Design, Development, and Evaluation of Monovinyl Acrylates Characterized by Secondary Functionalities as Reactive Diluents to Diacrylates

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ABSTRACT: This study focuses on the design and development of novel monovinylic (meth)acrylate monomers with enhanced polymerization kinetics and the evaluation of their performance as reactive diluents in diacrylate systems. Novel (meth)acrylic monomers characterized by several new secondary functionalities are developed in this study and are shown to exhibit reactivities 10−70 fold greater than traditional monoacrylates such as hexyl acrylate. These monomers were designed based on our understanding of interactions between monomer structure, polymerizations kinetics, and polymer properties. Performance of these monovinyl monomers as reactive diluents is also investigated in this study. Copolymerization of these monomers with diacrylates enhanced both the reactivity and the mechanical properties of the diacrylate system. Specifically, while copolymerization of a diacrylate system with traditional monoacrylates such as hexyl acrylate decreases the overall reactivity of the system, its copolymerization with the novel monomers led to comonomer mixtures that were 30−50% more reactive than either of the individual components, with initial polymerization rates increased by as much as 2 times that of the more reactive component. Furthermore, the copolymerization of these novel monovinyl systems with diacrylates also enabled formation of polymers with enhanced mechanical properties over the corresponding diacrylates including a more homogeneous network structure as indicated by a glass transition temperature that was narrowed by up to 55% while increasing the glass transition temperature by as much as 10 °C.

Introduction

Photopolymerization offers multiple advantages including spatial and temporal control, solventless polymerizations, and resistance to swelling in a wide variety of solvents. Hence, it has been used extensively for a range of applications including, stereolithography, coatings, dental materials, contact lenses, and adhesives.[1−13] However, it also suffers from various limitations including residual unsaturation[14,15] responsible for leakage of monomer, discoloration of the cured polymer due to the presence of photoinitiator, and oxygen inhibition,[16−18] which affects the polymer performance and properties.[19]

In order to increase the polymerization speed of the polymer formed, it is a common practice to use monomers containing multiple vinyl groups. Because of their cross-linking ability associated with the increase in monomer functionality, diffusional limitations are encountered early in the polymerization process which suppresses the termination reaction. The reduction in termination causes autoacceleration effects which increase the polymerization rate.[18] Furthermore, the cross-linked polymers achieved through the use of a monomer with multiple vinyl groups are characterized by a high elastic modulus and high glass transition temperature. Unfortunately, the increase in monomer functionality, which leads to increased cross-linking density, also leads to increased brittleness[20] and residual unsaturation.[15] While the increased brittleness adversely affects the mechanical properties of the polymer, the residual unsaturation is undesirable. To decrease the brittleness and residual unsaturation, monovinylic monomers are used as reactive diluents in copolymerizations with monomers containing multiple vinyl groups. However, the use of these reactive diluents generally reduces the rate, modulus, and glass transition temperature of the cured material. Thus, there is a tradeoff between polymerization rate, residual unsaturation, and the extent of cross-linking.

Therefore, the design and development of high performance monovinyl (meth)acrylates for the purpose of use as reactive diluents in multifunctional acrylate polymerizations is of significant interest. Recently, certain novel (meth)acrylates have been developed, which show enhanced polymerization kinetics rivaling those of traditional multivinylic acrylates while also achieving quantitative extents of conversion[21−33] Additionally these novel(mono)acrylates also form polymers characterized by high mechanical strength. Owing to their enhanced reactivity and polymer properties, these materials show excellent promise as reactive diluents. The applicability of these novel monomers as reactive diluents has been previously demonstrated.[23,25,29]

However, some of these novel monovinyl monomers are associated with disadvantages such as high viscosities and limited shelf stability.[29] Therefore, the overall objective of this work is to design reactive novel monomers with a diverse set of secondary functionalities as well as to characterize the superior reaction kinetics and network properties afforded by these systems as reactive diluents.

First, the existing knowledge of the relationships between monomer structure and polymerization kinetics was utilized to design shelf-stable and highly reactive novel (mono)acrylates,

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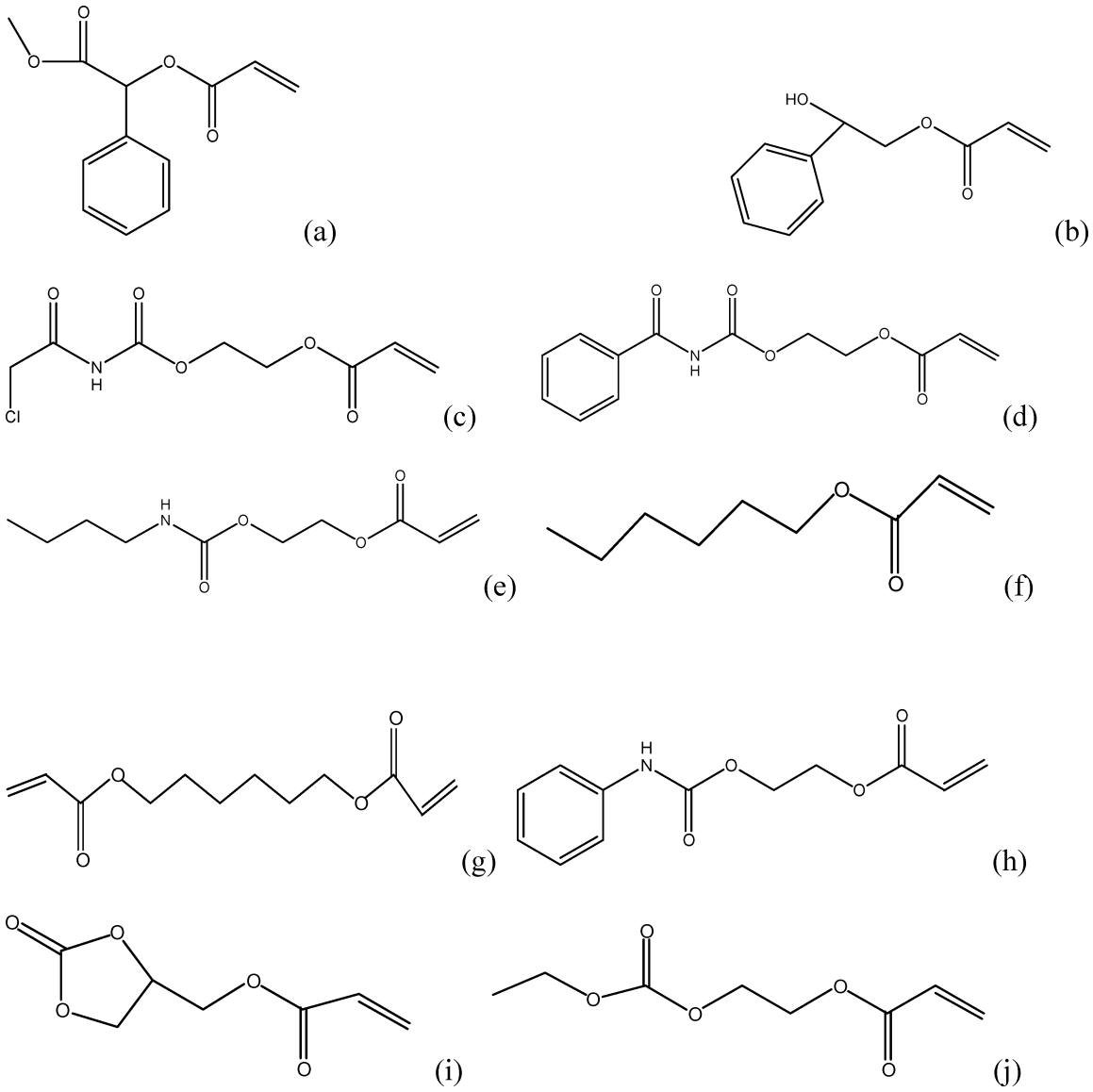

Figure 1. Structures of monomers used in the study: (a) phenylacetoxy acrylate methyl ester; (b) 2-hydroxy 2-phenylethyl acrylate; (c) chloroacetyl carbamate ethyl acrylate; (d) benzoyl carbamate ethyl acrylate; (e) *n*-butyl carbamate ethyl acrylate; (f) hexyl acrylate; (g) hexanediol diacrylate; (h) phenyl carbamate ethyl acrylate; (i) cyclic carbonate acrylate; (j) ethyl linear carbonate ethyl acrylate.

which would be expected to form polymers of high mechanical strength. The reactive monoacrylates, characterized by low viscosity, were then copolymerized with diacrylates to achieve highly reactive comonomer mixtures, more reactive than the individual components. Copolymerization of monoacrylates yielding high glass transition temperatures were conducted with diacrylates to yield polymers characterized by higher mechanical strength and increased homogeneity as compared to the individual components.

Experimental Section

Materials. The monomers phenyl carbamate ethyl acrylate, benzoyl carbamate ethyl acrylate, and chloroacetyl carbamate ethyl acrylate were prepared by a reaction of phenyl isocyanate, benzoyl isocyanate and chloroacetyl isocyanate (Aldrich Chemicals, Milwaukee, WI) with hydroxyethyl acrylate (Aldrich Chemicals, Milwaukee, WI).[21] The synthesis of cyclic carbonate acrylate and linear carbonate ethyl acrylate has been described elsewhere and will not be discussed here.[21,23] Phenylacetoxy acrylate methyl ester was prepared by reaction of manselic acid methyl ester with acryloyl chloride in the presence of triethylamine. 2-Hydroxy 2-phenylethyl acrylate was prepared by the reaction of 1-phenylethylene glycol with acryloyl chloride and subsequent separation of the diacrylate and the monoacrylate products. The 1-phenylethylene glycol was obtained by the ring opening reaction of styrene epoxide (Aldrich Chemicals, Milwaukee, WI) in the presence of carbon bromide as a catalyst. The monomers *n*-butyl carbamate acrylate, hexyl acrylate, and hexanediol diacrylate (HDDA) were obtained from Aldrich Chemicals (Milwaukee, WI) and used as received. The structures of all monomers utilized in this study are depicted in Figure 1. ^{1}H NMR spectroscopy was used to verify the structure of all synthesized monomers. The spectra were recorded at 500 MHz (Unity INOVA 500 spectrometer, Varian, Palo Alto, CA) with $CDCl_3$ as the solvent. Specifically, while the phenylacetoxy acrylate methyl ester and 2-hydroxy 2-phenylethyl acrylate are liquids at room temperature, the chloroacetyl carbamate ethyl acrylate (melting point = 65 °C) and benzoyl carbamate ethyl acrylate (melting point = 80 °C) are solid monomers at room temperature. Among the other monovinyl monomers employed in this study, while *n*-butyl carbamate acrylate and hexyl acrylate are both liquids at room temperature, phenyl carbamate acrylate is a solid monomer (melting point = 67 °C)

Methods

Fourier Transform Infrared Spectroscopy. FTIR studies were conducted with a Nicolet 760 Magna FTIR spectrometer (Nicolet, Madison, WI).[23] Samples were laminated between two NaCl crystals with approximate film thicknesses of 15−20 μm in a horizontal transmission apparatus. Samples were irradiated with a filtered ultraviolet light source (Ultracure 100SS 100 W high-pressure Mercury vapor short-arc lamp, EXFO, Mississaugua, Ontario, Canada) centered at 365 nm for a duration of 5 min. Irradiation intensity was monitored using a Cole-Parmer Instruments Co. Series 9811 radiometer (Vernon Hills, IL). The initiator used was 0.1 wt % of 2,2-dimethoxy-2-phenylacetophenone (DMPA) for all samples. The average polymerization rates for a given conversion range are calculated by measuring the slope of the linear fit for the conversion−time curves, in that particular range. The initial polymerization rates are estimated by dividing the increase in conversion by the time taken to achieve the conversion increase.

Dynamic Mechanical Analysis. Dynamic mechanic analysis in extension mode (Perkin-Elmer DMA-7, Perkin-Elmer, Norwalk, CT) was utilized for measurement of the material properties. Loss tangent and storage modulus were determined as a function of temperature, applying a sinusoidal stress at a frequency of 1 Hz. The rubbery modulus is estimated from the storage modulus observed in the rubbery plateau region of the storage modulus curve plotted as a function of temperature. The temperature of the sample was increased from −30 to +170 °C at a rate of 5 °C.

Results and Discussion

Numerous studies to date have led to an increased understanding of the interactions existing between monomer structure, polymerization kinetics, and polymer properties. Specifically, interactions such as hydrogen bonding, heteroatomic stacking, and aromatic ring stacking previously have been shown to impart superior polymerization kinetics to the reactive monovinyl monomers.[34] Utilizing this knowledge, this work attempts to both design and develop novel monomers with enhanced polymerization kinetics as well as to conduct copolymerizations of these systems with diacrylates to achieve more reactive mixtures with superior polymer properties.

Design of New (Meth)acrylic Monomers. Novel (meth)acrylic monomers, characterized by secondary functionalities such as carbonate, carbamate, acetal, oxazilidone, and phenyl rings, were previously shown to enhance the reactivity of (meth)acrylic monomers.[21−24,27,35] Specifically, phenyl carbamate acrylate (Figure 1h), characterized by both a carbamate and a phenyl ring, was one of the most reactive (mono)acrylate monomers synthesized to date. It was discovered that the dramatically enhanced reactivity of the phenyl carbamate ethyl acrylate is due to a combination of hydrogen bonding, carbamate stacking, and aromatic ring stacking interactions. Furthermore, as compared to other urethane acrylates, the conjugation of the phenyl ring with the carbamate functionality in this monomer greatly enhances its reactivity through increased stacking interactions.[34] Therefore, new reactive monomers, characterized by hydrogen-bonding features and aromatic ring stacking interactions with extensive conjugation, were designed in this study.

The structures of the designed monomers along with all the monomers used in the study are depicted in Figure 1. The monomer phenylacetoxy acrylate methyl ester is characterized by ester and aromatic ring stacking interactions while 2-hydroxy 2-phenylethyl acrylate is characterized by hydrogen bonding and aromatic ring stacking interactions. The monomers, chloroacetyl carbamate ethyl acrylate and benzoyl carbamate ethyl acrylate, are characterized by *N*-acyl carbamate stacking, extensive conjugation, and hydrogen bonding. The monomer benzoyl carbamate ethyl acrylate is further characterized by aromatic ring stacking interactions.

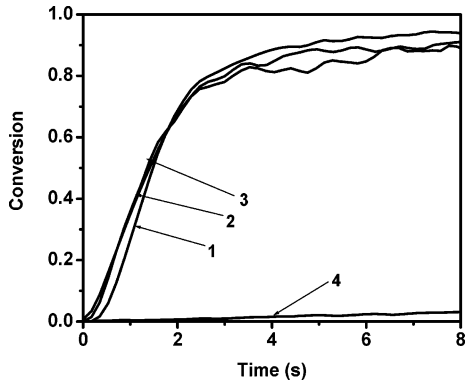

Figure 2. Acrylate conversion as a function of time for (1) chloroacetyl carbamate ethyl acrylate, (2) benzoyl carbamate ethyl acrylate, (3) phenyl carbamate ethyl acrylate, and (4) hexyl acrylate. Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %; temperature = 67 °C. Monomer benzoyl carbamate ethyl acrylate was polymerized at 81 °C, since it is characterized by a higher melting point of 80 °C.

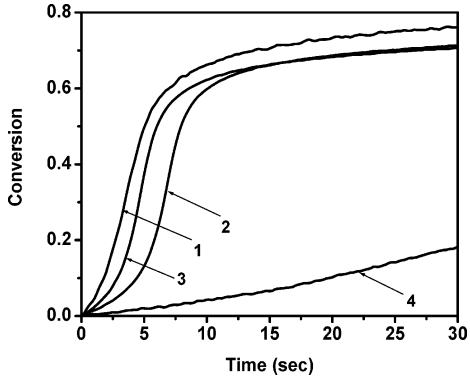

Figure 3. Acrylate conversion as a function of time for (1) phenylacetoxy acrylate methyl ester, (2) 2-hydroxy 2-phenylethyl acrylate, (3) cyclic carbonate acrylate, and (4) hexyl acrylate. Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %; temperature = 25 °C.

The reactivities of these monomers are presented in Figures 2 and 3 with the polymerization kinetics of a novel monoacrylate contrasted with that of traditional monoacrylate (hexyl acrylate). Figure 2 compares the polymerization kinetics of benzoyl carbamate ethyl acrylate and chlorocarbamate ethyl acrylate with hexyl acrylate and phenyl carbamate acrylate. Since the synthesized monomers are characterized by different melting points ranging from 65 to 80 °C, the polymerization kinetics of all the synthesized monomers have been compared at temperatures close to their melting points. Interestingly, monomers with benzoyl carbamate and chlorocarbamate functionalities were found to be extremely reactive, with reactivities equivalent to phenyl carbamate ethyl acrylate (Figure 2). Furthermore, these monomers were found to be around seventy times faster than hexyl acrylate when polymerized under the same conditions as can be inferred from Table 1.

While phenyl carbamate acrylate is one of the most reactive solid monomers known to date, cyclic carbonate acrylate is one of the fastest reacting liquid monomers. As there are inherent differences in diffusional limitations present during polymerization of liquid and solid monomers, this study compares the newly designed monomers with novel monomers of their class. Therefore, the reactivity of the liquid monomers, phenylacetoxy acrylate methyl ester and 2-hydroxy 2-phenylethyl acrylate, is contrasted with the fastest reacting liquid monomer, cyclic

Table 1. Initial Polymerization Rates, Average Polymerization Rates, and Time to Reach 60% Conversion for Various Monomer Systems[a]

monomer	melting point (°C)	$R_{p,initial}$ (2−10 % convn) (s^{-1})	$R_{p,average}$ (10−50 % convn) (s^{-1})	time to 60% convn (s)
hexyl acrylate	<25	0.006 ± 0.001	0.007 ± 0.001	103.0 ± 4.0
cyclic carbonate acrylate	<25	0.042 ± 0.003	0.130 ± 0.021	8.6 ± 0.4
phenylacetoxy acrylate methyl ester	<25	0.059 ± 0.015	0.123 ± 0.020	7.1 ± 0.3
2-hydroxy 2-phenyl-ethyl acrylate	< 25	0.028 ± 0.030	0.113 ± 0.010	10.3 ± 0.4
phenyl carbamate ethyl acrylate	67	0.358 ± 0.057	0.390 ± 0.051	1.8 ± 0.0
chloroacetyl carbamate ethyl acrylate	65	0.312 ± 0.031	0.479 ± 0.058	1.8 ± 0.0
benzoyl carbamate ethyl acrylate	80	0.348 ± 0.033	0.430 ± 0.038	1.8 ± 0.0

[a] Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %.

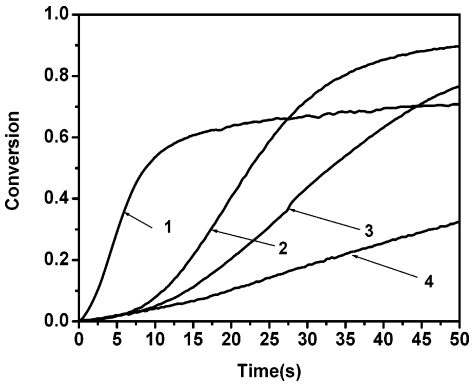

Figure 4. Acrylate conversion as a function of time (1) HDDA, (2) 70/30 wt % HDDA/hexyl acrylate, (3) 50/50 wt % HDDA/hexyl acrylate, and (4) hexyl acrylate. Polymerization conditions: light intensity = 5 mW/cm^2, initiator concentration = 0.1 wt %, and temperature = 25 °C.

carbonate acrylate. Figure 3 presents the polymerization kinetics of monomers phenylacetoxy acrylate methyl ester, 2-hydroxy 2-phenylethyl acrylate, cyclic carbonate acrylate, and hexyl acrylate. While the monomers methyl ester phenylacetoxy acrylate methyl ester and 2-hydroxy 2-phenylethyl acrylate have similar reactivity to the cyclic carbonate acrylate, they react 10−20 fold faster than hexyl acrylate (Table 1).

Copolymerization of Novel Acrylates with Diacrylates. As discussed earlier, traditionally, the addition of a reactive diluent to a multifunctional acrylate is associated with a decrease in the reactivity of the multifunctional monomer. Figure 4 presents the polymerization kinetics of HDDA upon the addition of varying amounts of hexyl acrylate. As anticipated, the polymerization rate of the reactive HDDA system decreases upon addition of increasing amounts of monovinyl hexyl acrylate monomer with a 44% decrease in the average rates from 10% to 50% conversion observed when going from pure HDDA to 30% HA as indicated in Table 2.

However, due to their enhanced monomer reactivity and superior polymer properties, the novel (meth)acrylates are well suited for use as reactive diluents. The addition of more highly reactive novel mono(meth)acrylates as reactive diluents to relatively less reactive diacrylate systems is expected to enhance the monomer reactivity of the diacrylates.[24] Furthermore, it can be theorized that upon the copolymerization of a suitable combination of a diacrylate and a more reactive monoacrylate, which differ marginally in their reactivity, there would be an increase in the reactivity of the monoacrylate component of the system, through increased autoacceleration effects. It is, therefore, hypothesized that copolymerization of a suitable combination of acrylate and diacrylate could lead to the formation of reactive mixtures more reactive than either of the individual components.

Table 2. Initial Polymerization Rates, Average Polymerization Rates, and Time to Reach 60% Conversion for Various Comonomer Systems[a]

monomer	$R_{p,initial}$ (2−10 % convn) (s^{-1})	$R_{p,average}$ (10−50 % convn) (s^{-1})	time to X = 60% convn (s)
HDDA	0.048 ± 0.013	0.063 ± 0.017	14.4 ± 0.4
hexyl acrylate (HA)	0.006 ± 0.001	0.007 ± 0.001	103.00 ± 4.0
HDDA:HA 70:30 wt %	0.014 ± 0.002	0.035 ± 0.004	25.5 ± 1.0
HDDA:HA 50:50 wt %	0.009 ± 0.002	0.017 ± 0.002	38.5 ± 1.2
phenylacetoxy acrylate methyl ester	0.059 ± 0.015	0.123 ± 0.020	7.1 ± 0.3
HDDA: phenylacetoxy acrylate methyl ester 70:30 wt %	0.067 ± 0.010	0.094 ± 0.009	7.1 ± 0.2
HDDA:phenylacetoxy acrylate methyl ester 50:50 w t%	0.062 ± 0.010	0.123 ± 0.021	8.5 ± 0.4
n-butyl carbamate ethyl acrylate (nBCA)	0.072 ± 0.013	0.130 ± 0.012	6.0 ± 0.3
HDDA:nBCA 70:30 wt %	0.06 ± 0.014	0.082 ± 0.005	9.0 ± 0.4
HDDA:nBCA 50:50 wt %	0.125 ± 0.023	0.154 ± 0.013	4.5 ± 0.2
HDDA:nBCA 30:70 wt %	0.096 ± 0.014	0.128 ± 0.014	5.3 ± 0.2
linear carbonate ethyl acrylate (LCA)	0.044 ± 0.007	0.072 ± 0.012	9.5 ± 0.3
HDDA:LCA 70:30 wt %	0.062 ± 0.014	0.087 ± 0.002	9.7 ± 0.1
HDDA:LCA 50:50 wt %	0.064 ± 0.014	0.093 ± 0.005	7.6 ± 0.3

[a] Polymerization conditions: light intensity = 5 mW/cm^2, initiator concentration = 0.1 wt %, and temperature = 25 °C.

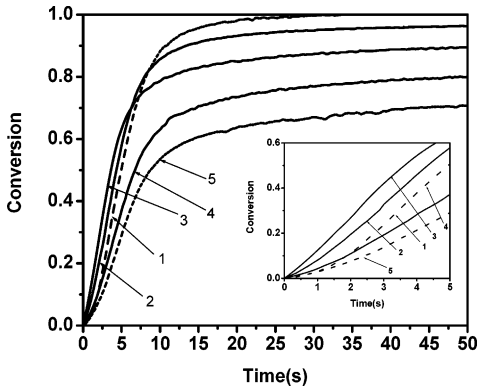

Figure 5. Acrylate conversion as a function of time for (1) *n*-butyl carbamate acrylate, (2) 30/70 wt % HDDA/n butyl carbamate acrylate, (3) 50/50 wt % HDDA /n butyl carbamate acrylate, (4) 70/30 wt % HDDA/n butyl carbamate acrylate, and (5) HDDA. Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %; temperature = 25 °C. The initial polymerization rates are depicted in the inset. The solid lines represent the monomer mixtures and the dotted lines represent the pure monomers.

Since *n*-butyl carbamate acrylate is a low viscosity liquid monomer previously[27] observed to exhibit enhanced reactivity, copolymerization studies of *n*-butyl carbamate acrylate were conducted (Figure 5). As can be inferred from Figure 5, *n*-butyl carbamate ethyl acrylate, in spite of being monovinylic in nature, reacts faster than HDDA. Furthermore, the 50/50 comonomer mixture of HDDA/*n*-butyl carbamate ethyl acrylate polymerized at an average polymerization rate (averaged from 10 to 50% conversion) 15% greater than the *n*-butylcarbamate acrylate and the initial polymerization rate (averaged over the first 10% conversion as, depicted in the inset of Figure 5) is approximately, 2-fold greater than *n*-butyl carbamate acrylate. This enhancement in the reactivity of comonomer mixture relative to the pure *n*-butyl carbamate acrylate is inferred to arise due to the contribution of the autoacceleration effects due to cross-linking. Also, the 70/30 HDDA/*n*-butyl carbamate ethyl acrylate mixture, which has a higher percentage of the diacrylate monomer, exhibits a reactivity intermediate to *n*-butyl carbamate

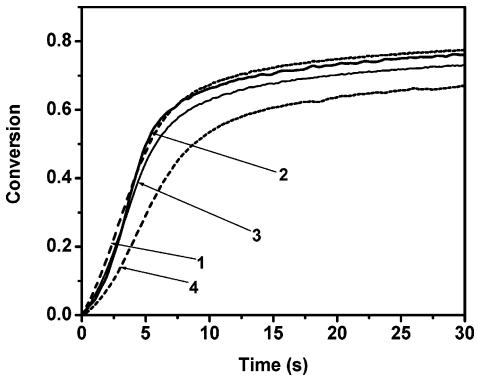

Figure 6. Acrylate conversion as a function of time for (1) phenylacetoxy acrylate methyl ester, (2) 50/50 wt % HDDA /phenylacetoxy acrylate methyl ester, (3) 30/70 wt % HDDA/phenylacetoxy acrylate methyl ester, and (4) HDDA. Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %; temperature = 25 °C. The solid lines represent the monomer mixtures and the dotted lines represent the pure monomers.

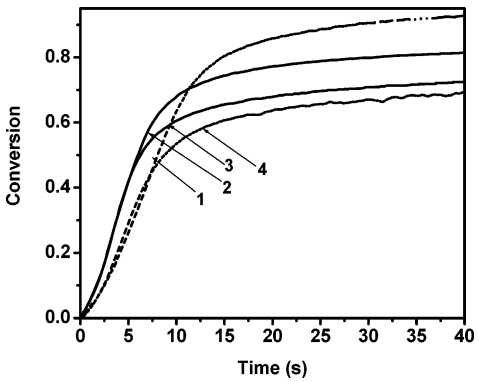

Figure 7. Acrylate conversion as a function of time for (1) linear carbonate ethyl acrylate, (2) 50/50 wt % HDDA /linear carbonate ethyl acrylate, (3) 30/70 wt % HDDA/linear carbonate ethyl acrylate, and (4) HDDA. Polymerization conditions: light intensity = 5 mW/cm^2; initiator concentration = 0.1 wt %; temperature = 25 °C. The solid lines represent the monomer mixtures, and the dotted lines represent the pure monomers.

acrylate and HDDA as is typically observed upon copolymerization of two (meth)acrylate monomers with different reactivities.

Figures 6 and 7 present the polymerization kinetics of HDDA with other reactive liquid monomers including phenylacetoxy acrylate methyl ester and ethyl linear carbonate ethyl acrylate. In these copolymerization mixtures, the 50/50 comonomer mixture of HDDA/phenylacetoxy acrylate methyl ester exhibits a polymerization rate equivalent to the more reactive phenylacetoxy acrylate methyl ester component. This result indicates that the contribution of autoacceleration effects due to cross-linking compensates for the lower polymerization rate of HDDA to yield a more reactive monomer mixture. The 70/30 comonomer mixture of HDDA/ethyl linear carbonate ethyl acrylate polymerized at an average polymerization rate (averaged from 10 to 50% conversion) 20% greater than the more reactive LCA component and 40% greater than HDDA. The 50/50 comonomer mixture of HDDA/ethyl linear carbonate ethyl acrylate polymerized at an average polymerization rate (averaged from 10 to 50% conversion) 30% greater than the more reactive LCA component and 50% greater than HDDA. Thus, it was observed that through the copolymerization of a combination of diacrylate and monovinyl acrylate marginally differing in their reactivity, the reactivity of the comonomer mixture can be significantly enhanced syngeristically.

It is also observed from Figures 5−7 that while bulk *n*-butyl carbamate acrylate and ethyl linear carbonate ethyl acrylate attain complete conversion, bulk phenylacetoxy acrylate methyl ester does not attain complete conversion. While this incomplete conversion of the phenylacetoxy acrylate methyl ester clearly indicates the diffusional limitations encountered during its polymerization, *n*-butyl carbamate acrylate and ethyl linear carbonate ethyl acrylate achieve complete conversion. This result indicates that they do not experience significant mobility restrictions prior to complete reaction. Since the phenylacetoxy acrylate methyl ester is already characterized by diffusional limitations during polymerization; the contribution of autoacceleration effects due to diffusional restrictions imposed by hexanediol diacrylate has a more limited effect. Hence, the enhancement in reactivity associated with the addition of HDDA system is reduced upon copolymerization with the phenylacetoxy acrylate methyl ester as compared to copolymerization with *n*-butyl carbamate acrylate and ethyl linear carbonate ethyl acrylate.

Copolymerization to Achieve Superior Mechanical Properties. Monovinyl (meth)acrylates typically lead to the formation of low mechanical strength polymers due to the absence of cross-linking. Therefore, the addition of a monovinyl (meth)acrylate as a reactive diluent to a multifunctional acrylate is typically associated with a decrease in the mechanical properties of the copolymer system due to decreasing cross-linking density. However, novel monovinylic (meth)acrylic monomers are observed to form high modulus materials, due to interactions such as hydrogen bonding and aromatic ring and heteroatomic functionality stacking. Hence, the addition of novel mono(meth)acrylates to a diacrylate may lead to a copolymer of superior mechanical properties.[22] Furthermore, while the traditional diacrylates form high modulus polymers due to cross-linking of the acrylate backbone, the mono(meth)acrylates form high modulus polymers due to hydrogen bonding and aromatic and heteroatomic stacking interactions associated with the side chains of the polymer. Hence, it is theorized that, upon copolymerization of these systems, both the effects of cross-linking in the polymer backbone and aromatic and heteroatomic stacking features along the side chains reinforce each other to lead to copolymers characterized by a higher modulus than either of the individual components.

Furthermore, this addition of monovinyl monomers to the diacrylate systems is also expected to increase the material properties of the copolymer due to its increased network homogeneity. This increased network homogeneity of copolymers as compared to pure diacrylates would be characterized by the copolymers having a more compressed glass transition region. Traditionally, diacrylates are known to form polymers with a very heterogeneous network structure[36,37] because of the unequal reactivity of functional groups in the monomer.[38,39] The reaction of the propagating acrylic radical with the pendant double bonds in the system leads to the formation of microgels, which are more extensively cross-linked than the remainder of the polymer.[36,37] At higher conversion, the acrylate radicals are trapped in highly cross-linked regions, resulting in incomplete curing of the system and thereby leading to network heterogeneity. However, the addition of a monoacrylate decreases the microgel formation. In this manner, the copolymerization of diacrylate monomers with monovinyl monomers is expected to increase the homogeneity of the system and reduce the T_g width.

Phenylacetoxy acrylate methyl ester, which forms a polymer with a T_g of 77 °C, was copolymerized with HDDA, which forms a polymer with a T_g of 86 °C to lead to formation of

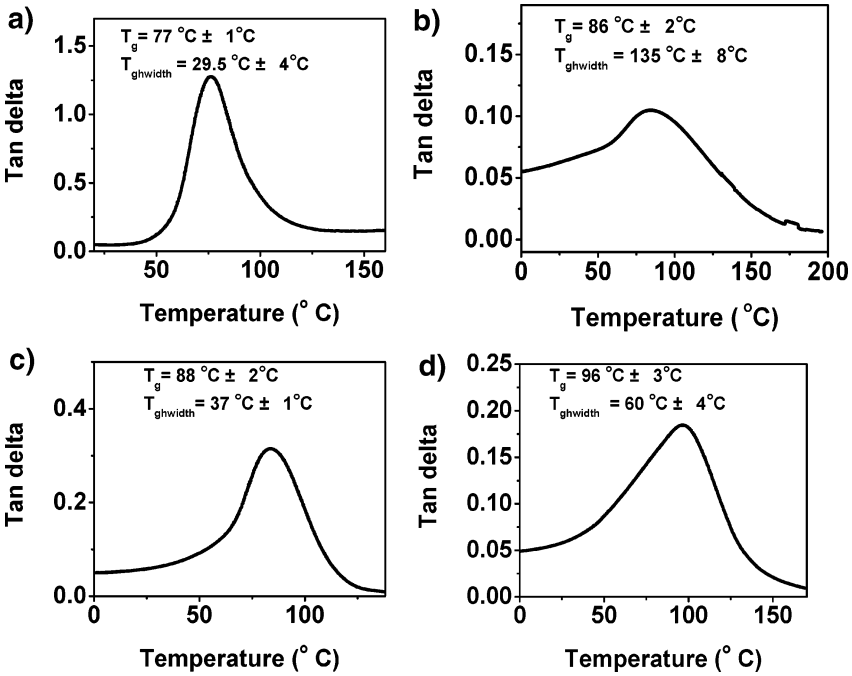

Figure 8. The tan δ curves for (a) phenylacetoxy acrylate methyl ester, (b) HDDA, (c) 50/50 HDDA/phenylacetoxy acrylate methyl ester, and (d) 70/30 HDDA/ phenylacetoxy acrylate methyl ester. All samples were cured at 5 mW/cm^2, for 5 min at T = 25 °C.

Table 3. Glass Transition Temperatures and T_g Half-Width for Various Copolymer Systems[a]

monomer	T_g (°C)	T_g half-width (°C)	final double bond conversion (%)
HDDA	86 ± 2	135 ± 8	78 ± 1
phenylacetoxy acrylate methyl ester	77 ± 1	30 ± 4	89 ± 1
HDDA:HA 70:30 wt %	77 ± 1	59 ± 2	87 ± 2
HDDA:nBCA 70:30 wt %	81 ± 2	59 ± 3	86 ± 3
HDDA: phenylacetoxy acrylate methyl ester 70:30 wt %	96 ± 3	60 ± 4	82 ± 2
HDDA:HA 50:50 wt %	44 ± 1	45 ± 4	95 ± 2
HDDA:nBCA 50:50 wt %	67 ± 0	35 ± 1	94 ± 2
HDDA:phenylacetoxy acrylate methyl ester 50:50 w t%	88 ± 2	37 ± 1	87 ± 1

[a] All samples were cured at 5 mW/cm^2, for 5 min at T = 25 °C.

copolymers with T_g greater than or equivalent to the diacrylate and with narrower T_g widths (Table 3 and Figure 8). The 50/50 wt % HDDA/phenylacetoxy acrylate methyl ester exhibited a T_g of 88 °C at 87% total acrylate conversion, equivalent to the T_g of HDDA, 86 °C, despite a decrease in the rubbery modulus to 0.06 GPa, compared to the 0.26 GPa for pure HDDA (Figure 8). The 70/30 wt % HDDA/phenylacetoxy acrylate methyl ester mixture also demonstrated a higher T_g of 96 °C at 82% total acrylate conversion and a rubbery modulus of 0.11 GPa (Figure 8). HDDA/HA mixtures copolymerized as a control exhibited a decrease in the glass transition temperatures as would be expected due to the decrease in the overall cross-linking density of the system. For instance, 50/50 wt % HDDA/HA and HDDA/*n*-butyl carbamate acrylate had T_g's of 44 °C and 67 °C, respectively, at approximately 95% and 94% acrylate double bond conversions, respectively, as compared to the T_g of 88 °C for the 50/50 wt % HDDA/ phenylacetoxy acrylate methyl ester mixture at 87% conversion.

Also, in addition to exhibiting higher T_g's, the HDDA/phenylacetoxy acrylate methyl ester mixtures also were more homogeneous. For instance, the 50/50 wt % HDDA/phenylacetoxy acrylate methyl ester had a T_g width at half-height of 37 °C, compared to 135 °C exhibited by HDDA for this same measure of heterogeneity. Similarly, the 70/30 and 50/50 HDDA/monoacrylate mixtures for all three monovinyl acrylates exhibit similar T_g half-height widths, of around 60 °C for the 70/30 HDDA/monoacrylate mixtures and 35−45 °C for 50/50 HDDA/monoacrylate mixtures as indicated from Table 3.

Conclusions

Advanced understanding of monomer-structure reactivity relationships was utilized to design, synthesize and characterize novel (meth)acrylic monomers with enhanced monomer reactivity and polymer performance. Liquid monomers characterized by low viscosities were developed and were shown to be highly reactive and well suited for performance as reactive diluents in multifunctional monomers. Furthermore, the performance of novel (meth)acrylates as reactive diluents in HDDA was evaluated. Copolymerization of the novel (mono)methacrylates was conducted with diacrylates to yield monomer mixtures with polymerization rates greater than the individual components. It was also presented that upon copolymerization of certain monoacrylate−diacrylate mixtures, a copolymer with a higher T_g than either of its components as well as a much narrower T_g width was obtained.

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