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Synthesis and photopolymerizations of new hydroxyl-containing dimethacrylate crosslinkers

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Abstract

Two new hydroxyl-containing di(meth)acrylate monomers were synthesized from the reaction of methyl α-chloromethylacrylate (MCMA) and of ethyl α-chloromethylacrylate (ECMA) with glycerol. The monomers were obtained as mixtures of two isomers in different ratios and in combination with the analogous trimethacrylate monomers. Each monomer was isolated by column chromatography. The photopolymerization of these isomer mixtures and the trimethacrylate monomers was investigated individually by photodifferential scanning calorimetry (photoDSC) at room temperature using 2,2′-dimethoxy-2-phenyl-acetophenone (DMPA) as a photoinitiator. The effect of hydrogen bonding on the rates of polymerizations and conversions was examined. The results obtained for the synthesized monomers were compared to the values obtained for commercial monomers. It was observed that the hydroxyl-containing dimethacrylates polymerize much faster and to considerably higher conversion than the trimethacrylate monomers. The maximum rates of polymerization of the hydroxyl-containing monomers were higher than that of the hexanediol dimethacrylate (HDDMA), comparable to glycerol dimethacrylate and lower than hexanediol diacrylate (HDDA) and 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM).

Keywords: Photopolymerization; Dimethacrylates; Hydrogen bonding

1. Introduction

Photoinitiated free radical polymerization of multifunctional monomers produces highly crosslinked networks with high thermal stability, mechanical strength and resistance to solvent absorption. These networks are widely employed in coatings for flooring and furniture, dental restorative materials, optical fiber coatings, hard and soft contact lenses, and photolithography [1–7]. The monomers that are widely used in such photopolymerizations are multifunctional acrylates and methacrylates [8–15]. It is important to understand the effect of monomer structure on the photopolymerization reactivities. For example, the type and number of functional groups present, the distance and flexibility between functional groups, hydrogen bonding and liquid crystallinity, and the presence of heteroatoms have drastic effects on the reactivity of monomers [9,14, 16–21]. For example, the reactivity of various acrylates containing chlorine, oxetane, dioxolane, oxazolidone and carbonate in photopolymerization has been evaluated by Decker et al. [9]. Cyclic carbonate moieties in these monomers were found to enhance the reactivity and allow complete conversion to polymer. The reasons for this behavior are not completely understood.

Jansen et al. investigated the rate of polymerization of different acrylates in terms of hydrogen bonding capability for systems containing amide, urethane and urea groups, and found that the monomers capable of forming hydrogen bonds exhibit 3–6 times higher polymerization rates compared to their non-hydrogen bonding analogues possessing ester and carbonate groups [18]. The high reactivities were suggested to be due to pre-organization via hydrogen bonding to bring the double bonds close to each other and enhances the rate of polymerization, although reduction in the termination rate may also be involved or be the cause. They also investigated the effect of monomer polarity on rate of polymerization and found a direct correlation between the maximum rate of polymerization and the

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dipole moment of the monomer above a certain value [22]. The presence of a heteroatom linkage in diacrylates also greatly enhanced rates of polymerizations in both argon and air [20].

We have been synthesizing a wide variety of derivatives of alkyl α-hydroxymethylacrylates (RHMA) for several years and discovered rate enhancements due to a variety of substituent effects. For example, various benzoate ester derivatives of ethyl α-hydroxymethylacrylate (EHMA) were synthesized and found to display unexpectedly rapid photopolymerizations [23]. In a previous article, we evaluated the influence of long-chain flexible linking units between double bonds of diacrylates and dimethacrylates on the rates of polymerization of materials based on RHMAs, hydroxyethyl acrylate (HEA) and hydroxyethylmethacrylate (HEMA) monomers [24]. In this work, we investigate the photopolymerization behavior of new multifunctional RHMA–ether derivatives containing hydroxyl groups in the pendent moiety.

2. Experimental

2.1. Reagents

Methyl α-chloromethylacrylate (MCMA), ethyl α-chloromethylacrylate (ECMA) were prepared according to literature procedures [25,26]. The photoinitiator, 2,2′-dimethoxy-2-phenylacetophenone (Irgacure 651 or DMPA from Ciba-Geigy), was recrystallized from hexanes before use. All other solvents and starting materials were reagent grade and used as received.

2.2. Characterization

The monomer characterization involved ^{1}H and ^{13}C NMR spectroscopy (Varian Gemini 200 MHz) and Fourier transform infrared (FT-IR) spectroscopy on thin films on NaCl plates (Mattson 5000). Photopolymerizations were carried out on a TA Instruments differential photocalorimeter (DPC) with a medium pressure mercury lamp.

2.3. Procedure for the synthesis of monomers

To a mixture of glycerol (1.84 g, 0.02 m), triethylamine (TEA, 7.68 g, 0.076 m) and 20 ml of tetrahydrofuran (THF), ECMA (5.94 g, 0.04 m) was added under stirring in an ice bath After 24 h of stirring at 60 °C, THF was evaporated. The residue was diluted with 25 ml of methylene chloride (CH_2Cl_2) and the solution was extracted with 3 × 12 ml of water. After drying of the solution with anhydrous magnesium sulfate and evaporation of the solvent, the crude product was obtained in a 68% yield. The products were separated and purified by chromatography on silica gel using ethyl acetate/hexane (2:1) as eluent. The crude yield for the MCMA–glycerol adduct was 77% and it was also purified by column chromatography using the same solvent system. Individual characterization data for each monomer are given below.

MCMA–glycerol dimethacrylate (isomer mixture). ^{13}C NMR ($CDCl_3$): 51.6 (CH_3), 62.1 (CH_2–OH), 68.7 ($\mathrm{O}C\mathrm{H_2C}{=}$), 69.1 ($\mathrm{O}C\mathrm{H_2}$–CH), 69.4 ($\mathrm{O}C\mathrm{H_2C}{=}$), 70.4 ($\mathrm{O}C\mathrm{H_2}$–C=), 71.7 ($C\mathrm{H_2}$–CH–OH), 79.0 ($C$H–$CH_2$), 125.8 ($C\mathrm{H_2}{=}\mathrm{C}$), 126.1 ($C\mathrm{H_2}{=}\mathrm{C}$), 126.8 ($C\mathrm{H_2}{=}\mathrm{C}$), 136.7 ($\mathrm{CH_2}{=}C$), 136.6 ($\mathrm{CH_2}{=}C$), 166.0 (C=O), 166.2 (C=O) ppm.

Anal. calcd for $C_{13}O_7H_{20}$: C, 54.17; H, 6.94. Found: C 53.89; H, 7.16.

ECMA–glycerol dimethacrylate (isomer mixture). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 60.5 ($C\mathrm{H_2CH_3}$), 62.1 (CH_2OH), 68.7 ($\mathrm{O}C\mathrm{H_2C}{=}$), 69.1 ($\mathrm{O}C\mathrm{H_2}$–C), 69.4 ($\mathrm{O}C\mathrm{H_2}$–$C{=}$), 70.5 ($\mathrm{O}C\mathrm{H_2}$–C=), 71.7 ($C\mathrm{H_2}$–CH–OH), 79.0 ($C$H–$CH_2$), 125.4 ($C\mathrm{H_2}{=}\mathrm{C}$), 125.7 ($C\mathrm{H_2}{=}\mathrm{C}$), 126.6 ($C\mathrm{H_2}{=}\mathrm{C}$), 136.9 ($\mathrm{CH_2}{=}C$), 137.2 ($\mathrm{CH_2}{=}C$), 165.6 (C=O), 165.8 (C=O). FT-IR: 3504 (OH), 2983 (C–H), 1712 (C=O), 1637 (C=C).

Anal. calcd for $C_{15}O_7H_{24}$: C, 56.96; H, 7.60. Found: C 56.73; H, 7.94.

2.4. Photopolymerization procedure

Approximately 3.0 mg of sample was placed at the bottom of an aluminum DSC pan that had been impressed with a smaller volume depression whose bottom was press flattened. A CH_2Cl_2 solution of the photoinitiator solution was added with a micro-syringe to give a final concentration in the monomer of 2.0 mol% after evaporation of the solvent. Heats of photoreactions were measured using a 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. The DSC chamber was purged with nitrogen to remove the air and CH_2Cl_2 for 10 min before polymerization; purging was continued during polymerization. The samples were irradiated for 10 min at room temperature. The heat flux as a function of reaction time was monitored using DSC under isothermal conditions, and both the rate of polymerization and conversion were then calculated as a function of time. The heat of reaction value $\Delta H_\mathrm{p} = 13.1$ kcal/mol was used as the theoretical heat evolved for methacrylate double bonds [27]. Rates of polymerization were calculated according to the following formula:

$$\mathrm{Rate}\,\frac{(Q/s)M}{n\Delta H_\mathrm{p}m}$$

where Q/s is heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule, and m the mass of monomer in the sample.

3. Results and discussion

3.1. Synthesis of monomers

The monomers were synthesized by the reaction of MCMA and ECMA with glycerol using TEA as catalyst in THF at 60 °C (Fig. 1). The ratio of MCMA or ECMA to glycerol was 2:1 to obtain hydroxylated dimethacrylate monomers. The crude product yields were 65–80%, containing a mixture of isomers of MCMA–glycerol dimethacrylate or ECMA–glycerol dimethacrylate with a very small amount of MCMA–glycerol trimethacrylate or ECMA–glycerol trimethacrylate monomer. The two isomers are formed from 1,3 or 1,2 substitution reactions on glycerol giving one isomer with primary hydroxyl group (unsymmetrical isomer) and the other with secondary hydroxyl group (symmetrical isomer). The substitution of the three hydroxyl groups of glycerol resulted in the formation of trimethacrylate monomers as by-products of these reactions.

The mixtures were subjected to a chromatographic separation on silica gel using ethyl acetate/hexane (2:1) mixtures. The first fractions obtained from the column were the less polar trimethacrylate monomers. The ^{13}C NMR spectrum of this fraction for ECMA–glycerol mixture (Fig. 2) showed characteristic peaks for ethyl carbons at 14.08 and 60.6 ppm, a tertiary carbon at 77.9 ppm and methylenes attached to this carbon at 69.5 ppm, two different methylene carbons attached to double bond carbons at 68.4 and 70.7 ppm (2:1 ratio), two sets of double bond carbons at 125.4, 137.2 and 125.5, 137.6 ppm in 2:1 ratio, and a carbonyl carbon at 165.8 ppm. The FT-IR spectrum of this fraction (Fig. 3) showed no hydroxyl peak, confirming complete reaction of the alcohol groups. The ^{1}H NMR spectrum of this monomer is characterized by methyl hydrogens at 1.25, methylenes of ethyl ester at 4.20, methylenes adjacent to double bond at 4.35, a tertiary hydrogen at 3.75, methylenes attached to this carbon at 3.6 and double bond hydrogens at 5.85, 5.92 and 6.3 ppm.

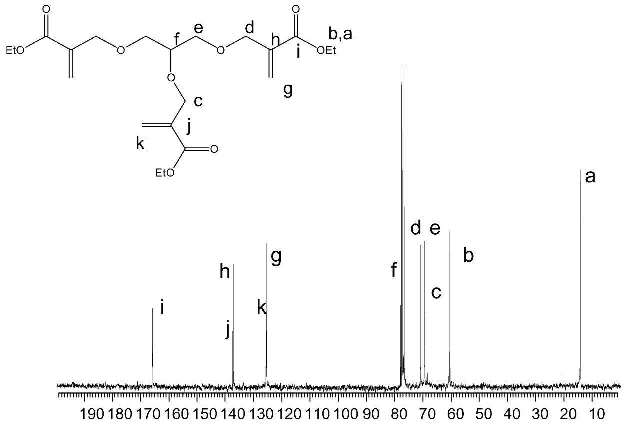

Fig. 2. ^{13}C NMR spectrum of ECMA–glycerol trimethacrylate monomer.

The ^{13}C NMR spectrum of the MCMA–glycerol trimethacrylate monomer showed a methyl carbon at 51.7 ppm, a tertiary carbon at 77.8 ppm, methylenes at 68.4, 69.4 and 70.6 ppm, double bond peaks at 125.7, 125.8, 126.3, 136.8 and 137.2 ppm and carbonyl carbons at 166.1 and 166.2 ppm.

The other fractions of column chromatography contained mixtures of the two isomers at different ratios. The ^{13}C NMR spectra of the two different isomer mixtures of ECMA–glycerol dimethacrylate monomer showed peaks for ethyl carbons at 13.9 and 60.5 ppm and a tertiary carbon at 79.0 ppm for both isomers (Fig. 4). The peak at 62.1 ppm is due to methylene carbon attached to primary hydroxyl group of the unsymmetrical isomer. The peaks at 68.7, 69.1, 70.5 ppm correspond to methylene carbons of the unsymmetrical isomer. Methylene carbons of symmetrical isomer appears at 69.4 and 71.7 ppm. The ratio of methylene carbons or carbonyl carbons (165.6 ppm for symmetrical isomer and 165.8 ppm for unsymmetrical isomer) indicates relative ratios of the isomers. For example, the mixtures in Fig. 4 show approximately 2:1 (mixture 1) and 1:1 (mixture

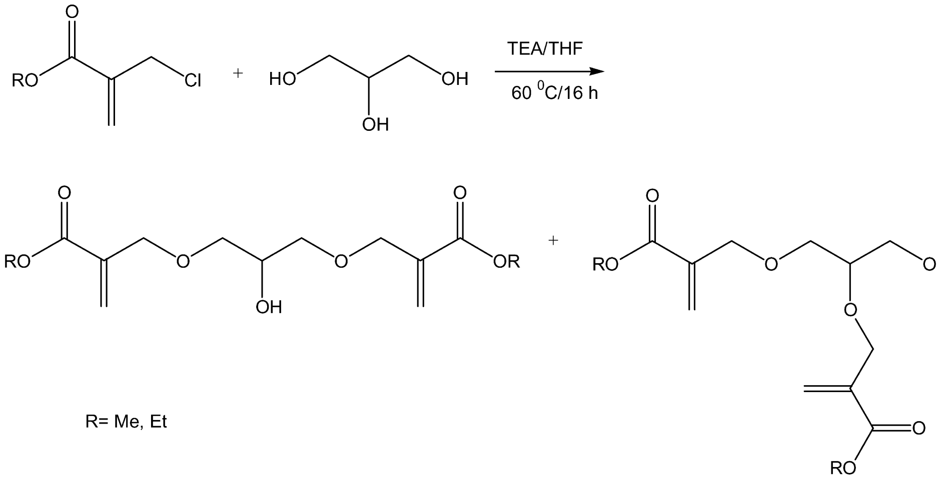

Fig. 1. Synthesis of hydroxyl-containing dimethacrylate monomers.

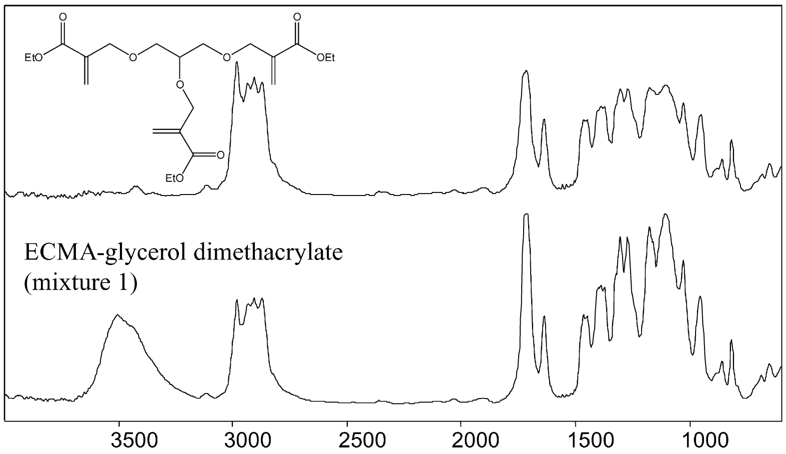

Fig. 3. FT-IR spectra of ECMA–glycerol dimethacrylate and ECMA–glycerol trimethacrylate monomers.

2) ratio of symmetrical to unsymmetrical isomers. The peaks at 20.8, 60.2 and 170.8 are due to residual ethyl acetate from column chromatography. ^{1}H NMR spectra of the isomers could not be used for the determination of isomer compositions due to overlapping peaks of the isomers. The FT-IR spectrum of this monomer (Fig. 3) showed the characteristic absorptions of hydroxyl, carbonyl and C=C groups at 3504, 1712 and 1637 cm^{-1}.

^{13}C NMR spectrum of MCMA–glycerol dimethacrylate monomer (Fig. 5, bottom spectrum) is characterized by methyl carbons at 51.6 ppm, methylene carbons for the unsymmetrical isomer at 62.1, 68.7, 69.1 and 70.4 ppm, those for the symmetrical isomer at 69.4 and 71.7 ppm, tertiary carbon at 79.0 ppm, three sets of double bond carbons and two carbonyls at 166.0 and 166.2 ppm for the symmetrical and unsymmetrical isomers. Comparison of peak heights of carbonyl peaks gave a 2.7:1 ratio of symmetrical to unsymmetrical isomer. Another fraction from the column chromatography gave a 3.2:1 ratio (symmetrical to unsymmetrical) of isomers. Fig. 5 (top spectrum) also shows a mixture of MCMA–glycerol dimethacrylate and MCMA–glycerol trimethacrylate monomers due to partial separation. The peaks at 77.8 and 79.0 ppm correspond to two different tertiary carbons of dimethacrylate and trimethacrylate monomers. Comparison of these peak heights showed approximately 1:1 ratio of MCMA–glycerol dimethacrylate to MCMA–glycerol trimethacrylate monomers.

3.2. Photopolymerizations

Photopolymerizations of the monomers were followed by DPC. All the polymerizations were performed under identical conditions of temperature (room temperature), initiator concentration (2.0 mol%) and UV light intensity. The hydroxyl-containing monomers were cured as mixtures of isomers. Fig. 6 shows the rates versus time plots for ECMA–glycerol trimethacrylate, ECMA–glycerol dimethacrylate (two slightly different isomer mixtures) and hexanediol dimethacrylate (HDDMA) monomers. The latter commercial monomer was polymerized under the same conditions for comparison. It is known that, as the monomer functionality is increased, the rate of polymerization increases while the conversion decreases. Thus, ECMA–glycerol trimethacrylate would be expected to have higher rates of polymerization than the dimethacrylate

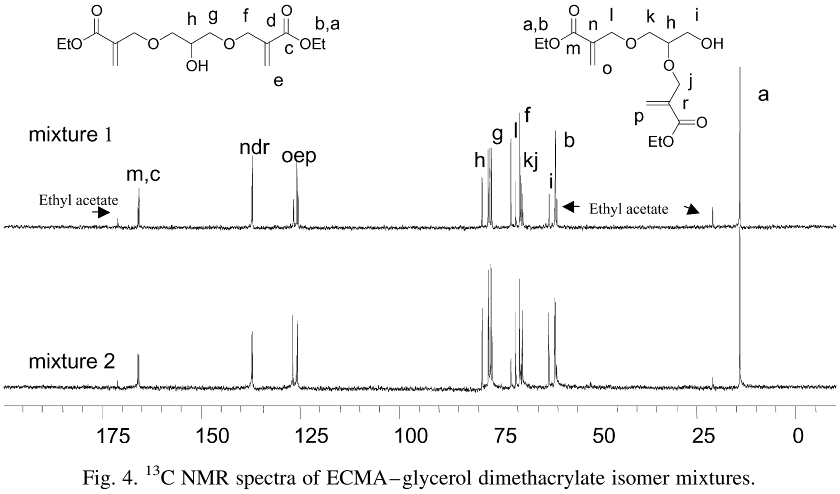

Fig. 4. ^{13}C NMR spectra of ECMA–glycerol dimethacrylate isomer mixtures.

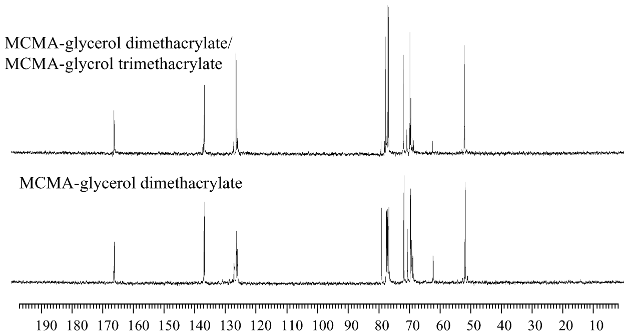

Fig. 5. ^{13}C NMR spectra of MCMA–glycerol dimethacrylate isomer mixtures.

monomers. However, the hydroxyl-containing dimethacrylate monomers described here showed higher rates of polymerizations than their trimethacrylate analogs. This may be due to the hydrogen bonding capability which brings the double bonds close to each other and enhances the rate of polymerization. Maximum rates of polymerizations for ECMA–glycerol trimethacrylate, hexanediol dimethacrylate, isomer mixtures of ECMA–glycerol dimethacrylate (mixture 2) and ECMA–glycerol dimethacrylate (mixture 1) were found to be 0.0088, 0.0357, 0.03 and 0.051 s^{-1}, respectively. It was observed that as the unsymmetrical monomer content in the isomer mixture increased, the maximum rate of polymerization decreased from 0.051 to 0.03 s^{-1}. Although the two isomers have similar chemical structures, the mixture 1 containing larger amount of symmetrical isomer (with secondary hydroxyl groups) showed higher polymerization rates than mixture 2. The reason for the higher reactivity of the symmetrical isomer is unclear but the change in polarity may also be important.

Fig. 7 shows the conversion of these monomers as a function of time. As the functionality of monomers increased, the double bond conversions decreased. The two ECMA–glycerol monomer mixtures showed the same conversions of 62–63%, while ECMA–glycerol trimethacrylate gave 56% conversion. The higher degree of conversion for HDDMA monomer (72%) may have resulted from autoacceleration that was not seen for the other systems.

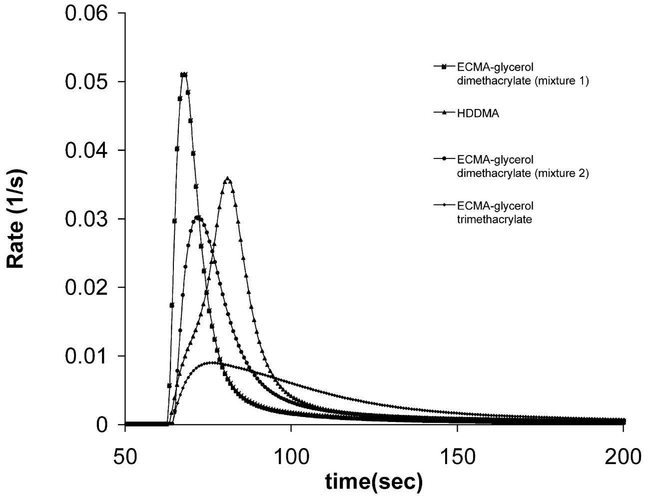

Fig. 6. Rate of polymerization of ECMA–glycerol dimethacrylate (mixture 1) (top), HDDMA, ECMA–glycerol dimethacrylate (mixture 2) and ECMA–glycerol trimethacrylate (bottom).

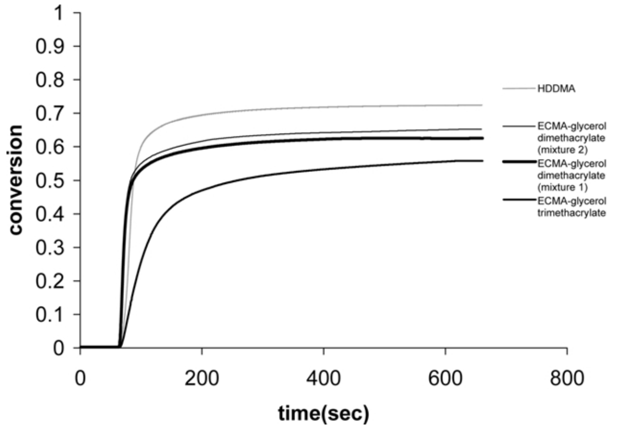

Fig. 7. Conversion-time plots of HDDMA (top), ECMA–glycerol dimethacrylate (mixture 2), ECMA–glycerol dimethacrylate (mixture 1) and ECMA–glycerol trimethacrylate (bottom).

Fig. 8 shows the rates versus time plots for MCMA–glycerol trimethacrylate, a MCMA–glycerol trimethacrylate–dimethacrylate mixture, MCMA–glycerol dimethacrylate (isomer mixture) and glycerol dimethacrylate monomers. The maximum rate of polymerization for MCMA–glycerol trimethacrylate monomer was found to be similar to ECMA–glycerol trimethacrylate, with respective values 0.0121 and 0.0088 s^{-1}. The monomer with smaller methyl ester groups showed a higher rate of polymerization than the ethyl ester monomer. MCMA–glycerol dimethacrylate mixture (3.2:1) showed a higher rate of polymerization (0.051 s^{-1}) than the trimethacrylate (0.0121 s^{-1}). The MCMA–glycerol dimethacrylate–trimethacrylate mixture (1:1) polymerized faster than pure trimethacrylate but slower than the dimethacrylate mixture (0.030 s^{-1}). The maximum rate of polymerization for

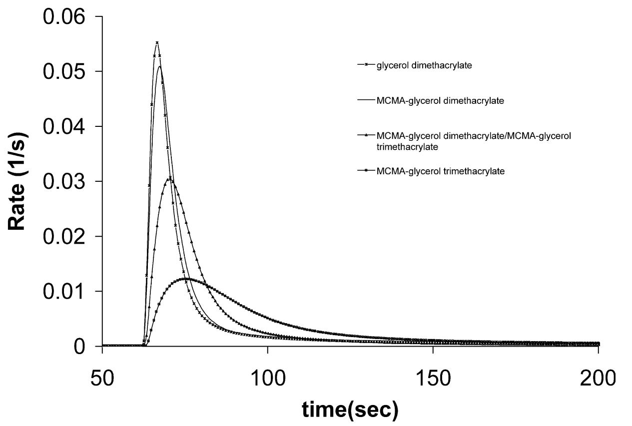

Fig. 8. Rate of polymerization of glycerol dimethacrylate (top), MCMA–glycerol dimethacrylate isomer mixture, MCMA–glycerol dimethacrylate/MCMA–glycerol trimethacrylate mixture and MCMA–glycerol trimethacrylate (bottom).

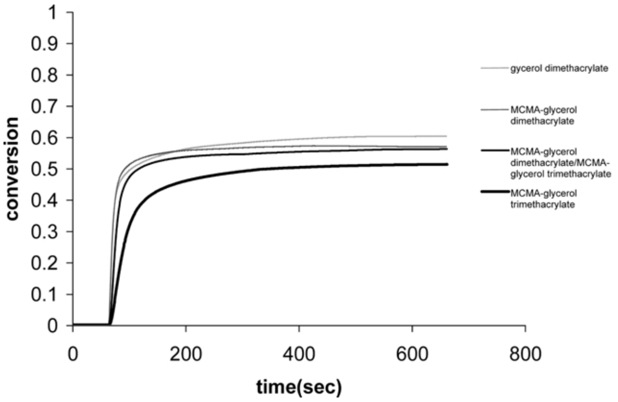

Fig. 9. Conversion-time plots of glycerol dimethacrylate (top), MCMA–glycerol dimethacrylate isomer mixture, MCMA–glycerol dimethacrylate/MCMA–glycerol trimethacrylate mixture and MCMA–glycerol trimethacrylate (bottom).

glycerol dimethacrylate was 0.055 s^{-1}. The conversion-time plots of these monomers are shown in Fig. 9. The MCMA–glycerol dimethacrylate monomer and trimethacrylate–dimethacrylate mixture showed similar conversions of 56–57%, while MCMA glycerol trimethacrylate polymerization gave 51% conversion. The high conversion of glycerol dimethacrylate (60%) was probably the result of late gelation.

The photopolymerization of two other commercial multifunctional monomers was carried out under the same conditions. One of them was a mixed acrylate/methacrylate monomer having a pendant hydroxyl group capable of hydrogen bonding, 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM). The other monomer was the well-known 1,6-hexanediol diacrylate (HDDA). Figs. 10 and 11 show the rates of polymerization and conversions of one of the synthesized monomers with AHM and HDDA as a function of time. It is known that diacryates have higher rates of polymerization than comparable dimethacrylates. Thus, it is not surprising that HDDA showed the highest rate of polymerization of all the systems evaluated here. On the other hand, AHM with mixed acrylate/methacrylate groups was less reactive than HDDA but polymerized faster than ECMA–glycerol dimethacrylate mixture (2:1). HDDA and AHM were found to polymerize 2.2 and 1.4 times faster than ECMA–glycerol dimethacrylate monomer with the maximum rates of polymerization of 0.051, 0.11 and 0.07 s^{-1} for ECMA–glycerol dimethacrylate, HDDA and AHM, respectively. It was observed that HDDA, with a very fast polymerization rate, reaches conversions up to 71%, while the conversions for ECMA–glycerol dimethacrylate and AHM were only 62 and 58%.

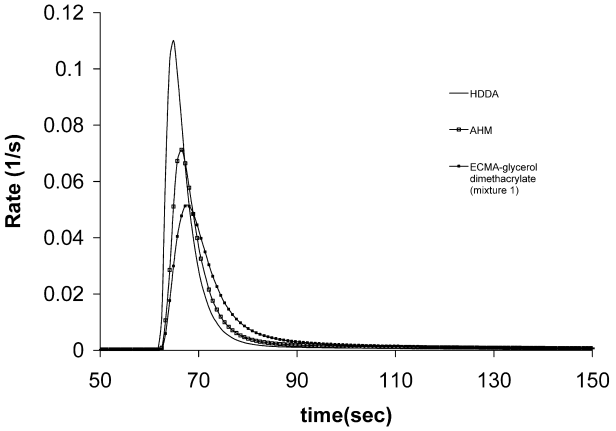

Fig. 10. Rate of polymerization of HDDA (top), AHM and ECMA–glycerol dimethacrylate (mixture 1) (bottom).

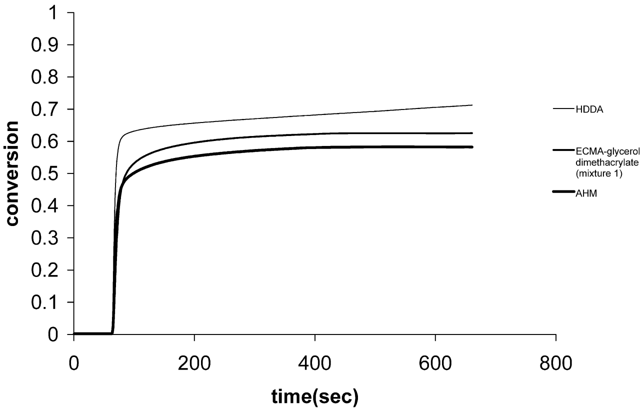

Fig. 11. Conversion-time plots of HDDA (top), ECMA–glycerol dimethacrylate (mixture 1) and AHM (bottom).

4. Conclusions

Two new hydroxyl-containing dimethacrylate monomers were synthesized as mixtures of two isomers plus a trimethacrylate analog. Photopolymerizations of the separated dimethacrylate isomer mixtures were investigated with respect to rates of polymerization and conversions. For comparison with these monomers, trimethacrylate monomers (isolated during the dimethacrylate monomer synthesis) and commercial dimethacrylate monomers were polymerized under the same conditions. It was observed that introduction of hydroxyl groups has an important effect on the bulk reactivities of these monomers: the maximum rates of the monomers followed the order HDDA > AHM > MCMA–glycerol dimethacrylate ~ ECMA–glycerol dimethacrylate ~ glycerol dimethacrylate > HDDMA > MCMA–glycerol trimethacrylate > ECMA–glycerol trimethacrylate.

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