increased termination. However, monomers characterized by hydrogen bonding depict a greater reduction, approximately 10−15-fold, upon dilution. Monomers such as phenyl acrylate and benzyl acrylate (Figure 5), which possess an aromatic ring but do not have strong hydrogen-bonding abilities, exhibited approximately a 5−10-fold reduction in polymerization kinetics with dilution.

As depicted in Table 1, the cyclic acetal acrylate monomers possessing the heteroatomic ring stacking interactions exhibited approximately a 13-fold rate reduction when diluted while monomers such as phenyl carbamate ethyl acrylate, which possesses both rate-enhancing features such as hydrogen bonding and $\pi-\pi$ stacking, exhibited a 50-fold reduction in polymerization kinetics.

Dilute solution polymerization studies conducted with the novel methacrylates also yielded similar results to the acrylates (Figure 6). The polymerization kinetics for methacrylates were drastically suppressed at 5 wt % dilution, relative to their kinetics in bulk. However, the novel methacrylic monomer cyclic carbonate methacrylate was observed to be more reactive compared to traditional methacrylates like hexyl methacrylate, even following extensive dilution. The observations with methacrylates also indicate the contribution of intramolecular conformational effects to enhanced monomer reactivity persists in both methacrylates and acrylates.

The exact mechanism through which the intramolecular interactions affect the reactivity is unclear. However, previously conducted studies suggest that the intramolecular effects could impact the nature of the propagating (meth)acrylic species and/or the (meth)acrylic double bonds.[24,25]

Relative Contributions of Various Factors to Monoacrylate Monomer Reactivity. While the relative rates of various

Table 2. Contribution of Bulk Interactions and Intramolecular Interactions to Monomer Reactivity[a]

monomer	ratio of rates upon dilution	ratio of rates in bulk	reactivity increase due to intramolecular interactions[b]	reactivity increase due to bulk interactions[b]
hexyl acrylate	1	1	1	1
cyclic carbonate acrylate	5.2 ± 0.5	12.7 ± 0.3	5.2 ± 0.5	2.4 ± 0.2
cyanoethyl acrylate	3.1 ± 0.2	10.3 ± 0.2	3.1 ± 0.2	3.3 ± 0.3
Acrylates with Carbamate Functionalities				
phenyl carbamate ethyl acrylate	3.0 ± 0.2	56.4 ± 5.2	3.0 ± 0.3	18.8 ± 2.1
ethyl linear carbonate ethyl acrylate	2.5 ± 0.2	9.8 ± 0.2	2.5 ± 0.2	3.9 ± 0.3
tert-butyl carbamate ethyl acrylate	2.4 ± 0.2	10.3 ± 0.2	2.4 ± 0.2	4.3 ± 0.4
benzyl carbamate ethyl acrylate	3.0 ± 0.3	19.6 ± 0.3	3.0 ± 0.3	6.5 ± 0.7
n-butyl carbamate ethyl acrylate	2.7 ± 0.2	16.9 ± 0.3	2.7 ± 0.2	6.3 ± 0.5
Acrylates with Aromatics and Heterocyclic Ring-Stacking Functionalities				
phenyl acrylate	2.0 ± 0.2	7.4 ± 0.1	2.0 ± 0.2	3.7 ± 0.4
benzyl acrylate	1.6 ± 0.2	4.0 ± 0.1	1.6 ± 0.2	2.5 ± 0.2
phenoxyethyl acrylate	2.0 ± 0.2	10.3 ± 0.2	2.0 ± 0.2	5.2 ± 0.5
cyclic acetal acrylate	1.8 ± 0.2	9.3 ± 0.2	1.8 ± 0.2	5.2 ± 0.3
Alkoxy-Functionalized Acrylates				
hydroxyethyl acrylate	2.8 ± 0.2	10.3 ± 0.6	2.8 ± 0.3	3.7 ± 0.3
methoxyethyl acrylate	2.2 ± 0.2	2.2 ± 0.1	2.2 ± 0.2	1.0 ± 0.1
4-hydroxybutyl acrylate	2.1 ± 0.2	8.5 ± 0.1	2.1 ± 0.2	4.0 ± 0.4
carboxyethyl acrylate	3.0 ± 0.3	16.9 ± 0.6	3.0 ± 0.4	5.6 ± 0.6

[a] Polymerization conditions: light intensity = 10 mW/cm^2, initiator concentration = 0.5 wt % with respect to the overall solution; solvent is 1,4-dioxane. [b] The average polymerization rates of these monomers divided by the average polymerization rate of hexyl acrylate gives relative reactivity increases at dilution, which are inferred to be reactivity increases associated with intramolecular interactions. Ratio of polymerization rates of various monomers in bulk with respect to polymerization rate of hexyl acrylate in bulk gives the contribution of both intramolecular and intermolecular interactions. Hence, through dividing the reactivity increases in bulk by the reactivity increases due to intramolecular interactions, we estimate the contribution of bulk interactions to monomer reactivity.

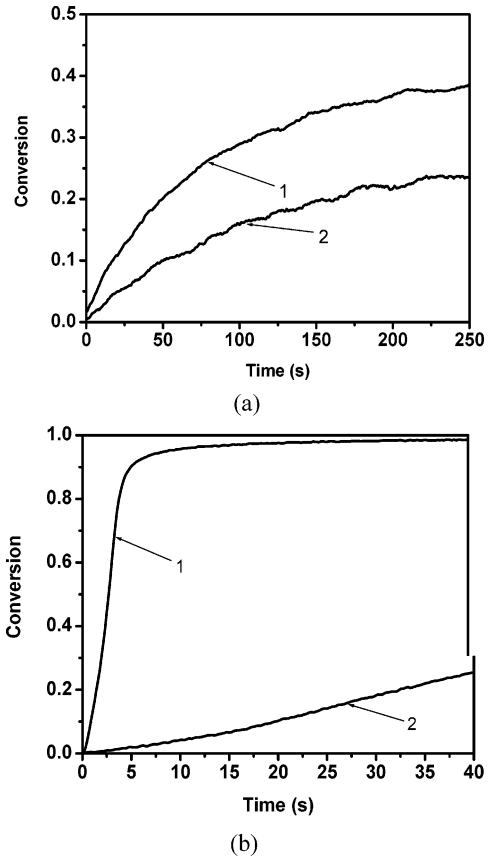

Figure 6. (a) Methacrylate conversion as a function of time for monomers polymerized at 5 wt % dilution in 1,4-dioxane and (b) methacrylate conversion as a function of time for monomers polymerized in bulk for (1) cyclic carbonate methacrylate and (2) hexyl methacrylate. Polymerization conditions: initiator concentration = 0.5 wt % DMPA with respect to overall solution, light intensity = 10 mW/cm^2, temperature = 25 °C.

monomers in bulk include contributions of both the intramolecular and intermolecular interactions, the relative rates upon extensive dilution would provide an estimate of the reactivity increases associated with the intramolecular interactions alone. Hence, the ratio of the reactivity increases in bulk with respect to the reactivity increases upon dilution provides an estimate of the contribution of bulk interactions to monomer reactivity. Table 2 presents the relative contributions of both the intramolecular interactions and intermolecular bulk interactions.

Methoxyethyl acrylate which does not possess any hydrogen bonding or ring stacking features did not depict any contribution to reactivity increase from bulk interactions as seen from Table 2. Thus, the entire difference of reactivity between hexyl acrylate and methoxyethyl acrylate both in bulk and in dilute solution is attributed to intramolecular interactions. For monomers such as hydroxyethyl acrylate, 4-hydroxybutyl acrylate, and carboxyethyl acrylate which are capable of hydrogen bonding, the reactivity increase due to bulk interactions is attributed to hydrogen bonding. The monomers, 4-hydroxybutyl acrylate and hydroxyethyl acrylate, showed a reactivity increase of 3.7 and 4.1, respectively, due to hydrogen bonding. Carboxyethyl acrylate, possessing strong hydrogen bonding interactions, exhibited a reactivity increase of 5.6. Work done by Nakamoto et al. relates the IR peak frequencies with bond distance from the crystallographic data, for different types of hydrogen bonds such as NH−N, NH−O, OH−O, and OH−N.[26] For a particular type of a bond, such as a NH−O bond or a NH−N bond, the strength of the hydrogen bonding is expected to scale inversely to the square of the bond distance. Thus, the bond distance obtained from the correlations developed by Nakamoto et al. provides a parameter for estimating the strength of the hydrogen bonding interactions as presented in Table 3.

For acrylates characterized by carbamate and carbonate functionalities, the stacking interactions between the carbamate and carbonate functionalities are also expected to contribute to the observed reactivity increase. The aliphatic carbamate acrylates, *tert*-butyl carbamate acrylate and *n*-butyl carbonate acrylate, depict a reactivity increase of 4.4 and 6.4, respectively, due to bulk intermolecular interactions. It can be inferred from the IR frequency−bond length data derived in Table 3 that the

Table 3. IR Peak Frequency Monomer Bond Length Data Derived from Nakamoto et al.

monomer	IR peak freq (cm^{-1})[a]	bond length (Å)
tert-butyl carbamate ethyl acrylate	3378	3.07
phenyl carbamate ethyl acrylate	3340	3.04
n-butyl carbamate ethyl acrylate	3347	3.05
benzyl carbamate ethyl acrylate	3352	3.05
hydroxyethyl acrylate	3434	2.87
4-hydroxybutyl acrylate	3344	2.88
carboxyethyl acrylate	2975	2.71

[a] IR peak frequency is the frequency in the NH stretching region (3200−3500 cm^{-1}) where the maximum absorption is observed.

Table 4. Reactivity Increases Caused by Incorporating Secondary Functionalities into the Acrylates

reactivity increases due to hydrogen bonding[a]	
urethanes	3.9−4.7
hydroxyl	3.4−4.4
carboxyl	5.0−6.2
reactivity increases due to aromatic and heteroatomic ring stacking interactions[a]	
phenyl ring	2.3−5.7
cyclic acetals	4.9−5.5
reactivity increases due to intramolecular interactions[a]	
carbamates and carbonates	2.2−3.3
cyclic carbonate	4.7−5.7
hydroxy/carboxy	2.6−3.3
cyano	2.9−3.3
cyclic acetal	1.6−2.0
phenoxy/methoxy	1.8−2.4

[a] The approximate ranges are calculated from the errors associated in the estimation of the reactivity ratios.

strength of the hydrogen bonding interactions in all of these urethanes is similar. Hence, the higher reactivity increase in *n*-butyl carbamate acrylate is attributed to the stacking interactions in the carbamate functionalities which are disrupted for the *tert*-butyl carbamate acrylate due to steric hindrance from the bulky *tert*-butyl group adjacent to the carbamate functionality.

Aromatic and heterocyclic ring stacking interactions were observed to contribute to a reactivity increase of 2−5-fold. Observed reactivity increases due to intramolecular interactions varied from 2- to 5-fold for various secondary functionalites obtained when the secondary functionalities are separated by an alkyl spacer length of two. The cyclic carbonate and cyano secondary functionalities exhibited higher rates upon dilution (Tables 1 and 2) and consequently higher contribution of intramolecular interactions to monomer reactivity. Table 4 summarizes the reactivity increases caused by to the presence of various functionalities both through bulk interactions and intramolecular conformational effects.

Conclusions

Here, it was clearly demonstrated that both intermolecular interactions, such as hydrogen bonding and aromatic and heterocyclic ring stacking effects, and intramolecular effects have a significant effect on the monomer reactivity. Depending on the nature of the monomer, its concentration, and the strength of both inter- and intramolecular interactions, the increase in polymerization rate is found to vary from no increase through as much as an approximately 50-fold increase. In this work the quantitative impact of various interactions was determined. Specifically, it was observed that hydrogen bonding, aromatic, and heteroatomic stacking interactions are all intermolecular interactions that lead to dramatically enhanced monomer reactivity.

However, it was also observed that monomers such as cyclic carbonate acrylate and ethyl linear carbonate ethyl acrylate, which do not possess significant intermolecular interactions, exhibit significantly higher reactivity. Further, all (meth)acrylates characterized by secondary functionalities such as cyclic carbonate, carbonate, and carbamate functional groups continue to exhibit significantly higher reactivity upon dilution. These reactivity differences, which are present even upon extensive dilution, cannot be attributed to bulk solvation effects due to the solvation of the monomer in itself. Thus, these reactivity differences upon dilution are suggestive of intramolecular conformational effects, which have a distinct contribution to monomer reactivity.

While the bulk interactions increase the reactivity by imposing diffusional limitations on the system, the intramolecular interactions affect monomer reactivity by impacting the radical vinyl chemistry. It was observed that these intramolecular interactions alone lead to a 2−5-fold polymerization rate increase.

As observed in this study, the contribution of the bulk and intramolecular interactions to monomer reactivity varies for different monomers, depending on the nature of the secondary functionalities. Since for each monomer different types of interactions contribute to its reactivity, there have been numerous theories to explain the reactivity of these systems, and a comprehensive theory to explain the reactivity of all novel (meth)acrylic monomers has not been found to date.

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