Effect of Aryl Substituents 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 that of typical monoacrylate monomers. Systematic studies were conducted by varying electron-withdrawing and electron-donating substituents on the aryl moiety. Two primary hypotheses were studied, which were that resonance and electronic effects or hydrogen-bonding effects lead to enhanced reactivity. Kinetic evaluations of these substituted monomers revealed that electronic and resonance effects are not the primary source of the increased reactivity. Moreover, correlations of dipole moment calculations with steady-state polymerization rate behavior revealed that dipole moment is also not the primary source of the increased reactivity. However, comonomer studies showed that, by adding the novel monoacrylate monomers to more slowly polymerizing traditional acrylate monomers, the overall reactivity of the mixture could be increased dramatically, revealing a possible use as reactive diluents. Additionally, hydrogen-bonding strength was analyzed and correlated with steady-state polymerization rate behavior. The hydrogen-bonding and N−H polarization strength of the monomers is not the primary source of the increased reactivity.

Introduction

Photopolymerization is a well-established technique for converting liquid monomer into a highly cross-linked solid polymer within seconds. These photopolymers are used in a wide variety of applications, which include inks, coatings, adhesives, stereolithography,[1−3] dental restoratives,[4−6] and contact lenses.[7,8] However, even though this photopolymerization practice is well established, there are still limitations to this process. These limitations include residual unsaturation, oxygen inhibition,[9] polymerization speed, and polymer properties. A typical method to increase the polymerization rate is to utilize monomers with more than one vinyl group. By increasing the monomer functionality, diffusion limitations are encountered earlier in the polymerization, and thus, termination is hindered earlier in the polymerization. This early reduction in termination leads to stronger autoacceleration and greater polymerization rates. Additionally, in this case, highly cross-linked materials are formed, which leads to increased modulus, hardness, and brittleness. Unfortunately, increasing the cross-linking density leads to the residual unsaturation. This tradeoff between polymerization rate and residual unsaturation is 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.

Recently, 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 upon polymerization.[3,10−14] Additionally, these polymers are characterized by a unique attribute exemplified by the combination of 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.[10,11] The polymerization rate was most rapid for a monoacrylate containing both cyclic carbonate and carbonate secondary functionalities. Unfortunately, the exact mechanism or mechanisms by which these unique polymer properties develop are yet to be fully understood.

Three main mechanistic theories for the possible enhanced reactivity of these monoacrylates have been hypothesized, which include hydrogen abstraction and subsequent chain transfer, hydrogen bonding, and electronic and resonance effects. Decker et al. first proposed a highly efficient hydrogen abstraction mechanism and subsequent chain transfer reaction to account for the increased reactivity and cross-linked polymer formation, implicating the labile hydrogens associated with the secondary functionality as the abstractable species.[1] In addition to hydrogen abstraction, hydrogen bonding may also contribute to the increased reactivity by increasing monomer order and subsequently increasing the efficiency of radical propagation through the aligned double bonds.[15] Furthermore, hydrogen bonding will increase the overall viscosity of the bulk monomer solution, thus hindering radical termination and causing an increase in radical concentration. This increase in radical concentration increases the polymerization rate. 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.[16,17] In this dipole moment theory, the polymerization rate

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Table 1. Chemical Formulas and Melting Point Ranges for the Phenyl Carbamate Acrylate Monomers Utilized in the Unsteady-State Analyses

monomer	chemical formula	mp (°C)
phenyl carbamate acrylate	$C_{12}H_{13}NO_4$	66−68
p-fluorophenyl carbamate acrylate	$C_{12}H_{12}FNO_4$	64−66
m-fluorophenyl carbamate acrylate	$C_{12}H_{12}FNO_4$	71−73
o-fluorophenyl carbamate acrylate	$C_{12}H_{12}FNO_4$	46−48
pentafluorophenyl carbamate acrylate	$C_{12}H_8NF_5O_4$	43−46
p-methoxyphenyl carbamate acrylate	$C_{13}H_{15}NO_5$	52−54
m-methoxylphenyl carbamate acrylate	$C_{13}H_{15}NO_5$	<25
o-methoxyphenyl carbamate acrylate	$C_{13}H_{15}NO_5$	<25

increases linearly with dipole moment when the overall dipole moment of the solution exceeds a threshold value of 3.5 D. 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.

This work develops and analyzes monoacrylate monomers with a carbamate secondary functionality that incorporates an aryl moiety with electron-withdrawing or electron-donating substituents to discern possible mechanisms for the enhanced monomer reactivity. Specifically, the base monomer is a phenyl carbamate ethyl acrylate, and substitutions to the phenyl ring of this monomer facilitate focusing on the electronic and resonance effects, with a minor emphasis on hydrogen bonding. This phenyl carbamate ethyl acrylate monomer was chosen for several specific reasons. First, this monomer exhibits one of the fastest polymerization rates of the novel monomers tested to date.[18] Thus, an increase in the polymerization rate of this monomer will be a large breakthrough into the novel monomer polymerization technology. Second, the aryl moiety allows for systematic variations with electron-withdrawing and electron-donating substituents, which vary both the electronic effects and hydrogen abstraction sites from the aryl moiety. Therefore, with this monomer, several hypotheses can be tested with systematic variations to the base monomer.

Experimental Section

Materials. All novel monoacrylate monomers were synthesized via a reaction of the appropriate phenyl isocyante with 2-hydroxyethyl acrylate and purified via column chromatography (room temperature liquid monomers) or recrystallization (room temperature solid materials), both using 3:1 by volume hexane:ethyl acetate eluent. Table 1 gives the chemical formula and melting point ranges for the monomers used in the unsteady-state analyses. All phenyl isocyanate reactants were purchased from Aldrich Chemical (Milwaukee, WI) and used as received. 2-Hydroxyethyl acrylate was purchased from Aldrich Chemical and vacuum-distilled prior to reaction. Inhibitors were removed from all starting materials and were not introduced into the final monomer products prior to polymerization. *p*-Fluorophenyl carbamate acrylate and *o*-methoxyphenyl carbamate acrylate were polymerized with 30 and 50 wt % propylene carbonate. The propylene carbonate was purchased from Aldrich Chemical and distilled prior to use. Comonomer systems were analyzed in a 50:50 wt % mixture with tetrahydrofurfuryl acrylate. Tetrahydrofurfuryl acrylate was purchased from Aldrich Chemical and vacuum-distilled prior to use. All samples were initiated with 0.1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA), purchased and used as received from Ciba Geigy (Hawthorne, NY).

FTIR Analysis. Conversion vs time profiles for all monomers were determined via steady-state analysis using real time Fourier transform infrared (RT-FTIR).[19−21] 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 a XT-KBr beam splitter and MCT/B detector. All samples were placed between NaCl salt 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 heated to a temperature of 67 °C for analysis using a house-built temperature cell, since most monomer samples are solids at room temperature.

Kinetic parameter data was determined via unsteady-state analysis, utilizing similar RT-FTIR methodology as described above.[6,21,22] 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:

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

where $\Delta[M]$ is the change in double-bond concentration in the dark, R is the reaction diffusion coefficient, defined as $k_t/k_p[M]$, R_{p0} is the polymerization rate at time equal to zero 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.

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

In eq 2, R_i is defined as the initiation rate.

Equation 1 requires that $\Delta[M] \ll [M]$ for valid determination of the reaction diffusion coefficient. For the more reactive monomers, such as the phenyl carbamate acrylate and the *m*-fluorophenyl carbamate acrylate, the $\Delta[M]/[M]$ was at most 0.15. For the less reactive monomers, such as the *p*-fluorophenyl carbamate acrylate and the *o*-fluorophenyl carbamate acrylate, the $\Delta[M]/[M]$ was at most 0.05. In all analyses, even in the cases of the higher $\Delta[M]/[M]$, the least-squares analysis utilizing eq 1 accurately predicted the dark polymerization over the dark conversion range studied, and thus accurate estimates of the kinetic constants were obtained.

Dipole Moment Calculations. Dipole moments of the monomers are determined via a Boltzmann-weighted average using a semiempirical AM1 simulation.[16,17,23] To determine the Boltzmann-weighted dipole moment, the following equation is utilized:

$$\langle D\rangle = \sum_j D_j \frac{e^{-\Delta E_j/RT}}{\sum_i e^{-\Delta E_i/RT}} = \sum_j D_j p_j \qquad (3)$$

where ΔE_j is the difference between the energy of conformation j and the global minimum conformation, R is the ideal gas constant, T is the absolute temperature, and p_j is the probability of finding the molecule in conformation j at the temperature T. Hyperchem 7.0 (Gainsville, FL) was utilized to determine the lowest energy conformations of the monomers. In this program, the dihedral angles of the molecule are varied, and the program compiles 1000 conformations based on randomization and optimization of the dihedral angles. The program keeps the low-energy molecules while the high-energy and duplicate molecules are rejected. Finally, the dipole moments and energies are inputted into eq 3, and the

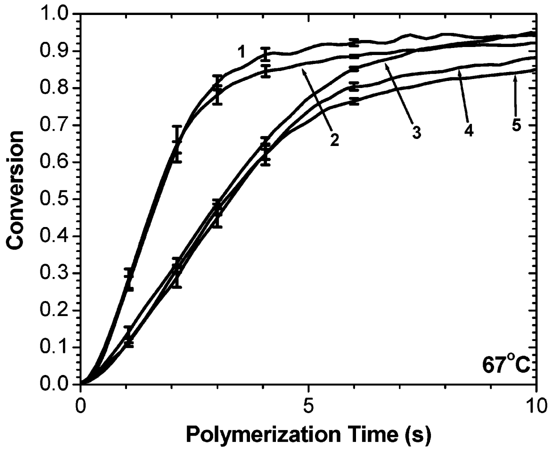

Figure 1. Acrylate conversion vs time for fluoro-substituted phenyl carbamate acrylate monomers studied. Phenyl carbamate acrylate (1), *m*-fluorophenyl carbamate acrylate (2), *o*-fluorophenyl carbamate acrylate (3), *p*-fluorophenyl carbamate acrylate (4), and pentafluorophenyl carbamate acrylate (5) are presented. An approximate 2-fold decrease in polymerization rate over the first 70% conversion is evident for the para-, ortho-, and penta-substituted monomers. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

Boltzmann-weighted dipole moment is determined. For the solution polymerizations, the overall dipole moment of the mixture is determined by the volume-weighted average of the calculated dipole moment for the monomer and the tabulated dipole moment of the solvent.

Results

Monomer reactivity is theorized to be dependent on three molecular contributions, which are hydrogen abstraction, hydrogen bonding, and electronic and resonance effects. Each of these mechanisms are interrelated, but specific experiments can be developed to vary a specific mechanism systematically and individually. This research will focus on electronic and resonance effects, with secondary effects due to hydrogen bonding. The comparison of electronic and resonance effects is accomplished by incorporating electron-withdrawing and -donating substituents at varying positions of the aryl moiety and examining the polymerization rate behavior of the monomer.

Electronic and Resonance Effects. Direct comparison of monomer reactivity can be accomplished via steady-state analysis. Specifically, the quantification of conversion vs time plots is presented for the fluoro-substituted aryl monomers studied (Figure 1). Figure 1 reveals that the meta-substituted and unsubstituted monomers attain approximately equivalent reaction rates. However, the para-, ortho-, and penta-substituted monomers each has approximately a 2-fold decrease in reaction rate as averaged over the first 70% conversion. Kinetic parameter studies were subsequently performed to decipher the cause for the polymerization rate differences among the monomers studied.

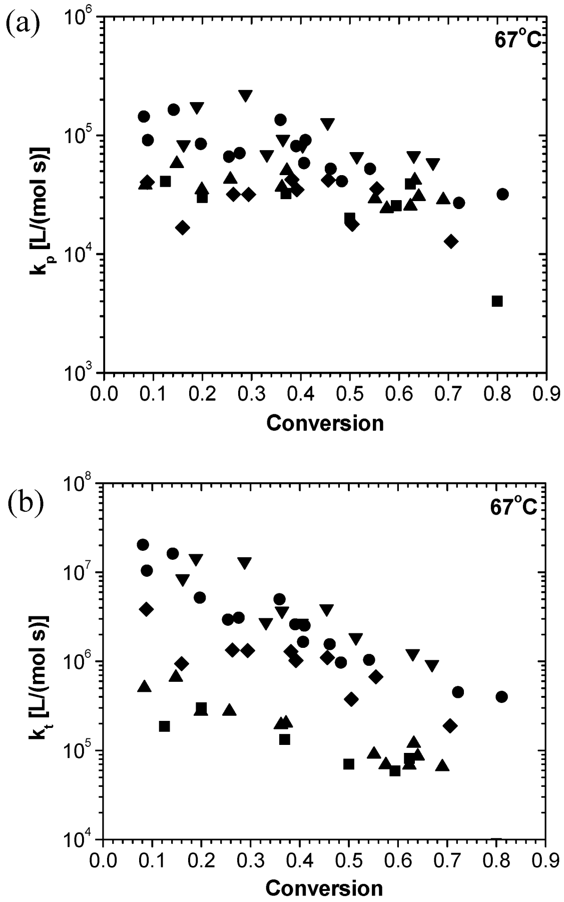

Figure 2. Kinetic constants vs conversion for the fluorinated monomers studied. Propagation kinetic constant (a) and termination kinetic constant (b) are shown. Phenyl carbamate acrylate (■), *p*-fluorophenyl carbamate acrylate (●), *m*-fluorophenyl carbamate acrylate (▲), *o*-fluorophenyl carbamate acrylate (▼), and pentafluorophenyl carbamate acrylate (◆) are presented. The polymerization rate reduction in the para-, ortho-, and penta-substituted monomers is due to the significant increase in termination with respect to the meta-substituted and unsubstituted monomers.

In addition to the steady-state kinetic investigation, unsteady-state analysis can be utilized to gain further insight into the polymerization rate behavior. Unsteady-state analysis involves extinguishing the irradiation source prior to complete conversion and monitoring the polymerization in the dark. On the basis of the dark polymerization reaction, the termination and propagation parameters are deciphered from eqs 1 and 2. The kinetic parameters yielded intriguing and unanticipated results for the monomers studied, as shown in Figure 2. First, for the para- and ortho-substituted monomers, there is an approximate 2-fold increase in the propagation kinetic constant over the unsubstituted and meta- and penta-substituted monomers for polymerization in the conversion range of 20−50%. However, there is a large increase in the termination kinetic constants for each of the para-, ortho-, and penta-substituted monomers over the unsubstituted and meta-substituted monomers for the equivalent range of 20−50% conversion. Specifically, the para- and ortho-substituted monomers show a 10-fold increase in termination, while the penta-substituted shows a 5-fold increase in termination over the meta-substituted and unsubstituted monomers. Upon analysis of the kinetic constants in the steady-state kinetic equation (eq 2), it is evident where the polymerization rate differences occur. All of the reactions have approximately equivalent double-bond concentrations ([M]) and initiation rates (R_i). Thus, the only difference in the steady-state polymerization will arise from the ratio of $k_p/k_t^{1/2}$. Therefore, the roughly 2-fold increase in k_p and the 10-fold increase in k_t translate into an approximate 2-fold decrease in the steady-state polymerization rate as observed over the first 70% conversion.

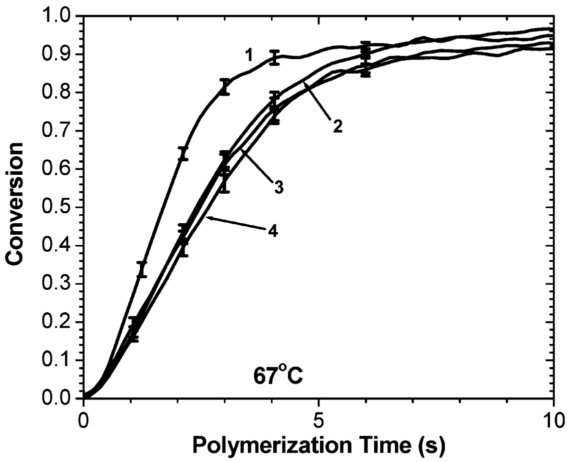

Figure 3. Acrylate conversion vs time for methoxy-substituted carbamate acrylate monomers studied. Phenyl carbamate acrylate (1), *m*-methoxyphenyl carbamate acrylate (2), *p*-methoxyphenyl carbamate acrylate (3), and *o*-methoxyphenyl carbamate acrylate (4) are presented. An approximate 2-fold decrease in polymerization rate over the first 70% conversion is evident for the substituted monomers, independent of substitution position. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

The electron-withdrawing fluorine substituent yielded interesting results with regard to polymerization rate and kinetic constants as compared to the unsubstituted monomer. However, to elucidate further possible mechanistic theories for the increased reactivity of the functionalized monomers, electron-donating substituents were also analyzed for their impact on the polymerization rate and kinetic constants. The combined results from the electron-withdrawing and electron-donating substituents help to clarify the role of electronic and resonance effects in these polymerizations. For these studies, the electron-donating methoxy substituent was incorporated into the monomer at differing positions of the aryl moiety. The steady-state analysis of these monomers is displayed in Figure 3. Figure 3 reveals an approximate 2-fold decrease in monomer reactivity in the first 70% conversion with the methoxy substitution. In comparison to the fluoro-substituted monomers, the meta-substituted methoxy monomer shows a depressed polymerization rate as compared to the unsubstituted monomer.

To gain an understanding of the rate decrease due to the methoxy substitution, unsteady-state analysis was performed. The resulting propagation and termination kinetic parameters are shown in Figure 4. The unsteady-state analyses shown in Figure 4 yielded results that are similar yet slightly differing from those of the fluorine substitution. Figure 4 reveals that methoxy substitution does not impact the propagation kinetic constant as compared to the unsubstituted monomer. Nevertheless, there is a polymerization rate reduction due to a roughly 4-fold increase in the termination kinetic constant for all of the methoxy-substituted monomers as compared to the unsubstituted monomer in the conversion range of 20−50%. Again, application of the steady-state kinetic equation demonstrates this approximate 2-fold decrease in polymerization rate over the first 70% conversion is due to changes in the ratio of $k_p/k_t^{1/2}$.

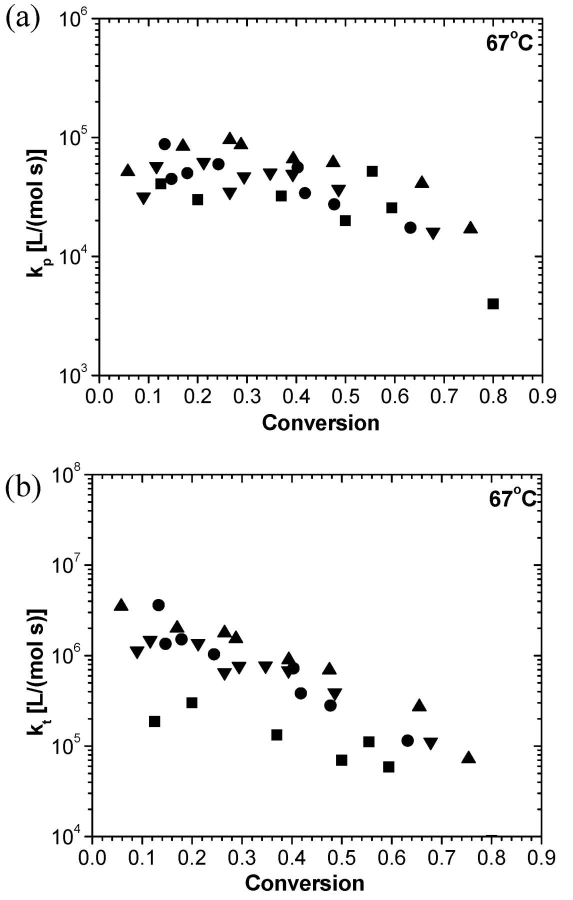

Figure 4. Kinetic constants vs conversion for the methoxy monomers studied. Propagation kinetic constant (a) and termination kinetic constant (b) are shown. Phenyl carbamate acrylate (■), *p*-methoxyphenyl carbamate acrylate (●), *m*-methoxyphenyl carbamate acrylate (▲), and *o*-methoxyphenyl carbamate acrylate (▼) are presented. Polymerization rate reduction of the substituted monomers is due to the significant increase in termination with respect to the unsubstituted monomer.

The results from the fluoro-substituted and methoxy-substituted monomers show that there is at best only equivalence in the polymerization rate, but in most circumstances there is a decrease in polymerization rate with aryl substitution. These polymerization rate results are a clear indication that resonance and electronic effects are not the dominant factor in the enhanced polymerization characteristics of these monomers. To be certain that resonance and electronic effects are not the primary source of the enhanced polymerization characteristics of the phenyl carbamate acrylate monomer, additional electron-withdrawing and electron-donating substituted monomers were synthesized, and a Hammett plot of the steady-state polymerization rate behavior was analyzed. The substituents of these monomers were a methyl group, a trifluorocarbon (CF_3) group, and a cyano group. The methyl group acts as an electron-donating substituent, and the trifluorocarbon and cyano groups act as electron-withdrawing moieties. Figures 5 and 6 show the Hammett plots for all of the para- and meta-substituted monomers studied, where the melting point of the monomer allowed for bulk polymerization. All polymerizations were performed at 67 °C, since most of the monomers studied had melting points above room temperature. However, several monomers synthesized had melting points that far exceeded the 67 °C temperature window, and these samples could not be polymerized in bulk. The Hammett equation utilized to create the Hammett plots is defined as follows:

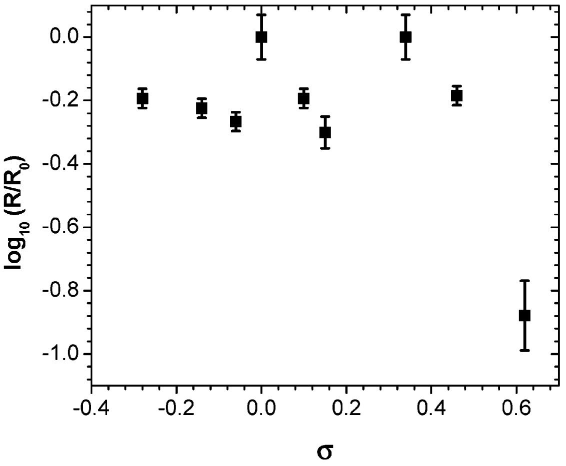

Figure 5. Effect of electron-withdrawing and electron-donating substituents on the reactivity of the phenyl carbamate acrylate. The ordinate of the Hammett plot is the log of the ratio of the polymerization rates averaged over 70% conversion. There is no apparent linear relationship between electronic effects and polymerization rate.

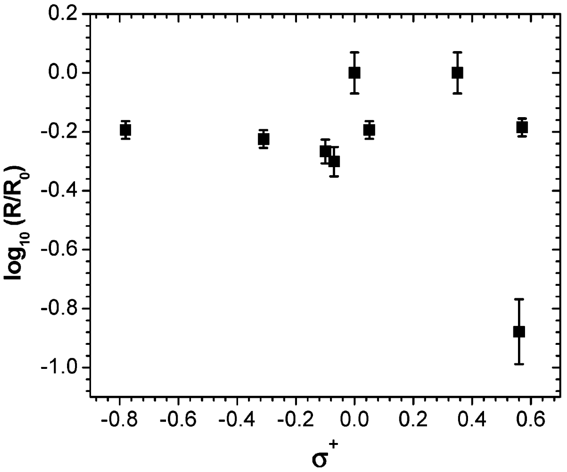

Figure 6. Effect of electron-withdrawing and electron-donating substituents on the reactivity of the phenyl carbamate acrylate where the reaction occurs directly on the aryl moiety. The ordinate of the Hammett plot is the log of the ratio of the polymerization rates averaged over 70% conversion. There is no apparent linear relationship between electronic effects and polymerization rate.

$$\log\left(\frac{R}{R_0}\right) = \sigma\rho \qquad (4)$$

where σ is a measure of the total electronic effects (resonance and electron density at the active center) of the substituent attached to the aryl moiety, where negative σ indicates an electron-donating group and positive σ an electron-withdrawing group, ρ measures the susceptibility of the reaction to electronic effects, and the left-hand side of the equation is the log of the ratio of the polymerization rates, where the polymerization rates are averaged rates from 0 to 70% conversion. In eq 4, a positive ρ indicates that the reaction is helped by electron-withdrawing substituents, and a negative ρ indicates that the reaction is helped by electron-donating substituents. To determine this averaged polymerization rate, the ratio of the polymerization time to reach 70% conversion was calculated since the polymerization rate is inversely proportional to polymerization time. For these ratios, the unsubstituted monomer polymerization time was always in the numerator and the substituted monomer polymerization time was in the denominator. Additionally, two Hammett plots were created—one for σ values and one for σ^+ values. In the first plot, σ measures the susceptibility of the reaction to the electronic effects at the active center, which is the carbamate functionality for this monomer. In the second plot, σ^+ measures the susceptibility of the reaction to the electronic effects when the reaction occurs directly on the aryl ring. In this reaction, an electron-donating group directly interacts with a developing positive charge in the transition state. The Hammett analysis evaluates the effect of electron-withdrawing or electron-donating substituents on the rate-determining step of the polymerization. The functionality under investigation can reduce the time necessary for the rate-determining step, thus allowing enhancing the polymerization rate.

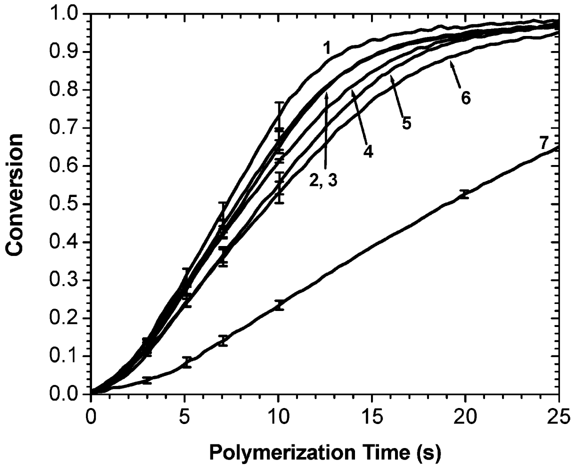

Figure 7. Acrylate conversion vs time for copolymerization studies of fluoro-substituted phenyl carbamate acrylate monomers with tetrahydrofurfuryl acrylate (THFFA) in a 50:50 wt % mixtures. Phenyl carbamate acrylate (1), 3,5-dimetafluorophenyl carbamate acrylate (2), *m*-fluorophenyl carbamate acrylate (3), *o*-fluorophenyl carbamate acrylate (4), *p*-fluorophenyl carbamate acrylate (5), and pentafluorophenyl carbamate acrylate (6) with THFFA are presented. Bulk THFFA (7) is given as reference. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

The results shown in Figures 5 and 6 do not show a clear correlation between electron density and an effect on the rate-determining step in the polymerization, as there is no distinct relationship between polymerization rate and σ or σ^+. These Hammett plot results, along with the results from the fluoro and methoxy substituents, decisively show that resonance and electronic effects do not affect the rate-determining step of the polymerization and thus do not increase the overall reactivity of the monomers studied here. One result seems to vary significantly from the rest of the results, and more work is necessary to deduce why this monomer shows a drastically lower polymerization rate. This anomalous result is the value at sigma equal to 0.62 and is due to the meta-cyano-substituted monomer.

In addition to the bulk polymerizations of the electron-withdrawing and electron-donating substituents, copolymerizations were performed using tetrahydrofurfuryl acrylate (THFFA) as the comonomer in 50:50 wt % mixtures. The THFFA molecule does not incorporate a strong hydrogen bond acceptor; thus, this molecule will act to dissipate some of the total hydrogen bonding in the system. Figure 7 displays the copolymerization

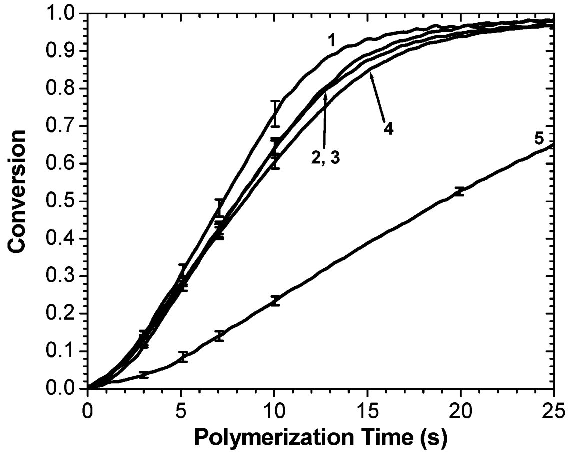

Figure 8. Acrylate conversion vs time for copolymerization studies of methoxy-substituted phenyl carbamate acrylate monomers with tetrahydrofurfuryl acrylate (THFFA) in a 50:50 wt % mixtures. Phenyl carbamate acrylate (1), *p*-methoxyphenyl carbamate acrylate (2), *m*-methoxyphenyl carbamate acrylate (3), and *o*-methoxyphenyl carbamate acrylate (4) with THFFA are presented. Bulk THFFA (5) is given as reference. All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

results for the fluorinated monomers with THFFA. As anticipated, the unsubstituted comonomer system displayed the fastest polymerization rate behavior. Additionally, the para-substituted and penta-substituted comonomer systems exhibited the slowest polymerization rate behavior. However, the comonomer systems in between these two extremes were slightly unanticipated. For instance, the meta-substituted comonomer system exhibited a polymerization rate behavior that was slightly lower than that of the unsubstituted comonomer system. Additionally, the ortho-substituted comonomer system displayed a polymerization rate behavior that was slightly greater than that of the para-substituted and penta-substituted comonomer systems. The aforementioned polymerization rate behavior results were slightly askew from the bulk polymerization results. For example, the meta-substituted comonomer system did not attain a polymerization rate equivalent to the unsubstituted comonomer system. From the data, it appears that the polymerization rates of the substituted monomers are only slightly hindered by the addition of the substituent at the meta position and significantly hindered by the addition of the substituent at the para position. One possible explanation for these comonomer results is due to the decreased overall hydrogen bonding. The decreased hydrogen bonding alters molecular interactions, favoring different conformations with increased or decreased intramolecular interactions. However, there is not a drastic difference in the reactivity trends of the comonomer systems; thus, this hydrogen-bonding reduction does not appear to have a drastic influence on the polymerization characteristics of the fluoro-substituted monomers.

In addition to the fluorinated monomers, the methoxy-substituted monomers were examined in 50:50 wt % mixtures with THFFA as the comonomer. Figure 8 displays the results of these experiments. From Figure 8, it is evident that the methoxy-substituted comonomer systems produced results that are similar to the bulk polymerization results. First, the fastest polymerization rate was observed for the unsubstituted comonomer system, with the substituted comonomer systems showing polymerization rates that are slower than the unsubstituted comonomer system. As seen in the bulk polymerization, the substituted comonomer systems also revealed that the meta-substituted monomer does not show an increase in reactivity over the para- and ortho-subsituted monomers. The reactivity trend similarity of the comonomer polymerizations to the bulk polymerizations indicates that the overall reduction in hydrogen bonding in the substituted monomer systems is approximately equivalent for each monomer, thus allowing for the similar trend in polymerization rates.

In studying these comonomer systems, one trait remained constant throughout all of the analyses, which is a reduction in the polymerization rate of the comonomer with respect to the novel monomer bulk polymerization. This reduction in polymerization rate is due to the addition of the less reactive THFFA to the system. Conversely, it should be noted that these comonomer systems exhibited greatly increased polymerization rates with respect to the bulk THFFA. Thus, these novel monoacrylate monomers are useful as reactive diluents to increase the polymerization rates of less reactive monomers.

Overall, these electronic and resonance effects experiments did not show significant increase in reactivity over the unsubstituted monomer. Only the meta-fluoro substituted monomer displayed a polymerization rate equivalent to the unsubstituted monomer. Aryl substitution appears to have a negative effect on the overall reactivity of the monomer, and the fastest polymerization kinetics are accomplished via unsubstituted monomers.

Dipole Moment Effects. As stated previously, monomer reactivity has been theorized to be directly related to dipole moment. By varying the position and chemistry of the substituents on the aryl ring, the overall dipole moment of the monomer can be altered. Using the Boltzmann-weighted dipole moment method described in eq 3, correlations between dipole moment and monomer reactivity for the novel monomers previously investigated were determined. Table 2 shows the calculated Boltzmann-weighted dipole moments for the fluorinated and methoxy monomers. From Table 2, it is evident that the position and chemistry of the aryl substituent do have a profound impact on the overall dipole moment of the monomer; there is an approximate 2 D variation in dipole moment for the monomers studied. Figure 9 displays the maximum normalized polymerization rate vs the calculated dipole moment. Figure 9 reveals no significant monotonic correlation between calculated dipole moment and monomer reactivity. More specifically, the molecule with the largest calculated dipole moment, pentafluorophenyl carbamate acrylate (3.7 D), was observed to exhibit the lowest maximum normalized rate. Additionally, from Figure 9, it is evident that there are three monomers with dipole moments near the hypothesized threshold of 3.5 D, and the reactivities of these monomers are approximately half that of the monomers with dipole moments far below the threshold dipole moment value. According to the theory proposed by Jansen et al.,[16,17,23] the polymerization rate will increase linearly, starting at approximately 3.5 D. However, 30:70 and 50:50 mixtures by weight of propylene carbonate (dipole moment = 5.0 D) with *p*-fluorophenyl carbamate acrylate and *o*-methoxyphenyl carbamate acrylate (approximate overall dipole moments are 4.0 and 4.3 D, respectively) polymerized with normalized maximum

Table 2. Calculated Boltzmann-Averaged Dipole Moment for the Fluoro-Substituted and Methoxy-Substituted Phenyl Carbamate Acrylate Monomers

monomer	calcd dipole moment (D)	monomer	calcd dipole moment (D)
phenyl carbamate acrylate	2.4	pentafluorophenyl carbamate acrylate	3.7
p-fluorophenyl carbamate acrylate	3.5	*p*-methoxyphenyl carbamate acrylate	2.8
m-fluorophenyl carbamate acrylate	2.9	*m*-methoxyphenyl carbamate	2.8
o-fluorophenyl carbamate acrylate	1.8	*o*-methoxyphenyl carbamate acrylate	3.5

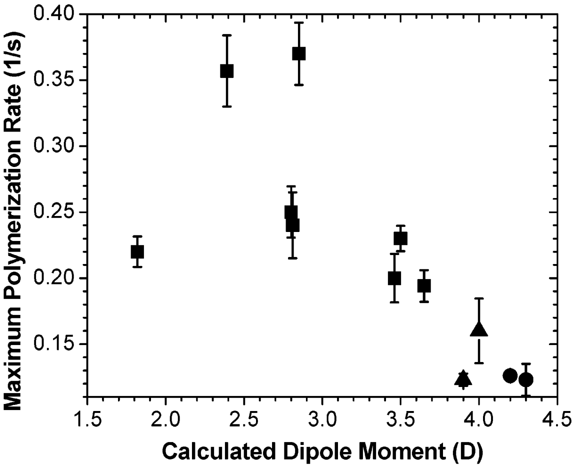

Figure 9. Maximum normalized polymerization rate vs calculated dipole moment. Bulk polymerizations (■), 30:70 wt % (▲), and 50:50 wt % solutions (●) of propylene carbonate in *p*-fluorophenyl carbamate acrylate and *o*-methoxyphenyl carbamate acrylate are presented. There is not an increase in polymerization rate with increasing overall dipole moment. Calculated dipole moments for all bulk monomers can be found in Table 2.

polymerization rates at best approximately equivalent, but in most cases approximately half that of the bulk monomers under identical polymerization conditions. Thus, with the overall dipole moment above the 3.5 D threshold, the theorized polymerization rate increase was not observed. These experiments indicate that the monotonic relationship does not hold for all solutions above the 3.5 D threshold, and the dipole moment theory is not applicable to all monomers.

Addition of a high dipole inert solvent to the monomer will have contrasting implications on the polymerization characteristics. First, simple dilution of the monomer reduces the monomer concentration and additionally influences the solvent cage surrounding the propagating radical. At both 30 and 50 wt % inert solvent, the solvent cage will be affected by the solvent presence, which is hypothesized by Jansen et al. to be partially responsible for the rate enhancement.[16] Dilution effects typically reduce polymerization rates, especially when diffusion-limited termination is occurring. However, it has been theorized that, with the addition of a high dipole moment solvent to create a higher overall dipolar medium, this effect is overcome and higher polymerization rates are achieved. Two theories have been proposed for explaining the limited results in which higher polymerization rates are achieved in the presence of a higher dipolar medium. The high dipole moment solvent leads to a greater charge on the propagating radical and reduced termination, or the higher dipole medium leads to a stronger solvent cage effect and less termination.[16] However, as shown in Figure 9 for the solution polymerizations with propylene carbonate, these theorized dipolar effects were not evident, and the more typical dilution effects were observed.

Cross-Linking Density. In addition to electronic and resonance effects, the ability to cross-link at low conversion has additionally been theorized as a possible mechanism for the enhanced reactivity. Decker et al. showed with oxazolidone and carbamate secondary functionalities cross-linked polymers could be formed nearly at the onset of polymerization.[11] Thus, with the formation of a gel at very low conversions, termination is hindered early in the polymerization and stronger autoacceleration occurs. In this research, cross-linking density was evaluated for the unsubstituted phenyl carbamate acrylate monomer by dynamic mechanical analysis.[24] This monomer was chosen due to the fact that this monomer attains the one of the greatest polymerization rates of all the monomers tested for this research. The DMA analysis on four distinct samples polymerized at 67 °C failed to yield a rubbery plateau, thus indicating that the samples did not obtain a cross-linking density within the tolerance of the apparatus. Additionally, the gel fraction was analyzed utilizing chloroform as the solvent, as chloroform was found to be the best solvent to dissolve the linear or branched polymer. The polymer samples had a gel fraction of 4 ± 1% at approximately 100% double-bond conversion. The small gel fraction is indicative of the typical backbiting and side reactions that allow for limited cross-linking at high conversions in conventional monoacrylates. Thus, low-conversion cross-linking does not appear to occur to great extents in these monomers at these conditions and does not appear to be major source of the enhanced reactivity of the novel monomers studied here.

Hydrogen Bonding. The enhanced reactivity of these novel monomers might be attributed to hydrogen bonding. With hydrogen bonding, molecules can attain a higher degree of alignment that would potentially allow for more efficient radical propagation through the acrylic double bonds.[15] Additionally, hydrogen bonding will increase the overall viscosity of the solution, thus allowing for increased reactivities. However, for the monomers studied in these experiments, initial monomer viscosity is not believed to have a large impact on the polymerization kinetics of these materials, as there is no apparent drastic difference in monomer viscosities. The N−H stretching vibration (~3350 cm^{-1}) gives insight into the prepolymerization extent of hydrogen bonding. However, the infrared band is influenced both by potential hydrogen bonding and the polarizability of the N−H bond. Both hydrogen bonding and N−H polarization will affect the intermolecular interactions of the molecules, with the monomers that have a high N−H polarization, such as the pentafluorophenyl carbamate acrylate, having a larger partial charge on the hydrogen atom.

Table 3 examines the N−H stretch vibrations of the aryl-substituted monomers before polymerization and relates the hydrogen bonding and polarization to the polymerization time necessary to react from 10% to 70% conversion. This analysis allows for a true polymeriza-

Table 3. FTIR Analyzed Prepolymer N−H Stretch of the Methoxy Phenyl Carbamate Acrylate Monomers and the Polymerization Time To React from 10 to 70% Conversion[a]

	$\nu^{NH}_{peak\ max}$ prepolymerization (cm^{-1})	time to reach $X = 10-70\%$ (s)
phenyl carbamate acrylate	3342	1.7
p-fluorophenyl carbamate acrylate	3339	3.7
m-fluorophenyl carbamate acrylate	3339	1.8
o-fluorophenyl carbamate acrylate	3340	3.4
pentafluorophenyl carbamate acrylate	3300	4.0
3,5-difluorophenyl carbamate acrylate	3335	4.8
p-methoxyphenyl carbamate acrylate	3342	3.0
m-methoxyphenyl carbamate acrylate	3342	2.8

[a] Spectra and polymerization measured at 67 °C.

tion rate comparison since any early polymerization effects are neglected. With the exception of the pentafluorophenyl carbamate acrylate, there is only minimal change in the absorption band, and no correlation is found between this band and the polymerization kinetics. Thus, it is evident that neither the strength of hydrogen bonding nor the polarization has a discernible effect on the overall kinetics of the polymerization. The unsubstituted and meta-substituted monomers exhibit the most rapid polymerization rate, while the disubstituted monomer achieves the least rapid polymerization rate. This result contradicts the proposed molecular alignment theory, as the disubstituted monomer has stronger hydrogen bonds and polarization than the unsubstituted or meta-substituted monomers.

Conclusions

Novel monoacrylate monomers were synthesized with varying substituents attached to the aryl ring of the base monomer phenyl carbamate acrylate. These monomers were evaluated using both steady-state and unsteady-state kinetics to decipher possible mechanisms relating to increased reactivity and ability to cross-link. Specifically, the electronic and resonance effects and hydrogen-bonding characteristics were examined. The steady-state analyses indicated that changing the electronic and resonance effects does not have a significant effect on polymerization rate. Additionally, results from the Hammett plot experiments suggested that there is not a strong correlation between electron density and polymerization rate. However, the copolymerization studies showed that, by adding the phenyl carbamate acrylate monomers to the slower tetrahydrofurfuryl acrylate, the polymerization rate of the mixture is significantly faster than the bulk traditional monoacrylate. Thus, these novel monoacrylate monomers can be used as reactive diluents. Dipole moment calculations were correlated with maximum normalized polymerization rates, and these correlations failed to show that dipole moment has an effect on the polymerization rate. Additionally, cross-linking density studies were performed and indicated that low-conversion cross-linking does not occur to a large extent. Thus, cross-linking at low conversion does not appear to be a source of the enhanced reactivity. Finally, hydrogen-bonding and N−H polarization effects were analyzed, and these results failed to yield any obvious polymerization rate correlations.

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References and Notes

(1) Decker, C. *Nucl. Instrum. Methods Phys. Res. B* **1999**, *151*, 22−28.
(2) Bernhard, P.; Hofmann, M.; Schulthess, A.; Steinmann, B. *Chimia* **1994**, *48*, 427−430.
(3) Decker, C.; Elzaouk, B. *J. Appl. Polym. Sci.* **1997**, *65*, 833−844.
(4) Lovell, L. G.; Stansbury, J. W.; Syrpes, D. C.; Bowman, C. N. *Macromolecules* **1999**, *32*, 3913−3921.
(5) Elliott, J. E.; Lovell, L. G.; Bowman, C. N. *Dent. Mater.* **2001**, *17*, 221−229.
(6) Lovell, L. G.; Berchtold, K. A.; Elliot, J. E.; Lu, H.; Bowman, C. N. *Polym. Adv. Technol.* **2001**, *12*, 335−345.
(7) Kunzler, J. F.; McGee, J. A. *Chem. Ind.* **1995**, *16*, 651−655.
(8) Martin, S. J.; O'Brien, J. E.; Dowling, J.; McBrierty, V. J. *Eur. Polym. J.* **1998**, *34*, 1817−1828.
(9) Finger, W. J.; Lee, K.; Podszun, W. *Dent. Mater.* **1996**, *12*, 256−261.
(10) Decker, C.; Moussa, K. *Macromol. Chem.* **1991**, *192*, 507−522.
(11) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 403−411.
(12) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 881−889.
(13) Moussa, K.; Decker, C. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2197−2203.
(14) Decker, C.; Elzaouk, B.; Decker, D. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 173−190.
(15) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Polym. Prepr.* **2001**, *42*.
(16) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2002**, *35*, 7529−7531.
(17) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861−3873.
(18) Berchtold, K. A. Ph.D. Thesis, University of Colorado, 2001.
(19) Decker, C.; Bendaikha, T. *Eur. Polym. J.* **1984**, *20*, 753−758.
(20) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381−2394.
(21) Berchtold, K. A.; Hacioglu, B.; Lovell, L. G.; Nie, J.; Bowman, C. N. *Macromolecules* **2001**, *34*, 5103−5111.
(22) Anseth, K. S.; Decker, C.; Bowman, C. N. *Macromolecules* **1995**, *28*, 4040−4043.
(23) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. Patent WO 02/42383, 2002.
(24) Hill, L. W. *J. Coat. Technol.* **1992**, *64*, 29−42.

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