

Influence of molecular dipole on monoacrylate monomer reactivity

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Abstract

Numerous acrylate monomers have been synthesized and evaluated extensively as a means to explore the relationship between molecular polarity and monomer reactivity. Various monomers, characterized by high values of dipole moment, were polymerized in bulk, and no correlation of dipole moment to monomer reactivity was established. Solution polymerization studies were performed on phenyl carbamate ethyl acrylate and several substituted derivatives to observe the effects of changing solvent polarity on the polymerization kinetics. The results of solution polymerization studies indicated that traditional dilution effects, which suppress the polymerization kinetics, dominate the reactions. Changes in solvent polarity had minimal impact on the polymerization kinetics.

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1. Introduction

Photoinitiated polymerization of acrylates and methacrylates is currently being used for a multitude of applications including dental materials, biomaterials, coatings, polymeric membranes, microfluidic devices and stereolithography [1–6]. However, currently used (meth)acrylates encounter a wide variety of limitations including oxygen inhibition, polymerization shrinkage, residual unsaturation, and photodegradation of the cured product due to the presence of initiator. Because of the wide variety of potential and current applications, design and development of high performance (meth)acrylates have been the focus of great interest.

The works of Decker et al. [7–12] and the more recent works of Bowman et al. [13–16] have shown that incorporation of secondary functionalities such as carbonates, carbamates, cyclic carbonates, and oxazolidones into a

(meth)acrylate functionalized monomer enhances the reactivity of the monomer, with the polymerization rate enhancement being as much as two orders of magnitude compared with typical acrylate esters. This class of novel (meth)acrylates exhibits cure rates rivaling or exceeding those of multifunctional acrylates while also achieving much higher extents of cure. The more rapid curing kinetics of these monomers enables the use of lower light intensities and reduced initiator concentrations. While lower light intensities are well suited for in vivo applications, reduced initiator concentrations facilitate overcoming the drawbacks associated with initiator usage such as discoloration, optical opacity, and photo-degradation of the cured product. Additionally, the combination of reduced initiator concentrations and higher cure extents reduce the risk of residual, unreacted monomer and/or initiator leaching from the cured polymer.

To design monomers having specific polymer properties, an understanding of the unique mechanistic factors leading to the enhanced reactivity would clearly be beneficial. Several theories have been put forward to explain the enhanced kinetics of this class of novel monomers including hydrogen abstraction, hydrogen bonding and molecular dipole. The hydrogen abstraction theory focuses on hydrogen abstraction as a means for leading to cross-linking

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and subsequently suppressed termination [13,14,16–18]. This hypothesis is supported by results that indicate that the termination kinetics are suppressed, whereas the propagation kinetics resemble those of traditional acrylic systems [17,19]. Others have explored the role of hydrogen bonding as a factor important to the enhanced reactivity [14,16,20–22]. Hydrogen bonding increases the viscosity of the system, particularly during early stages of polymerization. The resulting mobility restrictions inhibit termination reactions, which leads to a higher radical concentration, and hence higher reactivity [20]. Also, it has been shown that intermolecular hydrogen bonding between monomers acts like a non-covalent linkage between monomers, causing them to behave in many aspects like multifunctional monomers [20]. This phenomenon also leads to an increase in the polymerization rate.

Alternatively, Jansen and co-workers [21–24] have theorized that for molecules with a high dipole moment, the more polar medium reduces the activation energy for propagation, leading to acceleration in the propagation reaction rate. Also, in a highly polar medium there would be a more organized, tightly held solvent cage around the propagating radical, which would lead to a reduction in the termination rate [21]. Radicals may also have a greater partial charge in a polar medium, resulting in further reduced termination, due to electrostatic repulsion between the radicals. Overall these effects would lead to the observed propagation being favored over termination, causing an observed increase in reactivity. Furthermore, it has been claimed that for monomers or polymerizing mixtures where the average dipole moment exceeds 3.5 debye, the reactivity correlates monotonically with the dipole moment, with molecules possessing higher dipole moment having greater reactivity [24]. Additionally, it has been proposed that for monomers capable of hydrogen bonding, this interaction could further contribute to the enhanced reactivity. Since, both high dipole moment and hydrogen bonding are seen to enhance reactivity; it has been proposed that these effects are complementary [21]. However, though molecular dipole interactions would impact monomer reactivity, recent work done by our group has demonstrated that the molecular dipole does not appear to be the dominant, factor leading to enhanced reactivity [13,16]. Several highly reactive systems with low values of dipole moments have been characterized. Also, studies conducted to observe the impact of spacer length between the secondary functionality and acrylate [25] have shown that variations in the spacer length caused variations in the dipole moment. However, there was no marked difference in the reactivities of the molecules with spacer lengths greater than two.

This work focuses primarily on independently ascertaining the effect of dipole moment through both solution and bulk polymerizations. Solution studies were conducted to investigate the contribution of a high dipole moment solvent on the reactivity of the novel acrylic monomers. Bulk

polymerization studies were performed to examine possible correlations of molecular polarity to monomer reactivity.

2. Experimental section

2.1. Materials

2.1.1. Synthesis of the carbamate ethyl acrylates

The phenyl carbamate ethyl acrylate monomer (Fig. 1) was synthesized by the reaction of phenyl isocyanate with hydroxy ethyl acrylate [13]. Benzoyl carbamate ethyl acrylate and other substituted derivatives of phenyl carbamate ethyl acrylate were similarly synthesized by reaction with benzoyl isocyanate and substituted phenyl isocyanates, respectively [13]. All the isocyanates, and 2-hydroxy ethyl acrylate (HEA), were purchased from Aldrich Chemicals (Milwaukee, WI), and 2-hydroxy ethyl acrylate was vacuum distilled prior to its use in synthesis of other monomers. The monomer 2-cyanoethyl acrylate was purchased from polysciences (Warrington, PA). Hydrogenation of phenyl carbamate ethyl acrylate was carried out using 3 wt% Pd/active C (Aldrich Chemicals, Milwaukee, WI) as the catalyst. The solvents propylene carbonate and ethylene glycol diacetate were obtained from Aldrich Chemicals (Milwaukee, WI) are distilled prior to use. Cyclic carbonate acrylate was prepared by the reaction of 4-hydroxy methyl-1, 3-dioxolan-one (Huntsman, Salt Lake City, Utah), with acryloyl chloride in the presence of triethylamine [21].

2.1.2. Synthesis of cyclic acetal carbamate acrylate [16]

A solution of bis(1,1,1-trichloromethyl) carbonate (Aldrich Chemicals, Milwaukee, WI) in dichloromethane was reacted with a stoichiometric amount of glycerol formal (Aldrich Chemicals, Milwaukee, WI) in the presence of triethylamine. The formation of glycol chloroformate was confirmed by FTIR spectroscopy. The trimethylsilane (TMSi)-protected ethanolamine was prepared by dissolving ethanolamine and 1,1,1,3,3,3-hexamethyldisilazane in toluene and performing the reaction for 5 h at 95–100 °C. The TMSi-O-ethyleneamine solution was carefully added to the glycerol chloroformate solution and the reaction was conducted at ambient temperature overnight. Subsequently, the TMSi-protected glycerol carbamate alcohol

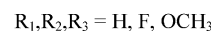
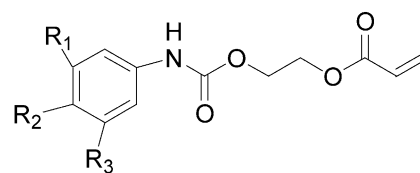


Fig. 1. The molecular structure of the monomer phenyl carbamate ethyl acrylate and its substituted derivatives.

(TMSi-U-acetal) was hydrolyzed at room temperature in a methanol/water solution ($\text{pH} \geq 10$) for 24 h which yielded the glycerol carbamate alcohol. The glycerol carbamate alcohol was reacted with acryloyl chloride in the presence of triethylamine and the resulting product was subsequently washed three times each with 1 wt% NaOH, 1 wt% aqueous HCl, and saturated NaCl then dried overnight using Na_2SO_4 . The product was purified by column chromatography using a silica gel column and a 1:1 volume ratio hexane/ethyl acetate solution as an eluent followed by vacuum distillation.

2.1.3. Synthesis of cyclic acetal acrylates [16]

Cyclic acetal acrylates were synthesized by the reaction of 5-ethyl-1,3-dioxane-5-methanol (Aldrich Chemicals, Milwaukee, WI) with acryloyl chloride in the presence of triethylamine. The resulting product was washed three times with saturated NaCl and dried overnight using Na_2SO_4 . The product was purified by column chromatography using a silica gel column and 3:1 volume ratio hexane/ethyl acetate as an eluent and followed by vacuum distillation. The synthesis of the cyclic acetal acrylates utilizes glycerol formal, which exists as an equilibrium mixture of both a five-membered and six-membered cyclic acetal alcohol. After reaction with acryloyl chloride, the two primary products are separated using flash chromatography and various fractions of mixtures of five-membered and six-membered acetal acrylates are obtained.

2.2. Polymerization

Samples were irradiated with 5 mW/cm^2 intensity light from an ultraviolet light source (Ultracure 100SS 100 W high pressure mercury vapor short-arc lamp, EXFO, Mississauga, Ont., Canada) filtered and centered at 365 nm for a duration of 5 min. Conversion versus time data for all monomers was obtained by using real time FTIR [14,26] either by monitoring the C=C stretching vibration at 1630 cm^{-1} or the C=C twisting vibration around 810 cm^{-1} . Samples were laminated between two NaCl crystals achieving approximate film thicknesses of 15–20 μm . The initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was used at 0.1 wt% for all polymerizations. However, since benzoyl carbamate ethyl acrylate melts at 80°C , the kinetic comparisons for benzoyl carbamate ethyl acrylate were performed at 81°C as shown in Fig. 2. In the remaining figures, the kinetic comparisons were made at 67°C .

2.3. Molecular dipole moment

Molecular modeling software (Hyperchem version 7.01, Hypercube, Gainesville, FL) was used to estimate molecular dipole moments. The program compiles varying conformations by changing the dihedral angle and calculates the energy of each conformation by a semi-empirical AM1

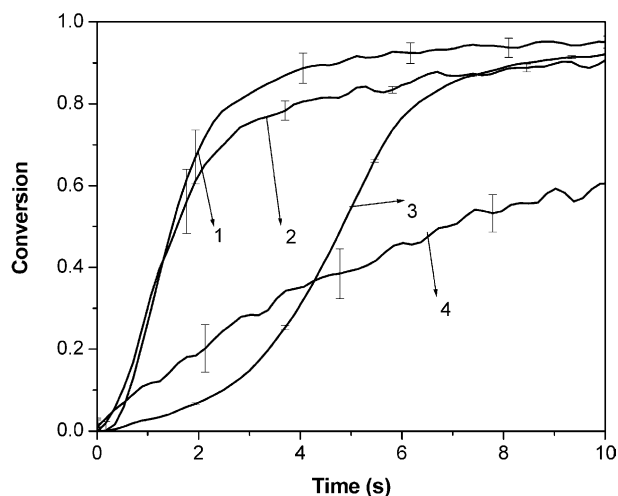


Fig. 2. Acrylate conversion versus time for (1) benzoyl carbamate ethyl acrylate, (2) phenyl carbamate ethyl acrylate, (3) cyclic carbonate acrylate, and (4) *meta*-cyano phenyl carbamate ethyl acrylate. Polymerization conditions: light intensity = 5 mW/cm^2 , initiator concentration = 0.1 wt%, temperature = 81°C .

simulation. All conformations up to 6 kcal higher than the minimum energy conformation are kept, and the remaining conformations are discarded, with the total number of conformations not exceeding 1000. The overall dipole moment is obtained by taking a Boltzmann weighted average dipole moment of all the conformations which is evaluated by the following formula [13,21,22],

$$\langle D \rangle = \sum_j D_j \frac{e^{(-\Delta H_j/RT)}}{\sum_i e^{(-\Delta H_i/RT)}}$$

Where, D_j is the dipole moment of a conformation j , ΔH_j is the energy difference between the heat of formation of conformation j and the heat of formation of the global minimum energy conformation, T is the absolute temperature and R is the ideal gas constant. For the solution polymerizations the volume fraction weighted average of the calculated dipole moments of the monomers and solvents is used as a measure of polarity in these mixtures [13,20].

4. Results

4.1. Bulk polymerization studies

Bulk polymerization studies of the monomers with high dipole moment were conducted to analyze the correlation of dipole moment with reactivity, above a threshold dipole moment of 3.5 debye. For this purpose various monomers were synthesized which incorporated functionalities that would allow high dipole moment values. Monoacrylate monomers containing functional groups such as carbamates, *N*-acyl carbamates, and cyclic carbonates were synthesized to increase the dipole moment. Then, kinetic comparisons

were made between monomers that differed considerably in structure but are characterized by similar values of dipole moment. Also, monomers sharing common structural features, but spanning broad ranges of dipole moments were polymerized and compared.

A study of monomers with carbamate functionalities conjugated with an aryl moiety revealed faster polymerization kinetics for benzoyl carbamate ethyl acrylate (6) having a dipole moment of 4.9 debye, as compared to cyclic carbonate acrylate (8) with a dipole moment of 6.1 debye (Fig. 2). The enhanced reactivity for (6) can likely be attributed to its hydrogen bonding ability, extensive conjugation and π - π stacking of the ring. Further, the cure kinetics of (6) are very similar to the cure kinetics of phenyl carbamate acrylate (1), (Fig. 2) which has a much lower dipole moment of 2.4 debye. A possible explanation for this fact could be that (6) and (1) share common structural and electronic features such as hydrogen bonding and extensive conjugation between the carbamate and the aryl moiety. Hence, the factors mentioned above will enhance the reactivity of both of the aforementioned monomers. Surprisingly, *meta*-fluoro phenyl carbamate ethyl acrylate (7) with a high dipole moment of 5.0 debye polymerizes much more slowly than the other monomers. The reason for the sluggish reaction behavior of (7) in comparison to all of the other substituted phenyl carbamate acrylate monomers is unclear.

A comparison of the cure kinetics of several monomers having similar estimated dipole moments is presented in Fig. 3. Cyano ethyl acrylate (4) and penta-fluoro phenyl carbamate ethyl acrylate (3), both having approximately the same estimated dipole moments of 3.7 debye, have different polymerization kinetics with the hydrogen bonding monomer possessing a higher reactivity (Fig. 3). Interestingly,

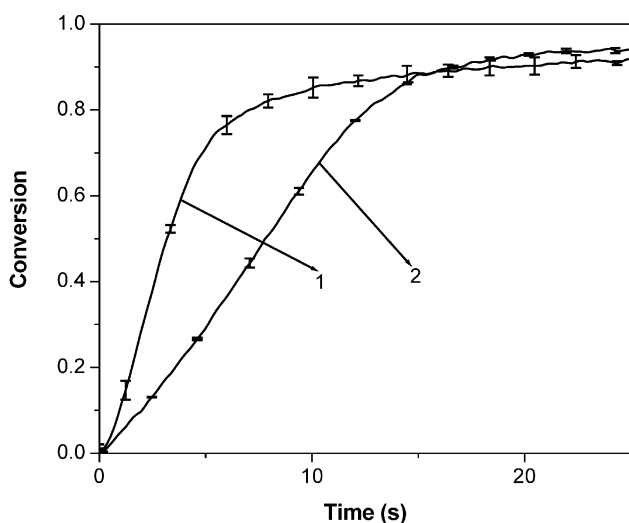


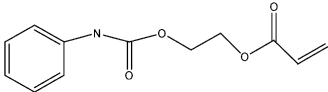
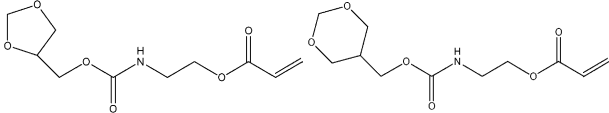
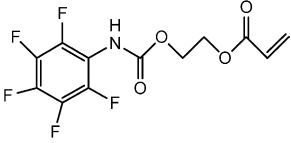
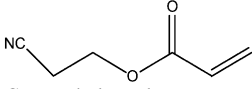
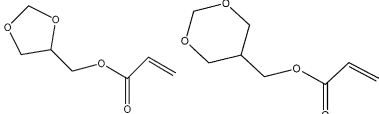
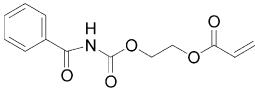
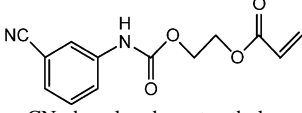
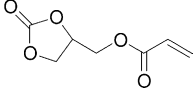
Fig. 3. Acrylate conversion versus time behavior for (1) cyano ethyl acrylate and (2) penta-fluoro phenyl carbamate acrylate both characterized by similar value of dipole moment of approximately 3.7 debye. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%, temperature = 67 °C.

mixture of cyclic acetal acrylates (5), also having a similar average dipole moment of 3.7 debye, polymerizes more rapidly than either of the above two systems [16]. Also, the mixture of acetal OCN acrylates (2) with a lower dipole moment of 3.1 debye is found to be the most reactive system [16]. While it is true that hydrogen bonding would increase the reactivity, and many high dipole moment systems are observed to be very reactive, our findings do not support an exclusively complementary relationship between hydrogen bonding and dipole moment. In molecules exhibiting intermolecular hydrogen bonding character, the energy of various conformations of the monomer is altered by hydrogen bonding with neighboring molecules. Correspondingly, such interactions and their effect on conformational energies would impact the Boltzmann average dipole moment significantly. For instance, due to intermolecular hydrogen bonding, a particular conformation having a lower value of dipole moment may be energetically favored over a conformation with a higher dipole moment. This case would lead to a lowering of the dipole moment if hydrogen bonding with neighboring molecules were taken into account. The present calculations, however, are based on single molecule simulations and do not take any intermolecular interactions into account. In actuality, it is not known how hydrogen bonding would itself impact the dipole moment of a system. Thus, the complementarity between dipole moment and hydrogen bonding is not obvious for several monomer systems. The maximum normalized polymerization rates for these monomers are summarized in Table 1, the rates being compared are maximum rates after normalization with respect to conversion, i.e. divided by (1-conversion). The rates are renormalized with respect to conversion because different monomers with varied structures would attain their maximum rates at very different conversions and hence, reactant monomer concentrations. Hence, since the maximum rate itself is also dependent on monomer conversion we believe for an ideal comparison of reactivity it is essential to normalize by this function of conversion. A plot of monomer reactivity versus molecular dipole, for all monomers depicted in Fig. 4, shows no monotonic correlation of monomer reactivity to molecular dipole.

4.2. Solution polymerization studies

Bulk polymerization studies did not indicate any significant correlation between molecular dipole and monomer reactivity. Solution polymerization studies were also conducted to observe the impact of the media polarity on monomer reactivity. Aryl substituents were systematically placed on a phenyl carbamate ethyl acrylate monomer template. Such substituents were utilized to manipulate the monomer dipole moment, allowing comparison of monomers with significantly different dipole moments but similar structural features. The solvents chosen for conducting the solution polymerizations were

Table 1
Bulk polymerization kinetic studies for monomers with high dipole moments

No.	Monomer structure	Dipole moment (debye)	Normalized maximum rate (s^{-1}) renormalized with respect to conversion
1	 Phenyl carbamate ethyl acrylate	2.4	0.62 ± 0.03
2	27/73 Mixture, 5 membered/6 membered cyclic acetal OCN acrylate  Cyclic acetal OCN acrylate	3.1	0.73
3	 Penta-fluoro phenyl carbamate ethyl acrylate	3.7	0.21 ± 0.01
4	 Cyanoethyl acrylate	3.7	0.11 ± 0.01
5	3/97 5 Membered/6 membered cyclic acetal acrylate  Cyclic acetal acrylate	3.7	0.3
6	 Benzoyl carbamate ethyl acrylate	4.9	0.64 ± 0.02
7	 <i>m</i> -CN phenyl carbamate ethyl acrylate	5.0	0.14 ± 0.04
8	 Cyclic carbonate acrylate	6.0	0.58 ± 0.01

The maximum polymerization rates have been normalized with respect to the initial double bond concentration, and also renormalized with respect to conversion i.e. divided by (1-conversion). Benzoyl carbamate ethyl acrylate (4) was polymerized and compared with other monomers at 81 °C. All other monomers were polymerized at 67 °C. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%.

propylene carbonate, possessing a high dipole moment of 5.0 debye, ethylene glycol diacetate with a relatively low dipole moment of 2.2 debye, and hydrogenated phenyl carbamate ethyl acrylate (with the acrylic double bond hydrogenated) with a dipole moment of 2.3 debye. Hydrogenated phenyl carbamate ethyl acrylate was included as a solvent to study the effects of dilution alone, while attempting to keep the electronic and structural characteristics of the solution similar to that of the bulk monomer.

The conversion-time plots for phenyl carbamate ethyl

acrylate depicted in Fig. 5 show that all polymerization kinetics are suppressed upon the addition of a solvent. Interestingly, upon comparing two solution polymerizations at similar dilutions for the same monomer, the polymerization kinetics in the more polar solvent (propylene carbonate) are not dramatically accelerated with respect to the less polar solvent (ethylene glycol diacetate). The solution polymerization rate suppression trend is independent of the dipole moment of the solvent, although the extent of the suppression varies. The polymerization kinetics of

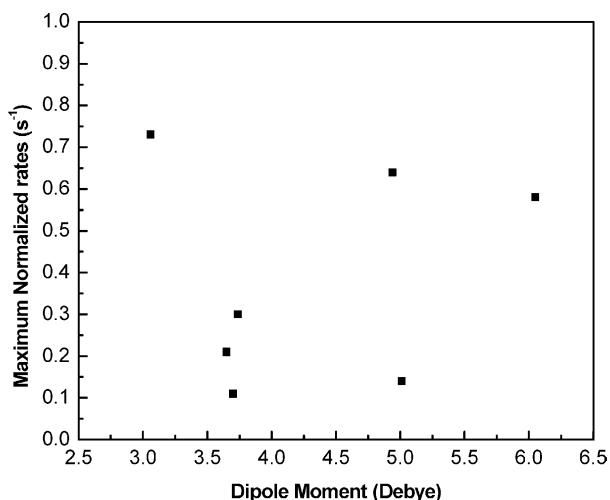


Fig. 4. Monomer reactivity versus dipole moment for monomers possessing high calculated values of dipole moment. The maximum polymerization rates are normalized with respect to initial double bond concentration and conversion at maximum rate, i.e. divided by (1-conversion). Benzoyl carbamate ethyl acrylate was polymerized and compared with other monomers at 81 °C. All other monomers were polymerized at 67 °C. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%.

para-fluoro phenyl carbamate ethyl acrylate at different dilutions in propylene carbonate are shown in Fig. 6. These results indicate that as the dilution is increased, the polymerization kinetics are suppressed further though the polarity of the polymerization medium increases. This decrease in reactivity with dilution is caused by the enhanced mobility that facilitates termination. Increased termination reduces the radical concentration, leading to slower polymerization, which is the primary dilution effect observed in traditional acrylic systems.

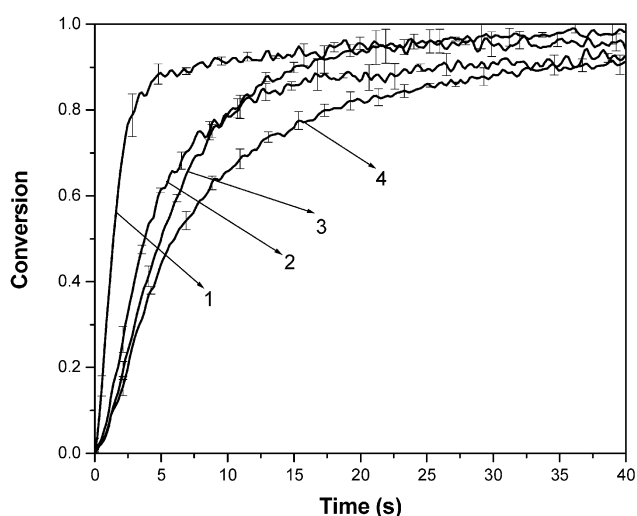


Fig. 5. Acrylate conversion versus time for monomer phenyl carbamate ethyl acrylate in different solvents at 50 wt% dilution. Bulk (1) hydrogenated phenyl carbamate ethyl acrylate (2) propylene carbonate (3) and ethylene glycol diacetate (4) Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%, temperature = 67 °C.

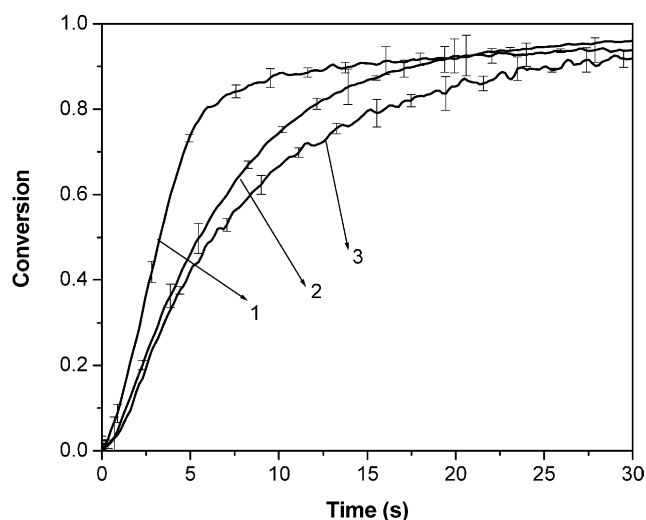


Fig. 6. Acrylate conversion versus time for *para*-fluoro phenyl carbamate acrylate at various dilutions (1) bulk, (2) 30 wt% dilution, and (3) 50 wt% dilution. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%, temperature = 67 °C.

Also, upon 50 wt% dilution of the different monomers in propylene carbonate, the average of the dipole moment of the components in many monomer solutions crossed the proposed threshold value of 3.5 debye (as can be inferred from Table 2). The proposed correlation of molecular dipole with monomer reactivity has been claimed to hold for solution polymerizations as well. However, as is depicted in Fig. 7, there was no definitive correlation found between polymerization kinetics and the average of the dipole moment of the components in various monomer solutions when this average dipole moment exceeded 3.5 debye.

The maximum polymerization rates and dipole moments

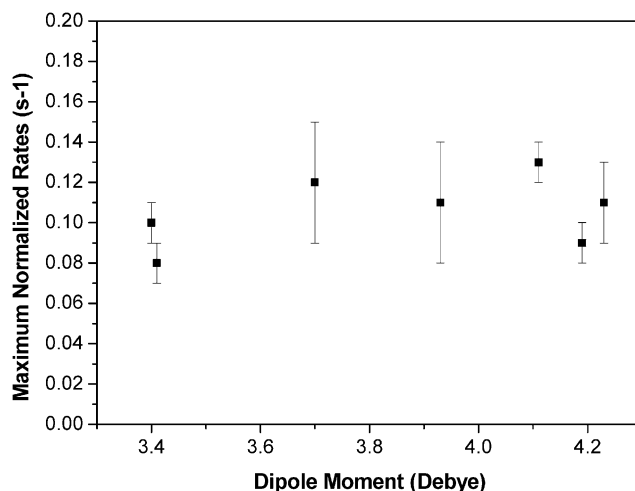


Fig. 7. Monomer reactivity versus calculated solution dipole moment for phenyl carbamate ethyl acrylate and its substituted derivatives diluted 50 wt% in the propylene carbonate. The maximum polymerization rates are normalized with respect to initial double bond concentration. All maximum polymerization rates occur between 10 and 20% conversion. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%, temperature = 67 °C.

Table 2
Comparison of polymerization kinetics for phenyl carbamate ethyl acrylate and its substituted derivatives in various solvents

Monomer	Bulk polymerization		Polymerization in 50 wt% ethylene glycol diacetate		Polymerization in 50 wt% hydrogenated phenyl carbamate ethyl acrylate		Polymerization in 50 wt% propylene carbonate	
	Dipole (debye)	Norm max rate (s^{-1})	Dipole (debye)	Norm max rate (s^{-1})	Dipole (debye)	Norm max rate (s^{-1})	Dipole (debye)	Norm max rate (s^{-1})
Phenyl carbamate ethyl acrylate	2.4	0.31 ± 0.03	2.3	0.11 ± 0.02	2.3	0.14 ± 0.02	3.7	0.12 ± 0.03
<i>o</i> -Fluoro phenyl carbamate ethyl acrylate	1.8	0.22 ± 0.01	2.0	0.08 ± 0.02	2.0	0.17 ± 0.01	3.4	0.08 ± 0.01
<i>m</i> -Fluoro phenyl carbamate ethyl acrylate	2.9	0.33 ± 0.02	2.5	0.1 ± 0.01	2.6	0.09 ± 0.02	3.9	0.11 ± 0.03
<i>p</i> -Fluoro phenyl carbamate ethyl acrylate	3.5	0.20 ± 0.02	2.8	0.11 ± 0.01	2.9	0.13 ± 0.01	4.2	0.11 ± 0.02
<i>o</i> -Methoxy phenyl carbamate ethyl acrylate	3.4	0.23 ± 0.01	2.8	0.06 ± 0.02	2.8	0.11 ± 0.02	4.2	0.09 ± 0.01
<i>m</i> -Methoxy phenyl carbamate ethyl acrylate	3.2	0.25 ± 0.02	2.7	0.07 ± 0.02	2.7	0.20 ± 0.03	4.1	0.13 ± 0.01
<i>p</i> -Methoxy phenyl carbamate ethyl acrylate	1.8	0.24 ± 0.03	2.0	0.08 ± 0.02	2.0	0.14 ± 0.01	3.4	0.10 ± 0.01

The maximum polymerization rates have been normalized with respect to the initial double bond concentration. All monomers were polymerized at 67 °C. Polymerization conditions: light intensity = 5 mW/cm², initiator concentration = 0.1 wt%. The maximum rate for all solution and bulk polymerization occurs between 10 and 20% conversion.

for all monomers and average dipole moments for solutions are presented in Table 2. Interestingly, at 50 wt%, solvent the polymerization rates in hydrogenated phenyl carbamate ethyl acrylate were slightly faster or comparable to polymerization kinetics in propylene carbonate, in spite of the dipole moment of the solvent being lower. Since hydrogenated phenyl carbamate ethyl acrylate is a solvent capable of hydrogen bonding with itself, it leads to an increase in the viscosity of the solution, hindering the termination reaction, and thereby increasing the reactivity. However, even in solvents without hydrogen bond donors, there is no pronounced difference in reactivity upon dilution with propylene carbonate and ethylene glycol diacetate, which are two solvents with very different polarities. These results thereby emphasize that polarity of the medium has minimal impact on the reactivity.

5. Conclusions

Bulk polymerization studies conducted on various monomers to correlate molecular dipole interactions with monomer reactivity, revealed systems with high dipole moments that polymerize relatively slowly as compared to many novel acrylic monomers as well as low dipole moment systems which are very reactive. No universally applicable monotonic correlation was found between monomer reactivity and molecular dipole for the systems studied herein. Solution polymerization studies were conducted to evaluate whether the introduction of solvents with varying dipole moments impact the reaction kinetics in a significantly different way. These studies demonstrate that these rapidly polymerizing systems are not dramatically accelerated in a high dipole solvent. Rather, the typical dilution

effects of enhanced mobility and reduced termination kinetics are apparent. Additional systematic studies must be undertaken to decouple and ascertain the contribution of other factors hypothesized to effect monomer reactivity.

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