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Influence of Secondary Functionalities on the Reaction Behavior of Monovinyl (Meth)Acrylates

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Photoinitiated polymerization of acrylates and methacrylates is currently being used for various applications including dental materials, contact lenses, coatings, polymeric membranes, stereolithography, and drug delivery applications.[1−5] Because of the wide variety of potential and current applications, development of high performance (meth)acrylates has been the focus of great interest. In the early 1990s, functionalization of an acrylate with certain secondary functional groups such as carbamates, carbonates, cyclic carbonates, ureas, and oxazolidones was discovered to lead to a dramatic enhancement in polymerization rate.[6−10]

However, the exact reasons for the enhancement in reactivity have been elusive to date.[8,11,12] The copolymerization ratios of the acrylates with other monomers were also observed to be altered drastically upon incorporation of the secondary functionalities.[13] The kinetic studies to investigate the mechanisms responsible for enhanced reactivity revealed that the addition of the secondary functionality alters the polymerization behavior through impacting the radical-vinyl chemistry in these systems and provides a potential anionic contribution to the radical photopolymerization.[10,13,14] If the addition of the secondary functionality alters the radical-vinyl chemistry, it may impact the reaction behavior of the acrylic monomers toward other reactions as well. In this study, we attempted to investigate these (meth)acrylic monomers, for reactivity toward nucleophilic addition reactions. We conducted a series of Michael addition reactions, which are base-catalyzed 1,4-nucleophilic addition reactions across α-unsaturated carbonyl compounds[15−18] involving intermediates of anionic nature.

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(1) Decker, C.; Elzaouk, B. *J. Appl. Polym. Sci.* **1997**, *65*, 833−844.
(2) Bernhard, P.; Hofmann, M.; Schulthess, A.; Steinmann, B. *Chimia* **1994**, *48*, 427−430.
(3) Finger, W. J.; Lee, K. S.; Podszun, W. *Dent. Mater.* **1996**, *12*, 256−261.
(4) Hutchison, J. B.; Haraldsson, K. T.; Good, B. T.; Sebra, R. P.; Luo, N.; Anseth, K. S.; Bowman, C. N. *Lab Chip* **2004**, *4*, 658−662.
(5) Decker, C.; Moussa, K. *Eur. Polym. J.* **1991**, *27*, 881−889.
(6) Decker, C.; Elzaouk, B. *Eur. Polym. J.* **1990**, *26*, 393−401.
(7) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861−3873.
(8) Moussa, K.; Decker, C. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2197−2203.
(9) Decker, C.; Moussa, K. *Macromol. Chem., Rapid Commun.* **1990**, *11*, 159−167.
(10) Kilambi, H.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2007**, *40*, 47−54.
(11) Berchtold, K. A.; Nie, J.; Stansbury, J. W.; Hacioglu, B.; Beckel, E. R.; Bowman, C. N. *Macromolecules* **2004**, *37*, 3165−3179.
(12) Kilambi, H.; Beckel, E. R.; Berchtold, K. A.; Stansbury, J. W.; Bowman, C. N. *Polymer* **2005**, *46*, 4735−4742.
(13) Kilambi, H.; Schneidewind, L.; Stansbury, J. W.; Bowman, C. N. Copolymerization and dark polymerization studies of novel (meth)acrylic monomers. *Polymer* **2006**, submitted.
(14) Beckel, E. R.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2005**, *38*, 9474−9481.
(15) Chatfield, D. C.; Augsten, A.; D'Cunha, C.; Lewandowska, E.; Wnuk, S. F. *Eur. J. Org. Chem.* **2004**, 313−322.
(16) Wabnitz, T. C.; Yu, J. Q.; Spencer, J. B. *Chem.*−*Eur. J.* **2004**, *10*, 484−493.

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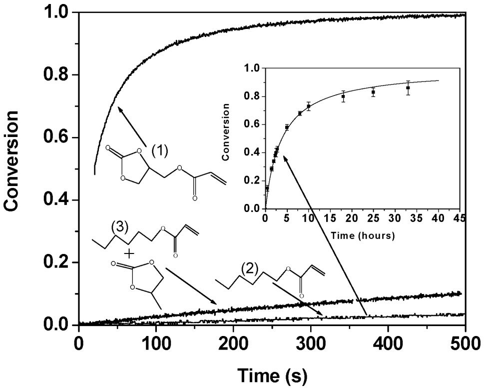

Figure 1. Acrylate conversion versus time for Michael addition. (1) CCA ($k = 2 \times 10^{-2}$), (2) HA ($k = 1 \times 10^{-5}$), and (3) propylene carbonate (HA = 1:1 molar, $k = 1 \times 10^{-4}$). Reaction conditions: 2.5 wt % triethylamine, temperature = 25 °C, 1:1 molar ratio of acrylate and butyl mercaptopropionate. The complete kinetics for HA were obtained in the time scale of hours. The experimental data points and the curve fit are depicted in the inset. Because CCA was observed to undergo considerable conversion in the initial few seconds of placing the sample in the apparatus, the initial conversion has been accounted for at the time the kinetics started to be monitored (see Supporting Information).

Amine-catalyzed Michael addition reactions of thiols[19] were performed on a variety of acrylic and methacrylic monomers incorporating carbamate, *N*-acyl carbamate, carbonate, and cyclic carbonate functionalities. Approximate reaction kinetic constants were calculated to fit the experimental conversion−time profiles, assuming a reaction first order in both the thiol and the (meth)acrylate concentrations. These studies revealed that the incorporation of a secondary functionality in an acrylate or a methacrylate compound increases the Michael addition reaction rates by 1 to 3 orders of magnitude (Figure 1).

Surprisingly, the methacrylated monomers with secondary functionalities also exhibited Michael addition reaction rates comparable to or greater than traditional acrylic monomers such as hexyl acrylate (HA; Figure 2).

This enhanced reactivity of the (meth)acrylates upon incorporation of secondary functionalities suggests an involvement of these functionalities, either in catalyzing the nucleophilic addition reaction or altering the overall medium polarity which could impact the Michael addition kinetics. Hence, the Michael addition studies of traditional acrylic and methacrylic compounds were conducted with equimolar amounts of solvents such as propylene carbonate and ethyl *N*-ethyl carbamate, which contain the cyclic carbonate and carbamate secondary functionalities. It was observed that the addition of these solvents caused minimal enhancement in the reactivity. Specifically, the kinetics for the addition of propylene carbonate are depicted in Figure 1. The addition of propylene carbonate as a solvent caused approximately a 10-fold enhancement in the reactivity of HA, but it remains 2 orders of magnitude less reactive than cyclic carbonate acrylate (CCA). Thus, the secondary functionalities appear to catalyze the Michael addition reaction only upon their incorporation into the monomer and not upon addition as a solvent, thereby suggesting the contribution of an intramolecular conformational effect.

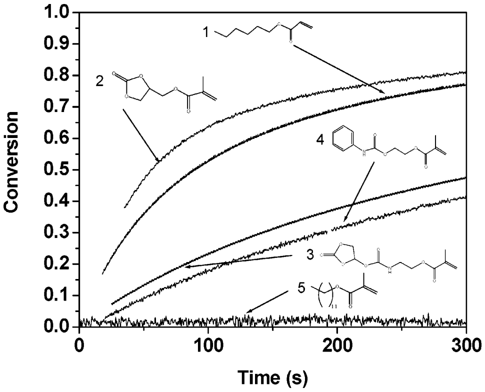

Figure 2. Acrylate and methacrylate conversion versus time for Michael addition of (1) HA ($k = 6 \times 10^{-3}$), (2) cyclic carbonate methacrylate ($k = 9 \times 10^{-3}$), (3) cyclic carbonate carbamate methacrylate ($k = 2 \times 10^{-3}$), (4) phenyl carbamate ethyl methacrylate ($k = 2 \times 10^{-3}$), and (5) lauryl methacrylate (no reaction in the observed time scale of 0.5 h). Reaction conditions: 2.5 wt % triethylamine, temperature = 25 °C, 1:1 molar ratio of acrylate and butyl mercaptopropionate thiol, in 50 wt % dimethyl sulfoxide. The kinetics of the monomers for the first few seconds could not be obtained. For the monomers which are reactive toward Michael addition, the initial conversion has been accounted for at the time the kinetics started to be monitored.

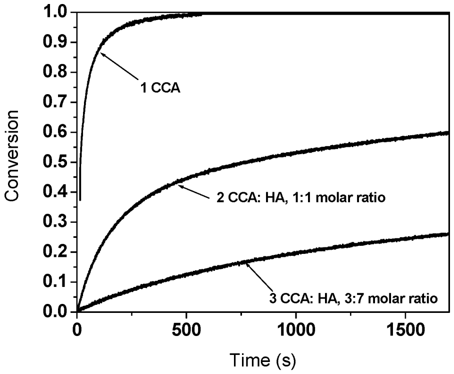

Figure 3. Acrylate conversion versus time for Michael addition. (1) $k_{CCA} = 2 \times 10^{-2}$; (2) $k_{CCA} = 2 \times 10^{-3}$, $k_{HA} = 5.5 \times 10^{-5}$; and (3) $k_{CCA} = 2 \times 10^{-4}$, $k_{HA} = 1.4 \times 10^{-5}$. Reaction conditions: 2.5 wt % triethylamine, temperature = 25 °C, 1:1 molar ratio of acrylate and butyl mercaptopropionate.

To investigate the contribution of the intramolecular conformational effect further, Michael addition studies were conducted for mixtures of CCA and HA in various stoichiometric ratios (Figure 3), and the total acrylate conversion was monitored. CCA is observed to attain complete conversion. For a 50:50 mixture of CCA/HA, the acrylate conversion curve tapers around roughly 56% conversion (Figure 3). For a 30:70 molar mixture, conversion curve tapers at around 31% conversion (Figure 3).

If the contribution to enhanced reactivity toward Michael addition is primarily due to an intramolecular conformational phenomenon, then we would expect the CCA to react faster than the HA while being a part of the same mixture. It was observed that the CCA and HA react over entirely different time scales and a single kinetic constant could not be used to predict the conversion−time profiles (see Supporting Information). Hence, two kinetic constants associated with the two acrylic monomers were used to fit the conversion−

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(17) O'Donnell, M. J.; Delgado, F.; Dominguez, E.; de Blas, J.; Scott, W. L. *Tetrahedron: Asymmetry* **2001**, *12*, 821−828.

(18) Hunt, D. A. *Org. Prep. Proced. Int.* **1989**, *21*, 705−749.

(19) Lee, T. Y.; Kaung, W.; Jonsson, E. S.; Lowery, K.; Guymon, C. A.; Hoyle, C. E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4424−4436.

time profiles. As the stoichiometric ratios of HA and CCA were altered, a reduction in the kinetic constants of both CCA and HA was observed with increasing HA fraction, which may be due to the alteration in the medium polarity due to dilution of CCA. Therefore, the alteration of the overall medium polarity due to the addition of the secondary functionality does contribute to the enhanced reactivity toward Michael addition. However, the catalysis of the Michael addition reaction through an intramolecular conformational phenomenon dominates that effect. The intramolecular conformational effect could lead to the stabilization of the incipient transition state toward Michael addition, thus lowering the activation energy.

The previous observations of diacrylates being distinctly more reactive[20] as compared to monoacrylates toward Michael addition can also be explained similarly, wherein the second ester functionality of the diacrylate intramolecularly assists the Michael addition. Since the Michael addition reaction involves a nucleophilic attack at the acrylic double bond site, differences in electrophilicity of the acrylic double bonds upon incorporation of the secondary functionality will also impact the reactivity.

To sterically hinder the possible intramolecular conformational stabilization of the incipient transition state, acrylates were designed and synthesized (see Supporting Information) with methyl groups in the spacer connecting the secondary functionality to the acrylic double bond. Because phenyl carbamate ethyl acrylate also demonstrated enhanced reactivity toward Michael addition, dimethyl substituted phenyl carbamate ethyl acrylates were synthesized. The kinetics presented in Figure 4 revealed that the β,β-substituted monomer underwent Michael addition at a rate approximately 2.5-fold slower than phenyl carbamate ethyl acrylate, while the α,α-substituted monomer underwent the Michael addition at an order of magnitude slower rate. These results further suggest that the enhanced reactivity toward Michael addition is primarily due to an intramolecular conformational effect. The dimethyl substitution may be disrupting the conformational stabilization to a larger measure and causing the α,α-substituted phenyl carbamate acrylate to behave similar to a bimolecular mixture of a traditional acrylate and the secondary functionality (carbamate) with respect to Michael addition.

The photopolymerization kinetics of the phenyl carbamate acrylates were also observed to be affected in a similar manner upon the α,α and β,β dimethyl substitution.[21] Further, there is a distinct correlation between reactivity toward photopolymerization and Michael addition reaction where the acrylates characterized by secondary functionalities exhibit enhanced reactivity toward both the reactions. The Michael addition kinetic constants and bulk photopolymerization rates have been summarized in Table 1 (see Supporting Information) for various acrylate monomers. It implies that the incorporation of the secondary functionality intramolecularly impacts both of these reactions by altering the radical-vinyl chemistry for these acrylates.

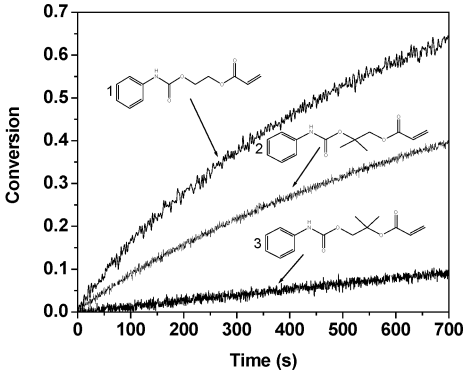

Figure 4. Acrylate conversion versus time for Michael addition of (1) phenyl carbamate ethyl acrylate ($k = 5 \times 10^{-4}$), (2) β,β-dimethyl-substituted phenyl carbamate ethyl acrylate ($k = 2 \times 10^{-4}$), and (3) α,α-dimethyl-substituted phenyl carbamate ethyl acrylate ($k = 4 \times 10^{-5}$). Reaction conditions: 10 wt % triethylamine, temperature = 25 °C, 1:1 molar ratio of acrylate and butyl mercaptopropionate diluted 50 wt % in tetrahydrofuran. As all of the monomers are solids at 25 °C, the Michael addition reactions were performed in solution.

In summary, we have demonstrated that functionalizing (meth)acrylates with certain secondary functionalities also impacts reaction behavior toward the amine-catalyzed Michael addition reaction with thiols and causes drastically enhanced reactivity toward Michael addition. These studies also support our previous hypothesis that incorporation of the secondary functionalities contributes significantly to reactivity toward photopolymerization by altering the radical-vinyl chemistry.

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Supporting Information Available: Synthesis, NMR, IR, and elemental analysis data of all the monomers synthesized (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] McCarthy, T. J.; Hayes, E. P.; Schwartz, C. S.; Witz, G. *Fundam. Appl. Toxicol.* **1994**, *22*, 543−548.

[21] Beckel, E. R.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2005**, *38*, 3093−3098.