Synthesis of New Hydroxylated Monomers Based on Methacrylate, Dimethacrylate, and Tetramethacrylate Michael Adducts and Photopolymerization Kinetics of Bulk Cross-Linkers

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ABSTRACT: A series of new hydroxylated monomers was synthesized from the Michael addition reaction between ethanolamine, diethylene glycol amine, triethylene glycol amine, tetradecylamine, and adamantanamine with 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM). Selective formation of secondary amine (mono adduct) or tertiary amine (bis adduct) products was obtained by controlling the stoichiometry of the reactants and reaction temperature. The Michael addition reactions were highly exothermic and carried out without the need of catalyst. The use of solvent, however, was required in some systems. The tetramethacrylate monomer was synthesized via the Michael addition reaction of 1,6-hexanediamine (HDA) to AHM. The photopolymerization kinetics of the synthesized monomers were investigated using differential scanning calorimeter. The rates of polymerization for the hydroxylated dimethacrylate systems were significantly higher than that of a typical dimethacrylate monomer (HDDMA) and approached that of the diacrylate HDDA, with overall conversions ranging from 80 to 87%.

Introduction

The photopolymerization of multifunctional monomers has been shown to produce highly cross-linked networks with high thermal stability, mechanical strength and resistance to solvent absorption.[1] These polymers have many industrial applications, especially in areas such as industrial coatings, dental composites, optical fiber claddings and contact lenses.[2,3] The most widely used monomers for this type of polymerization are multifunctional acrylates and methacrylates.[4−7]

The study of the relationship between the polymer formed and the network properties generated during the photopolymerization reaction is important to understand the polymerization mechanisms of the various multifunctional methacrylates. This is because the bulk polymerization of multifunctional systems is a complex process involving a plethora of reaction behaviors.[8] The various phenomena of autoacceleration, autodeceleration, unequal reactivity of different functional groups, multiple termination processes, volume shrinkage, and the heterogeneities of the networks formed make the understanding of the mechanisms difficult. For example, it has been shown that the presence of pendant hydroxyl groups in dimethacrylate compounds such as bisphenol A glycol dimethacrylate (Bis-GMA) enhances polymerization rates because it increases the viscosity of the system due to strong hydrogen bonding. This reduces termination rates and causes a pronounced maximum in the polymerization rate characterized as the immediate onset of autoacceleration.[9] Other important factors include flexibility and distance between functional groups. For instance, the distance between double bonds in cross-linker structures affects the cross-link density and formation of intrachain primary or secondary cyclic units rather than interchain cross-links.[10] In addition, final conversions are often limited by vitrification and topological factors governing steric crowding, accessibility of reactive sites, and kinetic access to pendant double bonds.[11] These problems can be partially overcome by incorporating long, flexible spacers between the vinyl groups, but this causes marked changes in physical properties.[12]

We have recently become interested in designing new cross-linkers with different degrees and types of functionality for coatings applications. Our most recent results involved the investigation of the photopolymerization kinetics of bulk multifunctional acrylates and their use in alkyl (α-hydroxymethyl)acrylate (RHMA) systems.[13] One interesting result was found for a mixed acrylate/methacrylate cross-linker system, 3-(acryloyloxy)-2-hydroxypropyl methacrylate (or AHM, Scheme 1).[14] This alcohol containing cross-linker showed very fast rates in bulk photopolymerization, being significantly faster than commonly used dimethacrylate systems.[13] Here, we describe one method for designing new hydroxylated methacrylate-based monomers based on AHM via Michael addition reactions.

The use of Michael addition reactions for the synthesis of polyfunctional methacrylate-terminated monomers has been recently investigated by others.[15,16] Frahani and co-workers used gas chromatography−mass spectrometry (GC−MS) to demonstrate the importance of the stoichiometry in the Michael addition reaction of arylamines to acrylic acids.[15] Muh and coworkers designed a hybrid organic−inorganic bismethacrylate monomer containing alkoxysilyl units by Michael addition of α−ω-alkoxysilylamines to ethylene glycol acrylate methacrylate and ethylene glycol bis(acrylate) in the presence of protic solvents. The low viscosity of the monomers obtained and their low volumetric shrinkage on polymerization were considered key parameters for their potential use in dental composite formulations.[16]

In this report, we describe an easy route to synthesizing secondary and tertiary amine-functionalized hydroxylated monomers via Michael addition with the

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remarkable advantage that this reaction can be usually carried out in bulk, is very fast, and is essentially quantitative even in the absence of catalysts. The photopolymerization kinetics of the series of new difunctional cross-linkers synthesized was also evaluated and was found to be facile.

Experimental Section

Materials. 3-(Acryloyloxy)-2-hydroxypropyl methacrylate (AHM), ethanolamine (EA), diethylene glycol amine (DGA), 1−6 hexanediamine (HDA), 1-adamantanamine (ADA), tetradecylamine (TDCA), 1,6-hexanediol diacrylate (HDDA), and 1,6-hexanediol dimethacrylate (HDDMA) were purchased from Aldrich Chemical Co. and used as received. Triethylene glycol monoamine (TGA) was purchased from Huntsman Corporation and used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba-Geigy) was used as received. Ethanol and choloroform (reagent grade solvents) were used as received.

Instrumentation. ^{13}C NMR solution spectra were recorded on a Bruker AC-200 spectrometer at room temperature using $CDCl_3$ with TMS as an internal reference. Fourier transform infrared spectra were obtained using a Mattson 5000 spectrometer. Photopolymerizations were initiated with Irgacure 651 using a DuPont Instruments 930 differential photocalorimeter (DPC). Results of the DPC experiments were evaluated using Microcal Origin 4.1 and Microsoft Excel. Glass transition temperatures (T_g's) of the polymers were measured by dynamic mechanical analysis (DMA) on a TA Instruments DMA Q800 using an 8 mm dual cantilever assembly at a frequency of 1 Hz. Polymer samples were rectangular in shape with approximate dimensions of 1 mm (thickness), 10 mm (width), and 20 mm (length). A heating rate of 5 °C/min was used over the range −30 to +250 °C. The T_g of the polymer was taken as the temperature at the maximum point of the tan δ peak.

General Procedure for Michael Addition Reactions. Typical Preparation of Secondary Amines (Mono Adduct Products). Equimolar amounts of AHM (3.8 mL, 20 mmol) and EA (1.2 mL, 20 mmol) were added to a 50 mL round-bottom flask and the mixture stirred for 24 h at ambient temperature using magnetic stirring. No catalyst was used. ^{13}C NMR spectroscopy was used to follow disappearance of acrylate peak resonances and appearance of Michael mono adduct peak resonances by sampling at 15 min, 90 min, and 24 h. The reaction was essentially complete after 15 min. All the products obtained were colorless, viscous oils.

3-(*N*-Propionate ethylene glycol amino)-2-hydroxypropyl Methacrylate (M1). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.95 (CH_3); 2.71, 3.74, 3.88, 3.98 (CH_2); 4.24 (CH), 5.61, 6.14 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.2 (CH_3), 34.6, 44.8, 50.8, 60.4, 65.0, 65.3 (CH_2); 67.4 (CH); 126.1, 135.7 (CH_2=C); 167.1, 172.3 (C=O). IR (neat), abs, cm^{-1}: 3323 (N−H), 1723 (C=O), 1560 (N−H def), 1621 (C=C).

3-(*N*-Propionate diethylene glycol amino)-2-hydroxypropyl Methacrylate (M2). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.90 (CH_3); 2.50, 2.79, 3.45, 3.52, 3.62 (CH_2); 4.15 (CH), 5.56, 6.10 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 17.9 (CH_3), 34.0, 44.5, 50.6, 60.1, 63.1, 64.8, 65.1, 69.7 (CH_2); 66.9 (CH); 126.0, 135.5 (CH_2=C); 166.9, 172.2 (C=O). IR (neat), abs, cm^{-1}: 3335 (N−H), 1725 (C=O), 1568 (N−H def), 1637 (C=C).

3-(*N*-Propionate triethylene glycol amino)-2-hydroxypropyl Methacrylate (M3). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.90 (CH_3); 2.53, 2.75, 2.86, 3.59, 3.65 (CH_2); 4.15 (CH), 5.55, 6.09 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.0 (CH_3), 34.3, 44.8, 48.5, 61.1, 64.9, 67.0, 69.5, 69.9, 72.4 (CH_2); 69.8 (CH); 125.9, 135.6 (CH_2=C); 166.9, 172.2 (C=O). IR (neat), abs, cm^{-1}: 3320 (N−H), 1726 (C=O), 1558 (N−H def), 1637 (C=C).

Typical Preparation of Tertiary Amines (Bis Adduct Products). A 2-fold molar ratio of AHM relative to the amine used was employed. The reactants were added to a 50 mL round-bottom flask and stirred at ambient temperature using magnetic stirring. No catalyst was used. The use of solvent was only required for systems in which the amine was not miscible with AHM. For instance, the formation of a bis adduct by Michael addition reaction of TDCA to AHM was carried out in chloroform, that of ADA to AHM was carried out in ethanol. ^{13}C NMR spectroscopy was used to follow disappearance of acrylate peak resonances and appearance of Michael bis adduct peak resonances over time. Reactions were usually complete after 72 h. All the products obtained were colorless, viscous oils.

A typical procedure for B1 preparation involved AHM (7.6 mL, 40 mmol) and EA (1.2 mL, 20 mmol) addition to a 50 mL round-bottom flask. The mixture was stirred at ambient temperature for 24 h. ^{13}C NMR spectroscopy was used to follow the reaction after 15 min, 90 min, 24 h, 48 h, 96 h, and 1 week. The product was obtained in quantitative yield.

A typical procedure for B5 preparation used AHM (3.76 mL, 20 mmol), TDCA (2.22 g, 10 mmol), and 10 mL of chloroform added to a 50 mL round-bottom flask. The mixture was stirred at ambient temperature for 24 h. The chloroform was evaporated under reduced pressure at 35 °C to give a clear, colorless viscous liquid.

3-(*N*,*N*-Bis(propionate) ethylene glycol amino)-2-hydroxypropyl Methacrylate (B1). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.95 (CH_3); 2.79, 3.68, 3.85, 3.99 (CH_2); 4.23 (CH), 5.61, 6.14 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.0 (CH_3), 32.5, 48.9, 55.4, 58.7, 64.9, 65.3 (CH_2); 67.2 (CH); 126.0, 135.5 (CH_2=C); 167.0, 172.6 (C=O). IR (neat), abs, cm^{-1}: 1723 (C=O), 1629 (C=C).

3-(*N*,*N*-Bis(propionate) diethylene glycol amino)-2-hydroxypropyl Methacrylate (B2). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.92 (CH_3); 2.52, 2.63, 2.79, 3.53, 3.66, 3.72 (CH_2); 4.18 (CH), 5.57, 6.11 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 17.7 (CH_3), 31.6, 49.3, 53.0, 60.9, 62.2, 64.6, 64.9, 71.9 (CH_2); 66.8 (CH); 125.7, 135.3 (CH_2=C); 166.7, 172.0 (C=O). IR (neat), abs, cm^{-1}: 1725 (C=O), 1637 (C=C).

3-(*N*,*N*-Bis(propionate) triethylene glycol amino)-2-hydroxypropyl Methacrylate (B3). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.92 (CH_3); 2.51, 2.66, 2.83, 3.59, 3.67 (CH_2); 4.19 (CH), 5.58, 6.12 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.1 (CH_3), 32.4, 49.8, 53.0, 61.3, 65.0, 67.4, 69.0, 70.0, 72.3 (CH_2); 70.0 (CH); 126.1, 135.6 (CH_2=C); 167.0, 172.4 (C=O). IR (neat): abs, cm^{-1}: 1722 (C=O), 1635 (C=C).

3-(*N*,*N*-Bis(propionate) adamantyl amino)-2-hydroxypropyl Methacrylate (B4). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.88 (CH_3); 1.46, 2.35, 2.67, 3.20, 3.49 (CH_2); 1.75, 3.99 (CH), 5.42, 5.95 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 17.8 (CH_3), 29.0, 34.0, 36.2, 41.5, 43.8, 51.3, 63.0, 65.0 (CH_2); 69.6 (CH); 125.7, 135.5 (CH_2=C); 167.1, 172.9 (C=O). IR (neat), abs, cm^{-1}: 1729 (C=O), 1637 (C=C).

3-(*N*,*N*-Bis(propionate) tetradecyl amino)-2-hydroxypropyl Methacrylate (B5). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 0.83, 1.90 (CH_3); 1.21, 2.43, 2.46, 2.73, 4.16 (CH_2); 5.56, 6.10 (CH_2=C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.1 (CH_3), 13.9, 22.5, 27.3, 29.5, 30.0, 31.7, 32.2, 49.0, 53.6, 65.0, 65.2 (CH_2); 67.4 (CH); 126.1, 135.6 (CH_2=C); 167.0, 172.4 (C=O). IR (neat), abs, cm^{-1}: 1726 (C=O), 1638 (C=C).

Preparation of the Tetrakis Cross-Linker 3-(*N*,*N*,*N*,*N*−Tetrakis(propionate) hexanediamino)-2-hydroxypropyl Methacrylate (T1). A 4:1 molar ratio of AHM (7.52 mL, 40 mmol) relative to the amine compound HDA (1.17 g, 10 mmol) and 10 mL of chloroform as a solvent were used in this case. The reactants were added to a 50 mL round-bottom flask, and the mixture was stirred at ambient temperature for 1 week using magnetic stirring. No catalyst was used, although the use of solvent was required due to immiscibility between the reactants at room temperature. The chloroform was evaporated under reduced pressure at 35 °C and the final product obtained as a clear and viscous liquid. The bulk reaction was also carried out between AHM and HDA at 45 °C for 2 h, using the same procedure described above. ^{13}C NMR spectroscopy was used to follow disappearance of acrylate peak resonances and appearance of Michael bis adduct peak resonances over time.

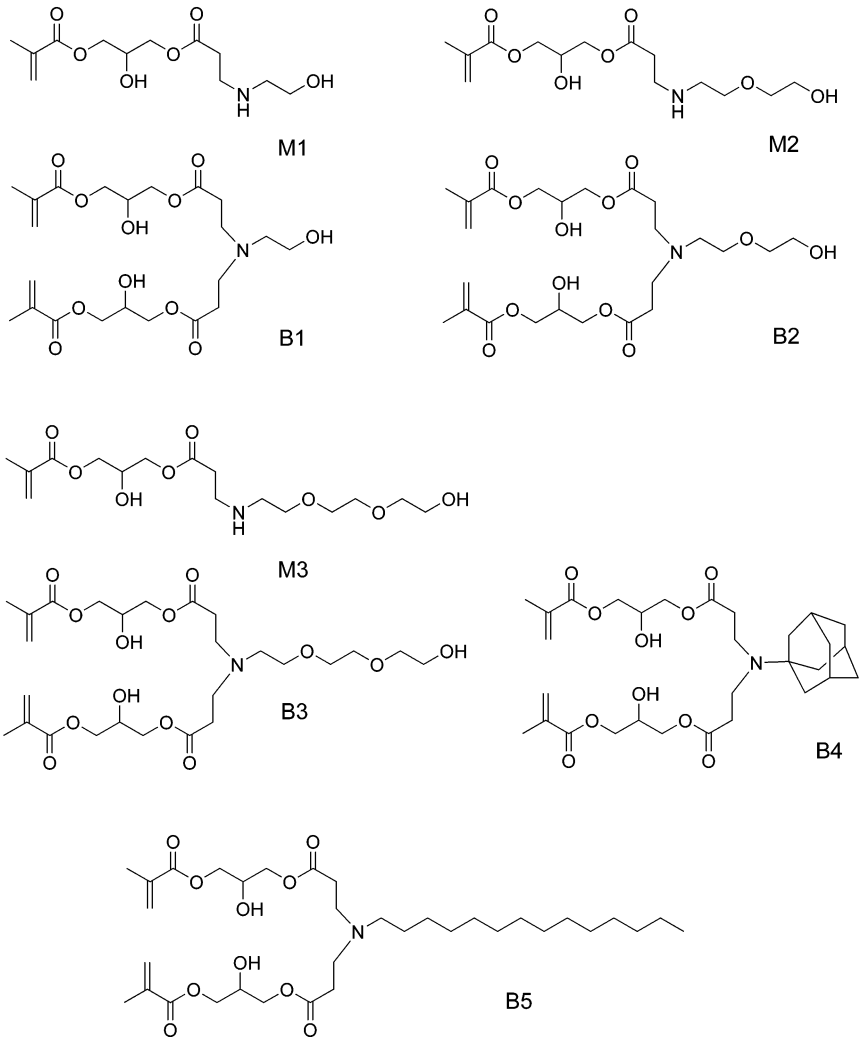


Figure 1. Structures of the hydroxylated methacrylate monomers synthesized via Michael addition reactions.

^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.93 (CH_3); 1.24, 1.41, 2.47, 2.50, 2.77, 4.19 (CH_2); 4.29 (CH), 5.59, 6.13 (CH_2═C). ^{13}C NMR ($CDCl_3$, 200 MHz), δ (ppm): 18.16 (CH_3), 25.94, 27.06, 32.31, 49.13, 53.44, 65.06, 65.232 (CH_2); 67.57 (CH); 126.20, 135.66 (CH_2═C); 167.16, 172.42 (C═O) ppm. IR (neat), abs, cm^{-1}: 3323 (N−H), 1723 (C═O), 1560 (N−H def), 1621 (C═C).

Photopolymerizations. For a typical photopolymerization, approximately 3 mg of the cross-linker with 1 mol % of Irgacure 651 relative to double bond functionality were placed in an aluminum DSC pan which had the bottom impressed and flattened (approximately 200 μm thickness). Heats of photoreactions were measured using a TA Instruments 930 differential photocalorimeter (DPC) equipped with a high-pressure mercury arc lamp. This unit emits radiation predominantly in the 220−400 nm range, and provides light intensity of 31 mW/cm^2 as measured by a UV radiometer capable of broad UV range coverage (UV Process Supply, Inc., Chicago, IL). The chamber of the DPC was purged with nitrogen for 10 min before irradiation, and a nitrogen blanket was maintained throughout the reaction. All the experiments were carried out sequentially so the light intensity during a given series of experiments would be as constant as possible. Each sample was irradiated for 6 min at 30 °C with the light shutter opening at 30 s after the beginning of data acquisition; i.e., the onset of photocure occurred at 30 s.

The enthalpy value, ΔH_{theor} = 13.1 kcal/mol, was used as the theoretical heat evolved for methacrylate double bonds, and for acrylate double bonds, the value of ΔH_{theor} = 20.6 kcal/mol was used.[17] The heat flux as a function of reaction time was monitored using DSC under isothermal conditions. Instantaneous rates of polymerization were calculated according to eq 1,[18,19] where ΔH_{pol} is the heat released per mole of double bonds reacted, Q/s is the heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule, and m is the mass of monomer in the sample. For the acrylate-methacrylate monomer, ΔH_{theor} was calculated using a weighted average of ΔH_{theor} for acrylates and methacrylates.

$$\text{rate} = \frac{(Q/s)M}{n\Delta H_{pol} m} \tag{1}$$

Results and Discussion

The structures of the novel hydroxylated monomers synthesized are shown in Figure 1.

The monomers were prepared according to the general synthetic routes shown in Figure 2 via Michael addition of different amines to the acrylate group of 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM), a mixed acrylate/ methacrylate monomer. It should be noted that this commercially available cross-linker contains a minor amount of the 2-substituted isomer, as shown in Scheme 1. This apparently results from competing attack of acrylic acid on the more hindered epoxide carbon of glycidyl methacrylate (Scheme 1). This minor isomer is present throughout the reactions and undergoes Michael addition as well.

Secondary or tertiary amine-based monomers were selectively formed by controlling the stoichiometry of the

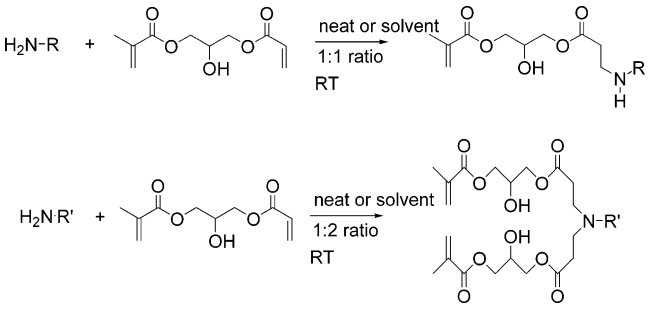
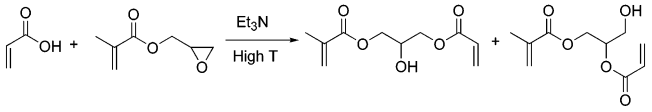


Figure 2. General synthetic schemes for the preparation of secondary amines (mono adducts) or tertiary amines (bis adducts) via Michael addition reactions to AHM.

Scheme 1. Hypothetical Synthetic Scheme for the Preparation of 3-(acryloyloxy)-2-hydroxypropyl Methacrylate (or AHM)



reagents. Different aliphatic amines with a variety of pendant groups were examined. These include long alkyl segments, ethylene glycol moieties with terminal hydroxyl groups, and bulky groups such as adamantane. Despite the fact that Michael addition reactions have been traditionally performed in the presence of catalytic amounts of base and/or protic solvents, in this work the reactions were generally carried out in bulk, without any added catalyst. The use of solvent was required only for systems in which the reactants were not miscible and the effect of the solvent in the medium will be discussed further below.

The first series of monomers were synthesized by the reaction of AHM with the amine-terminal ethylene glycol oligomers EGA, DGA, and TGA. These reacted at room temperature (25 °C) using equimolar quantities of reactants and without any solvent or catalyst. The products formed were clear, colorless and very viscous. The addition reaction to generate the secondary amine-based monomer (mono adduct) was generally highly exothermic and complete after 15−45 min at room temperature as monitored using ^{13}C NMR spectroscopy. For example, the disappearance of the ^{13}C NMR resonance peaks for the acrylate groups and the appearance of new signals corresponding to the methylene carbons of the Michael adduct allowed monitoring of the course of the reaction. Addition to methacrylate groups of the AHM monomer did not take place to any significant amount in any of the systems investigated based on NMR results.

It has been shown in the literature that a stoichiometric imbalance caused by the use of an excess of amines leads to predominant formation of the mono adduct of the Michael addition reaction.[20,21] The energy of activation of mono adduct formation is lower than that of bis-adduct formation, resulting in a very fast and highly exothermic initial addition reaction and slow reaction of the secondary amine thus formed.[22] This allows selective formation of mono or bis adducts by simply varying the ratio of reactants. Using a 2:1 molar ratio of the AHM relative to the amine, and allowing the reaction to proceed for longer time, led to the formation of the bis adducts by addition of the secondary amine to a second acrylate.

One explanation for the very fast rates of addition obtained during the first step could be the presence of

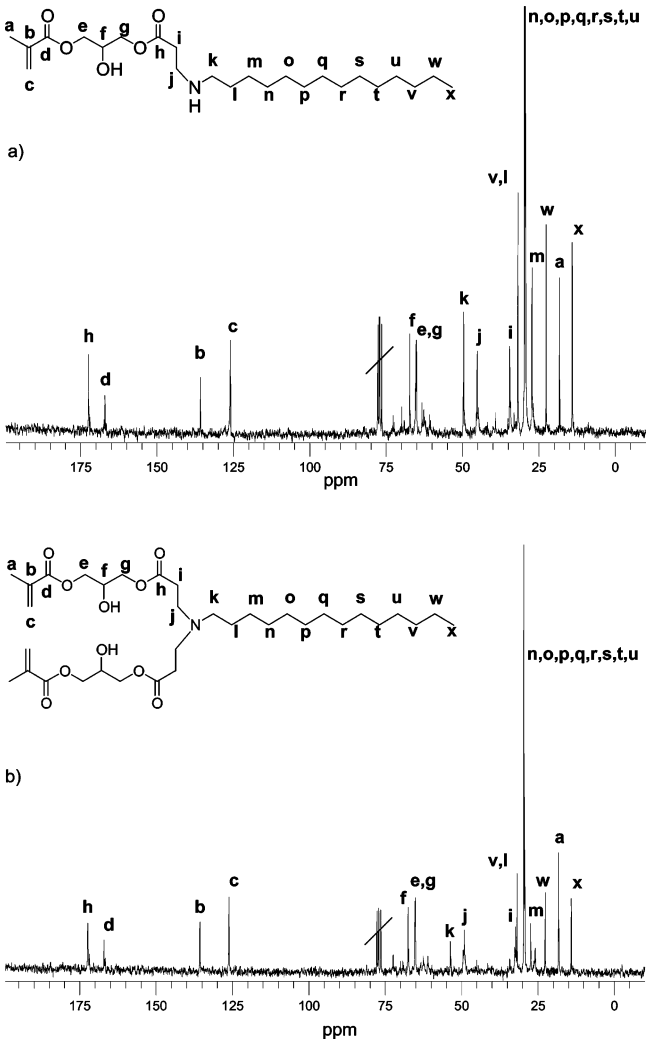


Figure 3. ^{13}C NMR of Michael adducts from reaction of tetradecylamine to AHM a) upper trace, mono adduct and (b) lower trace, bis adduct.

pendant hydroxyl groups in the AHM monomer leading to inter- and intramolecular hydrogen-bonding effects that facilitate hydrogen transfer during the formation of the Michael adduct. Remarkably high rates of Michael addition due to the presence of hydroxyl groups was also observed by Van de Mark and co-workers in the reaction of *n*-propylamine to hydroxyethyl acrylate.[22]

AHM was also reacted with a long aliphatic amine (tetradecylamine, TDCA) and a bulky amine (1-adamantanamine, ADA), as shown in Figure 2, to evaluate the general utility of this method. Because of poor miscibility between the reactants, the use of a solvent was necessary in both cases. The reaction of TDCA with AHM was carried out in chloroform at room temperature to give complete formation of both the mono adduct and the bis adduct after 72 h each. Figure 3 shows the ^{13}C NMR spectra of the mono and bis adducts formed from TDCA. The disappearance of the acrylate group resonances confirms clean formation of the Michael adducts. The carbonyl of the mono adduct ("h") appears at 172.3 ppm and at 172.4 ppm for the bis adduct, a slight but characteristic difference. The selectivity of the type of adduct formed is monitored by the chemical shift of the methylene carbon resonances of the amine functionality. For instance, the methylene carbons ("i", "j", and "k") appear at 34.5, 45.1, and 49.5 ppm in the

mono adduct (Figure 3a) and shift to 32.2, 49.0, and 53.6 ppm, respectively, after bis adduct formation (Figure 3b).

The reaction of 1-adamantanamine with AHM required the use of ethanol as solvent. Longer reaction times were required, even in the presence of polar, protic solvent, because of steric hindrance caused by the bulkiness of the adamantyl groups. For example, unreacted groups could still be detected by ^{13}C NMR after 48 h for the bis adduct reaction at room temperature. An increase in reaction temperature facilitated formation of the bis adduct, although a small amount of the mono adduct was still present even after 72 h at 40 °C.

The synthesis of a tetramethacrylate monomer was also achieved by reaction of hexamethylenediamine (HDA) with a 4:1 molar ratio of AHM. This reaction was carried out at room temperature in chloroform or at 45 °C in bulk, both gave complete formation of the tetrafunctional bis adduct after 1 week and 2 h, respectively.

As mentioned earlier, the changes in NMR chemical shifts going from mono adducts to bis adducts were clearly observed and consistent for all products. This is shown in Table 1 (see Supporting Information), which gives the ^{13}C NMR chemical shifts for all mono and bis adducts described here. Reaction monitoring was facile using these peaks, especially of the key methylene carbons "i", "j", and "k" in close proximity to the nitrogen of each reactant amine. ^{1}H NMR spectroscopy was also performed for these compounds and the absence of protons corresponding to the acrylate functionality of the starting material confirmed formation of desired products. The ^{1}H NMR chemical shifts were included in the Experimental Section. However, for the compounds M1 and M2 the detection of divinyl impurities in the mono adducts was not possible using proton NMR due to overlapping of key peaks. For the Michael adducts containing longer pendant groups linked to the amine functionality (compound M3), these key peaks were more clearly identified and the absence of divinyl impurities evidenced the purity of the mono adduct.

FTIR also confirmed selective formation of the Michael adducts. Figure 4 shows the FTIR spectra for M2 and B2. Formation of the bis adduct (tertiary amine) is monitored using the secondary amine peak at around 1560 cm^{-1} due to NH deformation. For example, this peak is present in the spectrum of the mono adduct but disappears in the spectrum of B2. This behavior is in agreement with that observed by Russell et al.[23] in the FTIR spectrum of the product of the Michael addition reaction of acrylate-functionalized poly(ethylene glycol) to a thin film of poly(allylamine) attached to gold surfaces.

Overall, the AHM-based hydroxylated monomers synthesized via Michael addition reactions had the appearance of clear, colorless viscous liquids. Products containing ethylene glycol moieties pendant to the amine, however, were more viscous than others, confirming strong intermolecular hydrogen bonding in this series beyond that involved with the internal tertiary alcohol.

Photopolymerizations. Figure 5 shows the polymerization rate vs time plots for the new hydroxylated dimethacrylate cross-linkers B1, B2, B3, B4, and B5, and for the tetrafunctionalized cross-linker T1. Repeatability of experiments was taken into account and the curves shown are the average of at least three runs obtained for each system evaluated.

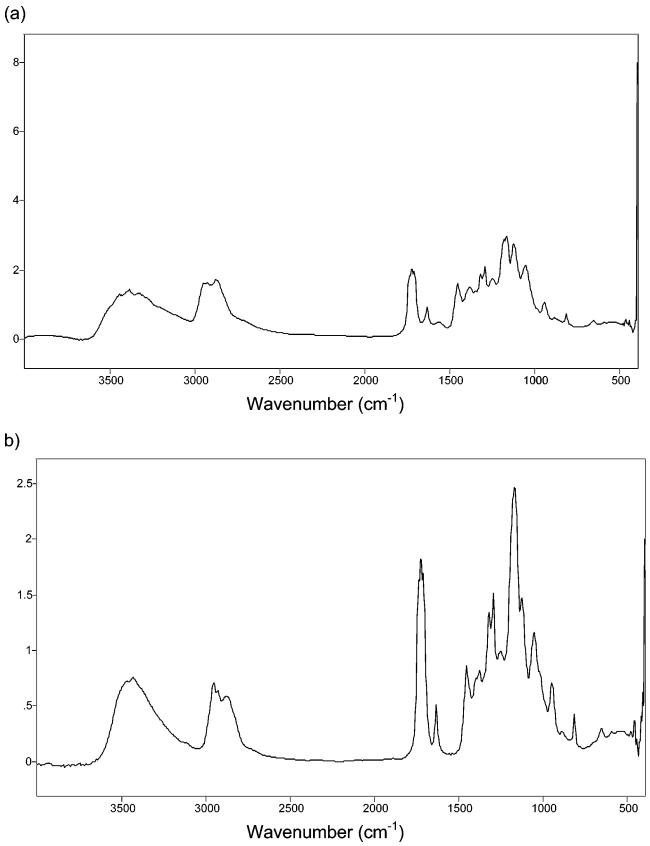


Figure 4. FTIR spectra of the mono adduct M2 (a) and the bis adduct B2 (b) formed after Michael addition of diethylene glycol amine (DGA) to AHM.

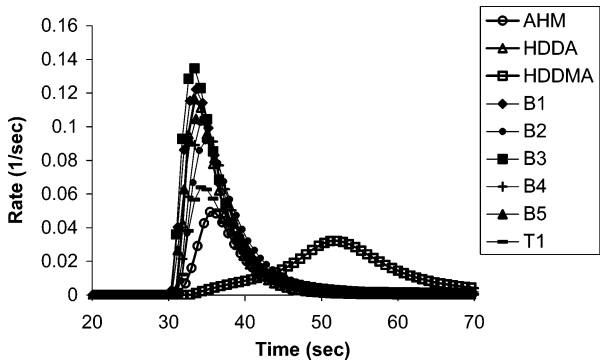


Figure 5. Polymerization rate vs time plots for bulk cross-linkers at 30 °C with onset of photocure occurring after 30 s.

Additional experimental data is given for the AHM cross-linker and for the well-known dimethacrylate and diacrylate cross-linkers, HDDMA and HDDA. These are included to provide qualitative and quantitative comparison with the systems discussed in this work. The plot of polymerization rate of HDDMA as a function of irradiation time followed the typical kinetic curve observed for dimethacrylate monomers.[12] However, the rates of polymerization of the hydroxylated monomers were significantly faster, even approaching that of HDDA. Moreover, final overall conversions were in the range of 81% (±5) for these systems as compared to 63% (±3) and 68% (±3) for HDDMA and HDDA, respectively, under similar conditions. The rate of polymerization of the tetrafunctionalized cross-linker T1 was slower than that of the dimethacrylate cross-linkers, likely due to rapid gelation and network formation, leading to trapped pendant double bonds and residual monomer and

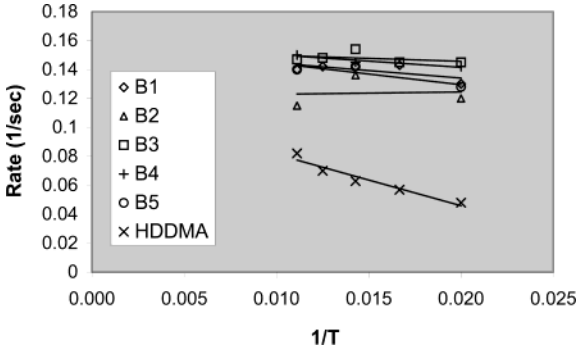


Figure 6. Polymerization rate change as a function of temperature for bulk cross-linkers polymerized in the range of 50 to 90 °C.

consequently limited conversion 65% (±5). However, its rate was faster and its conversion was much higher than that of pentaerythritol tetraacrylate.[13] AHM showed the slowest rate among all systems studied. As previously reported by us,[13] to calculate AHM conversions, a weighted average of ΔH_{theor} for acrylates and methacrylates was used. This assumes that an equal number of acrylates and methacrylates react, which may not be true given differences in reactivity; therefore, AHM conversions are only semiquantitative. The conversion value of 41% (±7) is similar to that of pentaerythritol multiacrylate derivatives (ranging from 35 to 46% conversion), and lower than HDDA and HDDMA. One important aspect of the cross-linkers investigated here is presence of one or more hydroxyl groups in the molecules. Many of the most rapidly polymerizing systems examined by Jansen et al. also possess strong hydrogen-bonding and/or dipole−dipole interactions.[24,25] Groups capable of H-bonding interactions could lead to preorganization of the molecules forcing the double bonds into close proximity for reaction or could decrease the rate of termination, causing an increase in the polymerization rate and overall conversion.[24,26]

It has also been proposed by Koosterboer et al. that the physical effect of volume shrinkage plays a role on the kinetics of systems polymerized at high reaction rates.[27] The polymerizing system cannot maintain its equilibrium volume at very fast polymerization rates because volume shrinkage occurs at a slower time scale than the chemical reaction, resulting in increased free volume formation. This excess free volume causes higher mobility of unreacted double bonds, and consequently, increased overall conversion. Topological factors governing accessibility of reactive sites and pendant double bonds have also been shown to have an effect on the degree of cure of difunctional monomers, particularly with regard to the length of the spacer, i.e., the distance and flexibility between functional groups.[11] The longer and more flexible the spacer is, the higher the overall double bond conversion, due to a delayed autoacceleration effect.[28] This same behavior has been previously observed in our group with dimethacrylate cross-linkers linked by a 18 carbon diacid.[28] In Figure 6 it can be observed that the difunctional cross-linkers B1, B3, and B5 show similar polymerization rates, and all three possess the same spacer length between methacrylate groups.

If strong hydrogen bonding is a controlling factor, a decrease in the polymerization rate with increasing temperature should be observed due to reduction of the extent of hydrogen bonding at elevated temperatures.[29] Of course, this behavior competes with normal increases in rates with increasing temperature in the absence of strong intermolecular interactions. Photopolymeriza-

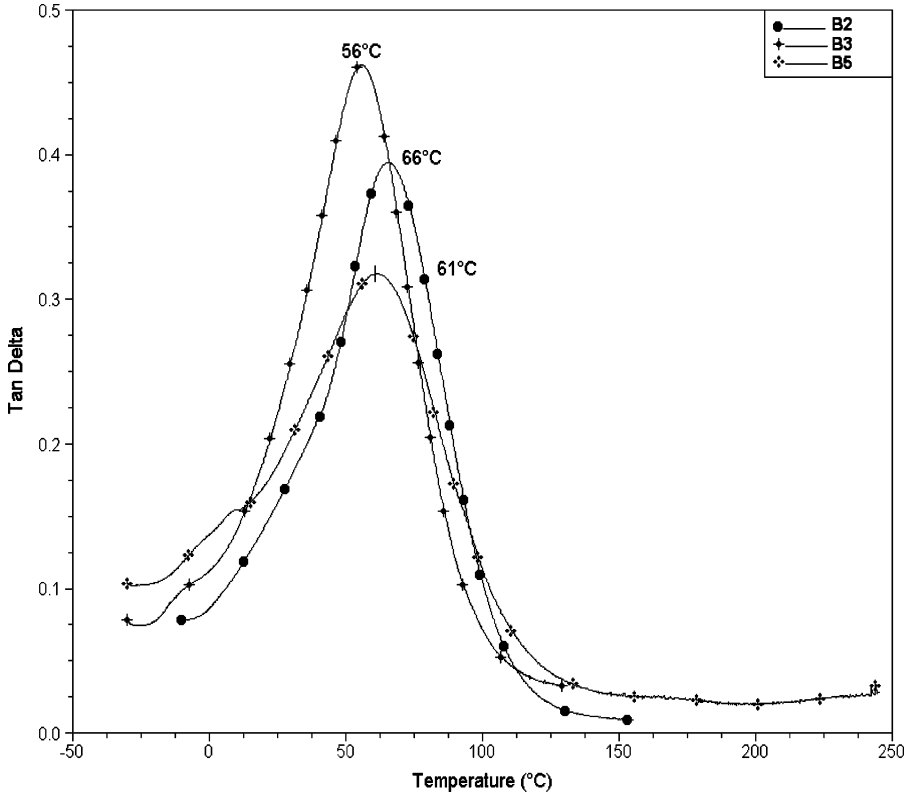


Figure 7. Dynamic mechanical analysis plots of the hydroxylated dimethacrylate cross-linkers investigated. Glass transition temperature (T_g) values are shown at the temperature corresponding to the peak maximum of the loss tangent δ observed for each sample.

tions of the bulk cross-linkers were thus carried out at 50−90 °C. Figure 6 shows the plots of polymerization rates as a function of the inverse of the temperature. While a decrease in rates was not observed, a clear decrease in the slope of these plots is evident. In fact, the slope of the HDDMA curve is at least four times higher than the slopes obtained for the hydroxylated cross-linkers. This indicates that hydrogen bonding does play a role in the behavior of these new cross-linkers.

The glass transition temperatures (T_g's) of the polymer networks obtained after photopolymerization of the hydroxylated dimethacrylate cross-linkers were determined using a dynamic mechanical analyzer. T_g values reported correspond to the temperature at which the peak maximum of the loss tangent δ was observed as shown in Figure 7. Cross-linkers were photopolymerized into rectangular shapes of approximately 1 mm in thickness, 10 mm wide, and 20 mm long using a poly(dimethylsiloxane) (PDMS) mold and UV light source; T_g values for B2, B3, and B5 were 66, 56, and 61 °C, respectively. These values are similar to those of Bis-GMA, tetraethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) cross-linkers.[9] The relatively high T_g values obtained for the polymer networks synthesized here at 30 °C imply formation of relatively rigid networks possessing hydrogen bonding. This is also consistent with faster onsets of the autoacceleration regions in the photoDSC plots (Figure 5). These T_g values, however, are significantly lower than those observed for common difunctional systems, such as HDDA or HDDMA and, as suggested by a reviewer, could be responsible for a delay of the autodeceleration effect, which would consequently allow the propagation rate (k_p) to remain unrestricted for longer periods of time leading to higher final overall conversions.

Conclusions

Novel hydroxylated methacrylate monomers with different nitrogen-linked groups were synthesized through the Michael addition of various amines to a commercial mixed acrylate/methacrylate monomer. Reactions carried out in bulk, without catalyst, gave reasonable rates and high conversions. The use of solvent was required only for systems in which the reactants were not miscible. Stoichiometric balance was used to selectively produce secondary amine (mono adducts) or tertiary amine (bis adducts) products. For highly hindered amines, such as 1-adamantanamine, the use of a protic solvent as reaction medium was not sufficient by itself for high conversion at short reaction times and higher temperatures were necessary. The isomer of AHM was present throughout the reactions and also underwent Michael addition reactions as evidenced by the disappearance of acrylate functionality in ^{13}C NMR spectra.

The photopolymerization kinetics of bulk cross-linkers was also evaluated. The rates of polymerization for these systems were significantly higher than that of a typical dimethacrylate monomer (HDDMA), approaching that of the diacrylate HDDA, with overall conversions approaching 81% (±5). Factors that contribute to the high rates and conversions achieved include strong hydrogen-bonding interactions as well as topological factors involving the length of the spacer between methacrylate groups.

Some potential applications of these new molecules include the design of materials with improved solvent resistance and adhesion, particularly useful in the coatings industry, where hardness, uniformity, toughness, durability and low shrinkage are important requirements.[19,30,31]

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Supporting Information Available: Table 1 containing ^{13}C NMR assignments used to monitor the selective formation of mono and bis adducts of the Michael addition reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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