Effect of Aliphatic Spacer Substitution on the Reactivity of Phenyl Carbamate Acrylate Monomers

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ABSTRACT: Novel monoacrylate monomers with a carbamate secondary functionality and a terminal aryl group were synthesized to study the mechanisms that allow for increased reactivity of these monomers compared to typical monoacrylate monomers. To test for the possibility of hydrogen abstraction from the two-carbon aliphatic spacer group, varying methyl substituents were added to one or both of the spacer carbons. Single methylation at the α and β carbons showed no drastic effect on the polymerization rate. However, dual methylation of the α carbon reduced the overall polymerization rate by approximately 5-fold. Conversely, dual methylation at the β carbon reduced the polymerization rate by only 2-fold. Unsteady state analysis of the α,α-methylated monomer showed that the apparent kinetic constants approach that of traditional monoacrylate monomers. Thus, hydrogen abstraction appears to be a likely explanation for these unique substitution effects on monoacrylate reactivity where the substitution number and location have a profound impact on the polymerization rate of these novel monomers. Disubstitution at the α-position has the most profound influence on the rate.

Introduction

The photopolymerization process is widely used in today's industrial market to convert liquid monomer rapidly to solid polymer for a variety of applications. These applications include inks, coatings, adhesives, stereo-lithography,[1−3] dental restoratives,[4−6] and contact lenses.[7,8] The photopolymerization curing mode is utilized for numerous reasons, which include solvent-free polymerizations, energy efficiency, and spatial and temporal control. However, there are several limitations to the photopolymerization process that restrict the industrial viability of these materials. These limitations include residual unstaturation,[9,10] oxygen inhibition,[11−13] low polymerization rate, and reduced polymer properties. A typical method to increase the polymerization rate of acrylic systems is to utilize monomers with more than one vinyl group. By increasing the monomer functionality, diffusional limitations are encountered earlier in the polymerization, and thus, termination is more restricted. The reduction in termination leads to more profound autoacceleration and increased polymerization rates. Additionally, in this case, cross-linked materials are formed, which leads to increased modulus and hardness. Unfortunately, increasing the cross-linking density additionally leads to brittleness and residual unsaturation, leading to polymer property variations with age and possible biocompatibility issues. These tradeoffs between polymerization rate, polymer properties, and residual unsaturation are a key constituent in the development and selection of monomers for use in polymerization applications. There has been a long-standing desire to counteract these limitations and develop monomers that polymerize to a higher extent of reaction with greater polymerization rates.

Decker et al. have developed a novel class of monoacrylate monomers that react extremely rapidly despite having only one vinyl group and still form cross-linked, insoluble polymer early in the polymerization.[3,14−18] These polymers are characterized by a unique combination of excellent hardness and flexibility in the same material. These novel acrylates were designed to include secondary functionalities such as carbonate, cyclic carbonate, carbamate, and oxazolidone moieties.[14,15] The polymerization rate was most rapid for a monoacrylate containing both cyclic carbonate and linear carbonate secondary functionalities.[14] Additional novel monoacrylate monomers that exhibit similar enhanced polymerization characteristics were developed and analyzed in our laboratory.[19−21] Unfortunately, the exact mechanism or mechanisms by which these unique polymer properties develop are yet to be fully understood.

Three distinct mechanistic theories to account for the enhanced reactivity of these monoacrylates have been advanced: (1) hydrogen abstraction/chain transfer, (2) hydrogen bonding, and (3) electronic and resonance effects. Decker et al. first proposed a highly efficient hydrogen abstraction mechanism to account for the increased reactivity and cross-linked polymer formation, implicating the labile hydrogens associated with the secondary functionality as the abstractable species.[2,22] In addition to hydrogen abstraction, hydrogen bonding may also contribute to the increased reactivity by increasing monomer ordering and subsequently increasing the efficiency of radical propagation through the prealigned double bonds.[23] Furthermore, hydrogen bonding increases the overall viscosity of the bulk monomer solution, thus hindering radical termination and causing an increase in radical concentration during polymerization. This increase in radical concentration will directly increase the polymerization rate. Recently, in a systematic study of monomethacrylate monomers with varying secondary functionalities and end groups, Berchtold et al. determined that hydrogen bonding appears

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to have an impact on the polymerization characteristics of these monovinyl monomers.[24] Nonetheless, by systematically varying the polymerization temperature, it was determined that the polymerization rate was relatively unaffected by temperature. This study demonstrated that hydrogen bonding may be important but is not the central factor affecting reactivity.

Finally, electronic and resonance effects may also impact the reactivity of these monoacrylate monomers. Specifically, resonance may allow for such mechanisms as an increase in the amount of labile hydrogens or (de)-stabilization of radicals. Recently, Jansen et al. have developed the theory of increasing polymerization rate with increasing dipole moment of the monomer.[25−27] In this dipole moment theory the polymerization rate increases linearly with dipole moment when the overall dipole moment of the solution exceeds a threshold value of 3.5 D. Recently, experimental data have shown that the resonance and electronic effects do not appear to be the primary source of the enhanced reactivity for a specific class of novel monomers. Novel acrylic monomers with a carbamate functionality and aryl end group were synthesized with differing electron-withdrawing and electron-donating substituents attached to the aryl end group.[28] These monomers have varying overall dipole moments, ranging from 1.8 to 3.7 D. Additionally, a high dipole moment solvent was added to the higher dipole moment monomers to create a greater overall dipole moment medium (∼4.3 D). In all cases, there did not appear to be a clear correlation between electronic and resonance effects and overall polymerization rate. These three mechanistic theories are interrelated and are extremely difficult to decouple in experimentation, but specific experiments can be developed to emphasize each of the above mechanisms individually to test their validity.

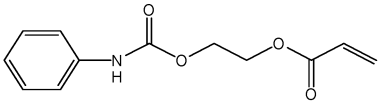
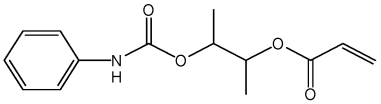
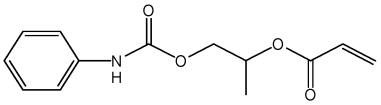
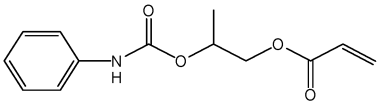
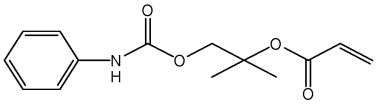
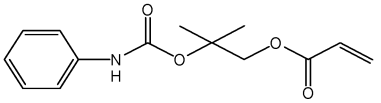
Each of the three mechanistic theories has been shown to affect polymerization rates in certain monomer systems. However, no clear explanation for the dramatically enhanced reactivity of these monomers relative to standard monoacrylate momomers has been identified. Hydrogen-bonding and electronic and resonance effects appear to contribute to the reactivity of the monomers but do not appear to be the primary contributors.

This work develops and analyzes the possibility of hydrogen abstraction from a two-carbon aliphatic spacer group between the acrylic moiety and the secondary functionality. This research expands on previous work where the base monomer is a monoacrylate with an aryl carbamate secondary functionality. However, in this research, the two-carbon aliphatic spacer group is methyl-substituted at the α and/or β carbon positions. This systematic aliphatic spacer group methylation is designed to test for the possibility of hydrogen abstraction from the spacer group and to provide an indication of the primary abstraction site, if present.

Experimental Section

Materials. All monomers evaluated in this work were synthesized in our laboratory. Table 1 gives the molecular structures of all monomers studied. Synthesis and purification information can be found in the Supporting Information. In all cases no inhibitors were added to the monomers. All samples were initiated with 0.1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA), purchased and used as received from Ciba Geigy (Hawthorne, NY).

Table 1. Molecular Structures of All Monomers Studied

Monomer	Monomer Stucture
Phenyl Carbamate Acrylate	
Phenyl Carbamate α,β-Methyl-Acrylate	
Phenyl Carbamate α-Methyl-Acrylate	
Phenyl Carbamate β-Methyl-Acrylate	
Phenyl Carbamate α,α-Dimethyl-Acrylate	
Phenyl Carbamate β,β-Dimethyl-Acrylate	

FTIR Analysis. Conversion vs time profiles for all monomers were determined via steady-state analysis using real time Fourier transform infrared (RT-FTIR) spectroscopy.[29−31] Conversion data were obtained by monitoring the decay of the acrylate double bond peak, either ∼1630 cm^{-1} (C═C stretching vibration) or ∼810 cm^{-1} (C═C twisting vibration), using a Nicolet Magna 760 FTIR spectrometer (Madison, WI) with an XT-KBr beam splitter and MCT/B detector. The temporal resolution for this instrument is approximately 200 ms. For ease of sample handling, a custom horizontal transmission accessory (HTA) was utilized to allow for the samples to remain in a horizontal configuration during analysis.[4,32] All samples were placed between NaCl crystals to form a laminate and were irradiated with 5 mW/cm^2 ultraviolet (UV) light (filtered and centered at a wavelength of 365 nm) from an EXFO Ultracure 100ss (Mississauga, Ontario, Canada) light source; steady-state irradiation duration was 5 min. Additionally, all samples were preheated to a temperature of 67 °C for analysis using a custom temperature cell,[19,24] since most of the monomer samples are solids or highly viscous liquids at room temperature.

Kinetic parameter data were determined via unsteady state analysis, utilizing similar RT-FTIR methodology as described above. Unsteady state analysis is equivalent to the steady state analysis, except the UV irradiation is extinguished prior to complete conversion and the dark polymerization is monitored. To calculate the kinetic parameters, the reaction diffusion coefficient is first determined from the following equation:[4,29,33]

$$\Delta[\mathrm{M}] = \frac{1}{2R}\ln(2RR_{\mathrm{p0}}t + 1) \qquad (1)$$

where Δ[M] is the change in double-bond concentration in the dark, R is the reaction diffusion coefficient, defined as the ratio of the termination kinetic constant over the propagation termination constant times the double-bond concentration ($k_t/k_p[\mathrm{M}]$), R_{p0} is the polymerization rate at time zero (shutter closed) in the dark, and t is the time that the double-bond concentration is monitored in the dark. To decouple the kinetic constants, the reaction diffusion coefficient is combined with

the steady state rate expression (eq 2) just prior to the extinction of light.

$$R_p = \frac{k_p}{k_t^{1/2}}[M]\left(\frac{R_i}{2}\right)^{1/2} \quad (2)$$

In eq 2, R_i is defined as the initiation rate.[34] It is very important to note that the kinetic constants for propagation and termination calculated by this method are apparent kinetic parameters that lump in many different reactions and radical types for both propagation and termination. For these systems, it is not possible to perform PLP/SEC experiments because of the extremely high chain transfer rates and the tendency to form gel at low conversions.

Molecular Modeling. Globally minimized molecular models of specific monomers were evaluated to determine possible conformational effects on the reactivity of these monomers. To perform these molecular models, CAChe 4.5 (Fujistu America, Inc., Sunnyvale, CA) was utilized to determine the lowest energy conformations of the monomers. In these simulations each molecule was first globally minimized twice via an augmented molecular mechanics MM2 simulation, followed by a semiempirical AM1 simulation to determine the lowest energy conformation of the molecule.

Results

The theory of hydrogen abstraction proposed is that the labile hydrogens associated with the secondary functionality lead to a highly efficient hydrogen abstraction/chain transfer reaction. Recent results that tested the possibility of electronic and resonance effects on the overall polymerization rate indicate a possible contradiction to this hydrogen abstraction theory from the secondary functionality and end group. In these experiments a monoacrylate with a carbamate secondary functionality and a perfluorinated aryl end group was synthesized, and subsequent steady state analysis of this monomer showed only a 2-fold decrease in polymerization rate with respect to the hydrocarbon analogue, with no major inhibition or slow initial polymerization rate.[28] On the basis of the assumption that abstraction occurs from the aryl ring, a more profound decrease in polymerization rate would be expected, since the fluorines are not prone to abstraction. Additionally, it was found that very little cross-linking occurred in these systems, including the unsubstituted monomer. Thus, the end group does not appear to be the location for abstraction in these molecules. Additionally, experiments by Berchtold with other monomer structures indicate that hydrogen abstraction from the secondary functionally may not be occurring.[19] Berchtold synthesized and analyzed a monoacrylate monomer with a carbamate secondary functionality and benzyl end group where the N−H of the carbamate was substituted with a methyl group (N−CH_3). Steady state polymerization of this monomer revealed that the polymerization rate of this monomer was slower than the unsubstituted monomer. However, the reduction in polymerization rate was solely attributed to the reduction in viscosity, leading to an increase in mobility, due to the elimination of the strong hydrogen bond donor. Thus, it appears that hydrogen abstraction from the secondary functionality and end group is not the primary mechanism for the enhanced polymerization rates.

Recent results utilizing the primary isotope effect of deuteriums have indicated the profound effect of hydrogen abstraction on the overall reactivity of several novel acrylate monomers.[19,35] Experiments were conducted where the hydrogens on the aliphatic spacer group between the carbamate secondary functionality and the acrylic moiety were exchanged with deuteriums. Deuterated acrylate monomers had a very slow initial polymerization rate that autoaccelerated into a maximum polymerization rate that was 4 times lower than that of the undeuterated monomer.[35] Therefore, hydrogen abstraction does appear to be a key and rate-limiting reaction in the overall reactivity of these monomers.

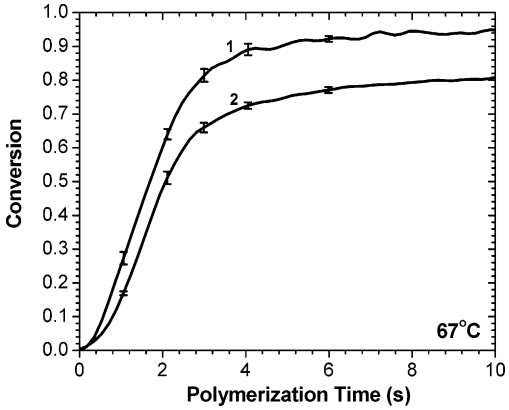


Figure 1. Acrylate conversion vs time for α,β-substituted monomer. Phenyl carbamate acrylate (1) and phenyl carbamate α,β-methyl acrylate (2) are shown. Only a slight initial decrease in polymerization rate is demonstrated by the substituted monomer; otherwise, polymerization rate profiles are similar. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2 and 67 °C.

Here, we explore further the possible importance of hydrogen abstraction from the aliphatic spacer group and the impact of this abstraction on the polymerization rate of the monomer. Systematic studies were performed where the aliphatic spacer group was substituted with methyl groups, and the effect on the steady state polymerization rate was analyzed.

α,β-Dimethyl Acrylate. Initial studies have implicated the aliphatic spacer group as the location for hydrogen abstraction; however, it is uncertain which carbon is the active site for this hydrogen abstraction. Systematic elimination of hydrogen abstraction sites by methylation allows for insight into the possible active center for the abstraction. The first methylation experiment utilized a single methyl at each of the α and β carbons of the spacer group. The addition of the methyl groups to the molecule has a 3-fold effect on hydrogen abstraction. First, each methyl group will remove a single hydrogen from the molecule that could have otherwise been abstracted. Second, the addition of the methyl group increases the stability of a radical at that specific carbon, thus allowing for the possibility of increased hydrogen abstraction from that site. Third, the methyl substituents will act as a steric hindrance to abstraction from the aliphatic spacer group, thus possibly reducing the total hydrogen abstraction from the spacer group. Because of the symmetry of the molecule, the single methylation of the α and β carbons will not reveal the major site of the hydrogen abstraction; however, it will give a greater indication into the possible abstraction mechanism hypothesized for enhanced reactivity of this novel monomer. Figure 1 shows the steady state polymerization rate of the unsubstituted and methylated molecules, and Table 2 gives the $R_{p,max}$ and time for the polymerization to proceed from 10 to 50% conversion for all monomers studied. Figure 1 and Table 2 show that there is not a significant

Table 2. Maximum Polymerization Rate, Polymerization Time Required To React from 10 to 50% Conversion, and Polyerization Time Required To React from 0 to 65% Conversion for all Unsubstituted and Substituted Monomers Studied

spacer substitution	$R_{p,max}$ (1/s)	$t_{x=10-50\%}$ (s)	$t_{x=0-65\%}$ (s)
unsubstituted	0.36 ± 0.03	1.2	2.1
α,β-methyl	0.35 ± 0.03	1.3	2.8
α-methyl	0.34 ± 0.02	1.3	2.7
β-methyl	0.28 ± 0.02	1.6	3.0
α,α-dimethyl	0.08 ± 0.02	20	39
β,β-dimethyl	0.16 ± 0.02	3.1	5.6

difference in reactivity between the methylated and nonmethylated phenyl carbamate acrylate monomer. There is a slight difference in initial reactivity, as the nonmethylated monomer reacts more rapidly at the initial stages of polymerization. Nevertheless, there is no significant difference in the maximum polymerization rates of the two monomers. Additionally, there is not a significant difference in the time for each monomer to polymerize from 10 to 50% conversion. The explanation for the steady state results is theorized to be dependent on the unique combination of reducing the number of abstractable hydrogens while simultaneously changing the resulting radical to a tertiary radical. In general, tertiary radicals are more stable than secondary radicals, and this stable tertiary radical may stifle secondary reactions at the onset of polymerization. Thus, the initial polymerization rate would be slower in the substituted monomer until the secondary reactions that may facilitate increased reactivities occur, allowing for approximately equivalent polymerization rates in the substituted and unsubstituted monomers.

Because of the symmetric nature of the aliphatic spacer group, the α,β-disubstituted monomer does not give much insight into the possible hydrogen abstraction location on the aliphatic spacer group. To gain greater insight into the possible hydrogen abstraction location, methylation solely on either the α or β carbon is required.

α(β)-Methyl Acrylate. To discern possible site-specific abstraction effects, monomers with single methylation at the α or β carbon were synthesized. These monomers allow the individual carbons in the spacer group to be analyzed for their effect on the polymerization rate. Figure 2 shows the steady state polymerization rate of the two singly methylated monomers. The steady state results of the singly methylated monomers greatly resemble that of the α,β monomer results. Specifically, there is a slightly lower initial polymerization rate, which autoaccelerates into a maximum polymerization rate that mimics that of the unsubstituted monomer. More specifically, the β-substituted monomer attains a maximum polymerization rate that is marginally slower than that of the unsubstituted monomer, and the α-substituted monomer nearly matches that of the unsubstituted monomer. Because of the initially slower polymerization rate, it is again hypothesized that the addition of the methyl groups promotes hydrogen abstraction and the formation of more stable tertiary radicals. Again, these stable tertiary radicals may suppress secondary reactions that could lead to increased polymerization rates at the onset of polymerization. Once these secondary reactions occur, the polymerization rates of the substituted and unsubstituted monomers would become approximately equivalent.

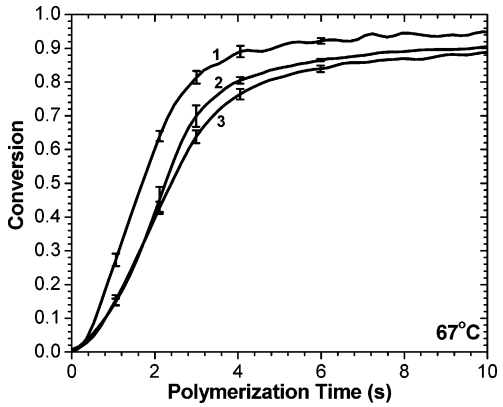


Figure 2. Acrylate conversion vs time for α- and β-substituted monomers. Phenyl carbamate acrylate (1), phenyl carbamate α-methyl acrylate (2), and phenyl carbamate β-methyl acrylate (3) are shown. Again, only a slight initial decrease in polymerization rate is demonstrated by the substituted monomers; otherwise, polymerization rate profiles are similar. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2 and 67 °C.

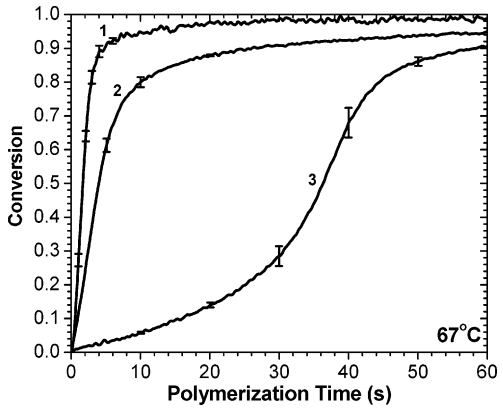


Figure 3. Acrylate conversion vs time for α,α- and β,β-substituted monomers. Phenyl carbamate acrylate (1), phenyl carbamate β,β-methyl acrylate (2), and phenyl carbamate α,α-methyl acrylate (3) are shown. The α,α-substituted monomer shows a greatly reduced polymerization rate profile as compared to the unsubstituted monomer. Additionally, the β,β-substituted shows a slightly decreased polymerization rate profile as compared to the unsubstituted monomer. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2 and 67 °C.

As with the α,β-disubstituted monomer, the results of the singly methylated monomer studies do not significantly indicate which, if either, of the spacer group carbons contribute to the enhanced reactivity. Thus, studies with dual methylation on either the α or β carbon are required to discern the possible effects of this proposed hydrogen abstraction. The dual methylation eliminates any possible hydrogen abstraction from one of the spacer group carbons.

α,α(β,β)-Dimethyl Acrylate. Figure 3 shows the steady state results of the α,α- and β,β-dimethylated monomers. From these steady state results it is evident that the α,α-dimethylated monomer shows a slow initial polymerization rate which autoaccelerates at about 20% conversion. This autoacceleration leads to a maximum polymerization rate that is approximately 4 times lower than the maximum rate of the unsubstituted monomer. Conversely, the β,β-dimethylated monomer does not show this slow initial polymerization rate. Instead, early in the polymerization, this monomer attains a maximum rate that is only approximately half that of the unsub-

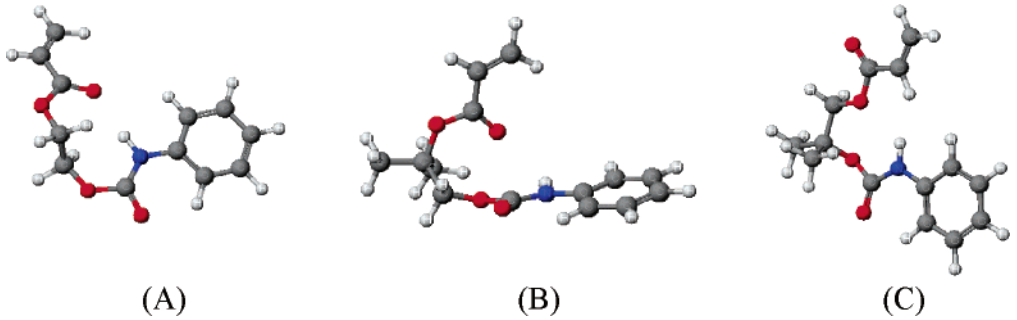


Figure 4. Globally minimized molecular structures of the unsubstituted (A), α,α-disubstituted (B), and *β*,*β*-disubstituted (C) monomers. From these molecular models, it does not appear that the secondary functionality sterically hinders the radical chain end to an extensive degree, except for the *β*,*β*-disubstituted monomer.

stituted monomer. From these steady state results, it appears that the α carbon is the predominate site for hydrogen abstraction, leading to enhanced reactivity of these novel monomers. The evidence stems from the extremely slow initial polymerization rate, delayed autoacceleration, and a maximum polymerization rate that is comparable to that of a typical monoacrylate.

Despite complex polymerization reactions that are not completely known, it is important to ascertain the kinetic relationships that lead to the variation in the reactivity of the disubstituted monomers. To discern the kinetic relationships of these monomers, unsteady state analyses were performed to determine the apparent or overall kinetic constants of each monomer at approximately 50% conversion. These unsteady state results entail extinguishing the light at various extents of conversion and monitoring the dark polymerization. It is important to note that numerous reactions are occurring during the polymerization process, such as propagation, backbiting, and chain transfer to monomer and polymer. The calculated kinetic constants reported here are apparent or overall values for propagation and termination. However, since a consistent method was utilized to determine these values for each monomer, qualitative analysis and comparison of the kinetic relationships with respect to reactivity is feasible.

Using the aforementioned unsteady state analysis, the average propagation and termination kinetic constants for the unsubstituted and α,α- and *β*,*β*-substituted monomers were determined. The average propagation kinetic constant for the unsubstituted, α,α, and *β*,*β* monomers are 2×10^4, 7×10^3, and 3×10^4 L/(mol s), respectively, while the average termination kinetic constant for the unsubstituted, α,α, and *β*,*β* monomers are 7×10^4, 2×10^5, and 7×10^5 L/(mol s), respectively. For comparison, the average propagation and termination kinetic constants for butyl acrylate at 20 °C determined via PLP/SEC and subsequent simulations are 7.6×10^3 and 3×10^7 L/(mol s), respectively.[36] The unsteady state results indicate that the α,α-disubstituted monomer exhibits a sharp decrease in the apparent propagation kinetic constant with a slight increase (2-fold) in the apparent termination kinetic constant. Moreover, the apparent propagation kinetic constant value for the α,α-substituted monomer is closer to that of a typical monoacrylate, such as butyl acrylate.[36] From inspection of the steady state polymerization rate equation (eq 2), it is the 3-fold decrease in propagation and 3-fold increase in termination that is responsible for the 5-fold decrease in the maximum polymerization rate of the α,α-disubstituted monomer as compared to the unsubstituted monomer. Thus, the kinetics of the α,α-disubstituted monomer are approaching that of traditional monoacrylate monomers. However, the *β*,*β*-substituted monomer still demonstrates the characteristics of enhanced reactivity associated with the novel class of monomers. More specifically, the apparent propagation kinetic constant for the *β*,*β*-disubstituted monomer is approximately 1.5 times greater than that of the unsubstituted monomer, but the apparent termination kinetic constant is approximately 10 times greater than the unsubstituted monomer. The large increase in the termination reaction does not have a obvious explanation at this point. Again, inspection of the steady state polymerization rate equation reveals that the 2-fold decrease in the *β*,*β*-substituted monomer rate is due to the approximately 10-fold increase in the termination kinetic constant. From the apparent kinetic constants it is evident that elimination of the hydrogens at the α-position decreases the reactivity of this monomer drastically.

A potential explanation for the increased reactivity of the unsubstituted monomer relies on steric blocking of the radical chain end by the bulky secondary functionality. This steric blocking of the radical chain end would limit the two sterically blocked chain ends from terminating, leading to a sharp decrease in the termination kinetic constant. This hypothesis is supported by the unsubstituted monomer kinetic constant evaluation, as the termination in this monomer is greatly decreased over traditional monoacrylates. However, this hypothesis is not supported by molecular modeling data of the three monomers studied herein. Figure 4 shows the globally minimized conformations of the unsubstituted and α,α- and *β*,*β*-disubstituted monomers, with intramolecular hydrogen bonding taken into consideration. As seen from this figure, in the unsubstituted and α,α-disubstituted monomers, the bulky secondary functionality is distant from the radical chain end and does not appear to cause significant steric blocking. However, in the *β*,*β*-disubstituted monomer (Figure 4C), the secondary functionality does appear to have a potential steric blocking effect on the radical chain end despite having the largest apparent termination kinetic constant of the three monomers. Thus, steric blocking of the radical chain end leading to decreased termination does not appear to be the primary source of the increased reactivities in these monomers.

From the results presented here, hydrogen abstraction from the α carbon remains as a likely primary mechanism leading to the enhanced polymerization kinetics of these novel monoacrylates. However, from the steady state polymerization characteristics of the α,α-substituted monomer, it appears that substitution

at the β-position may also contribute to the reduced reactivity. There are two distinct indications of the substitution effect at the β-position. First, apparent kinetic constants for the α,α-disubstituted monomer, specifically the propagation kinetic constant, remain elevated as compared to traditional monoacrylate monomers. If abstraction were occurring only from the α-position, removal of all hydrogens from this position would render the kinetic constants much closer to traditional monoacrylate monomers. The shape of the steady state polymerization conversion of the α,α-substituted monomer is indicative of the remaining importance of the β-position. As shown, the conversion curve initially shows a slow polymerization rate and begins to autoaccelerate at approximately 20% conversion, thereafter attaining the maximum polymerization rate. If abstraction were occurring solely from the α-position, the monomer would polymerize in a fashion more characteristic of a monoacrylate forming linear polymer and exhibit little to no autoacceleration.

Conclusions

Novel monoacrylate monomers were synthesized with methyl substituents attached to the two-carbon spacer group between the acrylic moiety and the secondary functionality. These monomers were designed to test for the effect of hydrogen abstraction on the polymerization rate. Steady state results indicated that single methylation on one or both of the carbons had little impact on the polymerization characteristics. However, steady state results of the α,α-dimethylation showed a drastic polymerization rate reduction. Unsteady state results for the α,α-dimethylated monomer showed that the apparent propagation kinetic constant is decreased 3-fold, while the apparent termination kinetic constant is increased 2-fold; moreover, these kinetic constants approach those of traditional monoacrylate monomers. Conversely, β,β-dimethylation showed only a mild polymerization rate reduction. These results are consistent with the majority of the hydrogen abstraction occurring at the α carbon, while hydrogen abstraction from the β carbon contributes minimally to the polymerization rate characteristics. Thus, the polymerization rate is most drastically influenced by substitution at the α carbon.

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Supporting Information Available: Synthesis and purification methods for all monomers analyzed herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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