Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Polymer 44 (2003) 5131–5136

polymer

www.elsevier.com/locate/polymer

Photopolymerization of urethane dimethacrylates synthesized via a non-isocyanate route

Heidi J. Assumption[a,b], Lon J. Mathias[a,*]

[a]*Department of Polymer Science, School of Polymers and High Performance Materials, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, MS 39406-0076, USA*
[b]*Sasol Technology Research and Development, P.O. Box 1, Sasolburg 1947, South Africa*

Received 24 February 2003; received in revised form 27 May 2003; accepted 4 June 2003

Abstract

Urethane dimethacrylate monomers were synthesized via a non-isocyanate route from the reaction of a urethane diol with methacrylic anhydride. The urethane diols were synthesized through the reaction of ethylene carbonate with 1,6-hexanediamine, 3-amino-1-propanol and 2,2-dimethyl-1,3-propanediamine. ^{1}H NMR, ^{13}C NMR and FTIR spectroscopies confirmed the structure of the monomers. Elemental analysis confirmed the purity of the monomers. Photopolymerization of these multifunctional monomers was investigated with respect to polymerization rates and conversions using photoinitiated differential scanning calorimetry. Irgacure 651® was used as an initiator at 2 mol%. Photopolymerization results indicate high peak polymerization rates, 0.09 s^{-1} compared to 0.06 s^{-1} for bis-GMA and 0.07 s^{-1} for HDDMA polymerized under the same conditions. Overall bulk conversions were 70–78%, compared to 68 and 76% for bis-GMA and HDDMA, respectively.

The methodology developed here utilizes diamines and amino-alcohols that are members of commercially available families possessing a large range of structures, thus allowing synthetic flexibility in obtaining new urethane dimethacrylates with desirable properties.

Keywords: Urethane dimethacrylates; Cyclic carbonate; Photopolymerization

---

1. Introduction

Multifunctional urethane methacrylates produce densely crosslinked networks with high thermal stability and mechanical strength. These resins find applications in areas such as coatings, adhesives, stereolithography and dental restorative materials [1–3]. The commonly used dental monomer of this type is 1,6-bis-(2-methacryloyloxy-ethoxycarbonylamino)-2,4,4-trimethyl-hexane, or UDMA for short. The photopolymerization of UDMA results in flexible materials, and it is mostly used in combination with the less flexible 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane (bis-GMA) [2], the latter being the most commonly used dimethacrylate monomer in dental composites. Some advantages of bis-GMA over smaller dental monomers such as methyl methacrylate include lower cure shrinkage, higher modulus, and reduced toxicity due to lower volatility and diffusivity into tissues [1]. The hydroxyl groups of bis-GMA provide desirable adhesion to various materials like tooth enamel, bone and glass [4]. However, bis-GMA hydroxyl groups increase resin viscosity and cured polymer water uptake at room temperature [5]. A common practice when using bis-GMA is to add a less viscous comonomer such as triethylene glycol dimethacrylate (TEGDMA) or UDMA as a reactive diluent. TEGDMA, however, has been shown to adversely affect the properties of the matrix resin by increasing final equilibrium water absorption and cure shrinkage [1]. Current research goals in this area include identifying new dimethacrylates of moderately low viscosities, which can eliminate or minimize the use of diluent monomers for this type of application [6,7]. For example, Moszner and coworkers [2] prepared urethane dimethacrylates with more rigid structures. Their aim was to synthesize multifunctional urethane methacrylates that can result in materials with mechanical properties comparable with those of bis-GMA-based resins.

Urethane dimethacrylates are usually synthesized from

---

[*] Corresponding author. Tel.: +1-601-266-4871; fax: +1-601-266-5504.
E-mail address: lon.mathias@usm.edu (L.J. Mathias).

0032-3861/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00530-5

the reaction of diisocyanates with hydroxyalkyl methacrylates. UDMA is the reaction product of two equivalents of 2-hydroxyethyl methacrylate (HEMA) reacted with 2,4,4-trimethylhexamethylene diisocyanate (TMDI) [2]. In fact, commercial diisocyanates are synthesized by non-phosgene processes, which make them environmentally more attractive. One example is the montmorillonite-catalyzed dealcoholysis of mono- and dicarbamates to mono- or diisocyanates [8]. However, the production of urethane dimethacrylates excluding both types of hazardous monomers (phosgene and isocyanates) would be advantageous for health and environmental reasons. In this paper, we report on the synthesis and photopolymerization of urethane dimethacrylates prepared via such a non-isocyanate and non-phosgene route.

2. Experimental

2.1. Reagents

Ethylene carbonate (Aldrich), 1,6-hexanediamine (Aldrich), 2,2-dimethyl-1, 3-propanediamine (Aldrich), 3-amino-1-propanol (Aldrich), 4-(dimethyl-amino)pyridine (DMAP, Acros Organics), 1,6-hexanediol dimethacrylate (HDDMA, Aldrich), Bisphenol A glycerolate (1 glycerol/-phenol) dimethacrylate (bis-GMA, Aldrich), 2,2-dimethoxy-2-phenyl acetophenone (Irgacure 651®, Ciba-Geigy), and dichloromethane were used as received. Methacrylic anhydride (MAAn, Aldrich, 94%) and tetrahydrofuran (THF) were purified by distillation and *N,N*-dimethylformamide (DMF) was dried over 4A molecular sieves prior to use.

2.2. Characterization

Monomer characterization included ^{1}H and ^{13}C NMR spectroscopies (Varian Unity Inova 500 MHz, DMSO-d_6) and FTIR spectroscopies on NaCl plates (Mattson 5000). Standard acquisition parameters were used. NMR data was referenced to internal solvents.

2.3. Synthesis of urethane diols

2.3.1. Reaction of ethylene carbonate with 1,6-hexanediamine (Urdiol **1**)

Ethylene carbonate (26.4 g, 0.3 mol), 1,6-hexanediamine (17.4 g, 0.15 mol) and 20 mL dichloromethane were stirred at room temperature in a 250 mL round-bottomed flask according to the procedure of Rokicki and Piotrowska [9]. A white precipitate formed after 1 h. The precipitate was filtered, washed with cold dichloromethane and further purified by recrystallization from acetone to give a white solid in 70% yield with a melting point of 93–94 °C.

2.3.2. Reaction of ethylene carbonate with 3-amino-1-propanol (Urdiol **2**)

Ethylene carbonate (13.21 g, 0.15 mol), 3-amino-1-propanol (11.27 g, 0.15 mol) and dichloromethane (20 mL) were stirred at room temperature in a 250 mL round-bottomed flask for approximately 16 h during which the mixture phase-separated. The product (top layer) was removed and the residual dichloromethane evaporated. The final product was a clear liquid (87% yield) with a viscosity close to that of water.

2.3.3. Reaction of ethylene carbonate with 2,2-dimethyl-1,3-propanediamine (Urdiol **3**)

Urdiol 3 was prepared using the same procedure as for Urdiol 2. From 6.6 g (0.075 mol) of ethylene carbonate and 3.8 g (0.0375 mol) of 2,2-dimethyl-1,3-propanediamine, 10.16 g of the product was obtained (97% yield). The final product was a clear liquid with a higher viscosity than Urdiol 2.

2.4. Synthesis of urethane dimethacrylates

2.4.1. Reaction of Urdiol 1 with methacrylic anhydride (UDMA **1**)

Urdiol 1 (0.01 mol) was dissolved in 30 mL DMF at room temperature. DMAP catalyst (0.0025 mol) was added to the reaction mixture, followed by dropwise addition of methacrylic anhydride (0.025 mol). The reaction mixture was stirred at room temperature for 3–4 h under a nitrogen atmosphere. Approximately 10 mg $CuCl_2$ was added to the reaction mixture before the removal of DMF and residual methacrylic anhydride under reduced pressure. The resultant oily product was washed with deionized water to remove trace amounts of DMF, methacrylic acid and the $CuCl_2$ inhibitor. The residue was dried in a vacuum oven and precipitated from hexane. The final product was a white solid (70% yield) with a melting point of 56–57 °C.

UDMA 1. $C_{20}H_{32}N_2O_8$ (428.48) calcd: C, 56.06; H, 7.53; N, 6.54; O, 29.87. Found: C, 56.17; H, 7.64; N, 6.57.

^{13}C NMR: δ (ppm) = 18.6 (CH_3), 26.6 (CH_2), 29.9 (CH_2), 40.8 (CH_2NH), 62.2 ($OCH_2\mathit{CH_2}OCONH$), 63.8 ($O\mathit{CH_2}CH_2OCONH$), 126.7 ($\mathit{CH_2}{=}C$), 136.4 ($CH_2{=}\mathit{C}$), 156.6 (C=O, carbamate), 167.1 (C=O, ester). ^{1}H NMR: δ (ppm) = 1.21 (m, CH_2), 1.35 (m, CH_2), 1.87 (s, $CH_2{=}C{-}\mathit{CH_3}$), 2.93 (m, CH_2NH), 4.19 (m, $OCH_2\mathit{CH_2}OCONH$), 4.25 (m, $O\mathit{CH_2}CH_2OCONH$), 5.68 and 6.03 (2s, $\mathit{CH_2}{=}C$), 6.92 (br, NH), 7.26 (t, NH). FTIR (neat): 3330, 2939, 1712, 1641, 1537, 1454 cm^{-1}.

2.4.2. Reaction of Urdiol 2 with methacrylic anhydride (UDMA **2**)

UDMA 2 was prepared using the same procedure as for UDMA 1, except the mixture was stirred for 24 h. Trace amounts of DMF, methacrylic acid and $CuCl_2$ inhibitor was removed by washing the oily residue with deionized water. The product was dissolved in 20 mL dichloromethane and dried over anhydrous sodium sulfate. The solvent was removed and the final product obtained as a pale yellow liquid (40% yield) with a viscosity similar to that of the starting material, Urdiol 2; that is, similar to water.

UDMA 2: $C_{14}H_{21}NO_6$ (299.32) calcd: C, 56.18; H, 7.07; N, 4.68; O, 32.07. Found: C, 55.98; H, 7.28; N, 4.59.

^{13}C NMR: δ (ppm) = 18.57 and 18.6 (CH_3), 29.1 (CH_2), 37.8 (CH_2NH), 62.3 ($OCH_2\mathit{CH_2}OCONH$), 62.7 (CH_2CH_2-$\mathit{CH_2}OCO$), 63.8 ($O\mathit{CH_2}CH_2OCONH$), 126.2 and 126.7 ($\mathit{CH_2}{=}C$), 136.4 and 136.6 ($CH_2{=}\mathit{C}$), 156.7 (C=O, carbamate), 167.1 and 167.2 (C=O, ester). ^{1}H NMR: δ (ppm) = 1.72 (m, CH_2), 1.84 (s, CH_3), 3.06 (m, $\mathit{CH_2}NH$), 4.06 (m, $OCH_2\mathit{CH_2}OCONH$), 4.20 (m, $CH_2CH_2\mathit{CH_2}OCO$), 4.24 (m, $O\mathit{CH_2}CH_2OCONH$), 5.62, 5.64 and 6.00 ($\mathit{CH_2}{=}C$), 6.92 (br, NH), 7.26 (t, NH). FTIR (neat): 3346, 2960, 1714, 1637, 1531, 1454 cm^{-1}.

*2.4.3. Reaction of Urdiol 3 with methacrylic anhydride (UDMA **3**)*

UDMA 3 was synthesized in the same manner as UDMA 2, except THF was used as solvent. The final product was isolated as a pale yellow liquid (54% yield) with a viscosity close to that of its syrup-like urethane diol analogue.

UDMA 3: $C_{19}H_{30}N_2O_8$ (414.45) calcd: C, 55.05; H, 7.30; N, 6.76; O, 30.88. Found: C, 55.16; H, 7.53; N, 6.60.

^{13}C NMR (*$CDCl_3$*): δ (ppm) = 18.5 (CH_3), 23.3 ($C(\mathit{CH_3})_2$), 36.6 ($\mathit{CH_2}NH$), 47.7 ($\mathit{C}(CH_3)_2$), 62.9 (OCH_2-$\mathit{CH_2}OCONH$), 63.2 ($O\mathit{CH_2}CH_2OCNHO$), 126.2 ($\mathit{CH_2}{=}C$), 136.2 ($CH_2{=}\mathit{C}$), 157.3 (C=O, carbamate), 167.4 (C=O, ester). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.83 (m, $C(\mathit{CH_3})_2$), 1.91 (s, CH_3), 2.93 (m, $\mathit{CH_2}NH$), 4.29 (m, $O\mathit{CH_2CH_2}O$), 5.56 and 6.10 (2s, $\mathit{CH_2}{=}C$). FTIR (neat): 3352, 2960, 1716, 1635, 1525, 1471 cm^{-1}.

2.5. Photopolymerization procedure

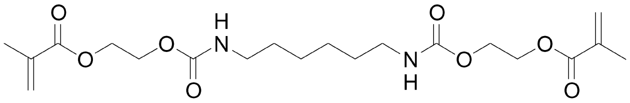
Photopolymerizations of monomers were carried out on a TA Instruments Photo-DSC (model 912S) using Irgacure 651® as the primary initiator system. Bis-GMA and HDDMA were used as standards for comparison purposes. Initiator was added at 2 mol% to a typical monomer sample size of 3 mg. The initiator was first dissolved in dichloromethane and a specific amount of this solution was added to neat monomers. The monomer (ca 3 mg) was placed in an aluminum DSC pan and carefully weighed. Then initiator solution was added and the sample transferred to the sample holder in the photo-DSC. The samples were purged with nitrogen for 10 min to remove air and to allow for complete solvent evaporation prior to the polymerization. Samples were photocured for 6 min at 80 °C under nitrogen purge and the heat flux as a function of reaction time was monitored using isothermal conditions. The light shutter was opened at the 60 s point during data acquisition. Both rate of polymerization and conversion were calculated as a function of time. Calculations were based on the heat of reaction (ΔH_p) of 54.8 kJ/mol for the methacrylate double bond [10]. The following equation was used to determine the rate of polymerization:

$$R_P = \frac{(Q/s)M}{n\Delta H_p m}$$

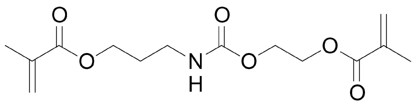
where Q/s is heat flow per second during reaction, M the molecular weight of the monomer, n the number of double bonds per monomer molecule, ΔH_p the heat released per mole of double bonds reacted and m the mass of monomer in the sample [10–12].

3. Results and discussion

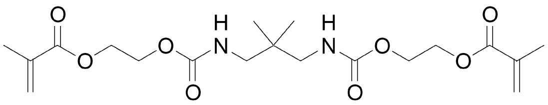
The mono- and bis-urethane monomers (Fig. 1) were synthesized from ethylene carbonate. The latter was first converted to a urethane diol by reaction with an appropriate diamine or amino-alcohol. The urethane diol products were reacted with methacrylic anhydride to give the corresponding urethane dimethacrylates. Fig. 2 gives a representative example of the overall synthetic approach used here to obtain the mono- and bis-urethane materials. Urdiol 1 and 2 were obtained using the procedure of Rokicki et al. [9]. Our product (Urdiol 1) was further purified by recrystallization from acetone and has a melting point 10 °C higher than the literature melting point of 83–84 °C, indicating a different crystal form or higher purity. Urdiol 2 was a clear liquid with a relatively low viscosity when compared to water. According to the procedure of Rokicki et al. [9] the product



UDMA 1



UDMA 2



UDMA 3

Fig. 1. Chemical structures of urethane dimethacrylates synthesized.

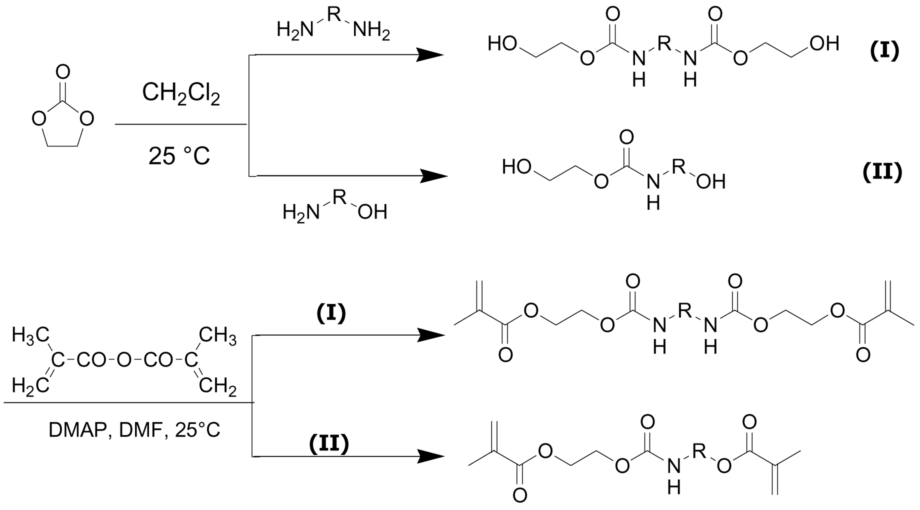


Fig. 2. Synthetic scheme to obtain mono- and bis-urethane dimethacrylates.

was obtained as a white solid. We repeated the synthesis and in both cases the product was obtained as a clear liquid. NMR analysis confirmed the structure of the diol synthesized here; the discrepancy remains unexplained. Urdiol 3 obtained from 2,2-dimethyl-1, 3-propanediamine is also a clear liquid, but with a higher viscosity.

UDMA 1 is a white solid with a melting point of 56–57 °C, while both UDMA 2 and UDMA 3 are pale yellow liquids with UDMA 3 being more viscous than UDMA 2. UDMA 2 and 3 are both reactive monomers and may polymerize spontaneously on solvent removal on the rotary evaporator. For this reason $CuCl_2$ was added to inhibit radical formation on solvent removal. The characterization of the synthesized monomers was carried out by ^1H NMR, ^{13}C NMR and IR spectroscopies. The spectral data are in agreement with the expected structures. For example, the ^1H NMR analysis of the products showed two signals for the NH protons, which correspond to the pseudo *E* and *Z* urethane conformers previously reported for similar systems [13]. The methacrylic groups are supported by the presence of two singlets ($\delta = 5.7$ and 6.0 ppm) on the ^1H NMR spectrum as well as the peaks at 126.7 and 136.4 ppm on the ^{13}C NMR assignable to the double bond of a methacrylate group.

The purity of the urethane dimethacrylate monomers was confirmed by elemental analysis and was acceptable (see Fig. 3) for subsequent photopolymerizations. In order to evaluate the radical polymerization behavior of the monomers, the polymerization rates and degrees of double bond conversion were determined by photo-DSC using Irgacure 651® as initiator at 2 mol%. All the polymerizations were performed under identical conditions of temperature (80 °C), initiator concentration (2 mol%) and light intensity. The photopolymerization was done in triplicate and an average rate and conversion are reported.

Fig. 4 shows the time dependencies of the instantaneous bulk polymerization rate, R_p for each of the synthesized monomers. Immediate auto-acceleration (initial increase in polymerization rate with conversion) was observed for all three monomers. High peak polymerization rates were observed for UDMA 1 and 2 ($0.09\ s^{-1}$) compared to $0.06\ s^{-1}$ for bis-GMA and $0.07\ s^{-1}$ for HDDMA polymerized under the same conditions. The polymerization rate for UDMA 3 was slower at $0.07\ s^{-1}$. However, the maximum rate of polymerization, R_p^{max}, for UDMA 1 and 3 were reached at 4.6 and 4.2 s into the polymerization, respectively, whereas R_p^{max} for UDMA 2 was reached only after 5.1 s. UDMA 1 and 3 both have a bis-urethane core, but UDMA 3 is sterically hindered by two methyl groups on the carbon beta to the urethane linkage. UDMA 2 can be considered as a mono-urethane analogue of UDMA 1. We ascribe the differences observed in the polymerization rates to the different spacer groups connecting the two methacrylate groups. The observed high rates can be accounted for by hydrogen bonding pre-association in these systems. This is in accordance with work done by Jansen et al. [14], where the effect of hydrogen bonding on the rate of photo-initiated acrylate polymerizations was investigated: acrylate monomers capable of hydrogen bonding exhibited 3–6 times higher polymerization rates than their non-hydrogen bonding counterparts. Steric effects for the neopentyl group in UDMA 3 apparently counteract this, perhaps by breaking up intermolecular hydrogen bonding to a certain degree. Hence, the pre-organization of molecules due to hydrogen bonding forcing the methacrylate double bonds in close vicinity of each other is not as effective for UDMA 3 as it is for UDMA 1. The result is vitrification of the system for UDMA 3 at much lower conversions and a corresponding decrease in the polymerization rate (auto-deceleration) earlier in the polymerization process.

Fig. 5 shows the effect of monomer structure on conversion. The highest conversion was observed for UDMA 1, followed in order by UDMA 2 and 3. Overall conversions were 78 and 75% for UDMA 1 and 2, respectively compared to 70% for UDMA 3. The overall conversions for bis-GMA and HDDMA were 68 and 76%,

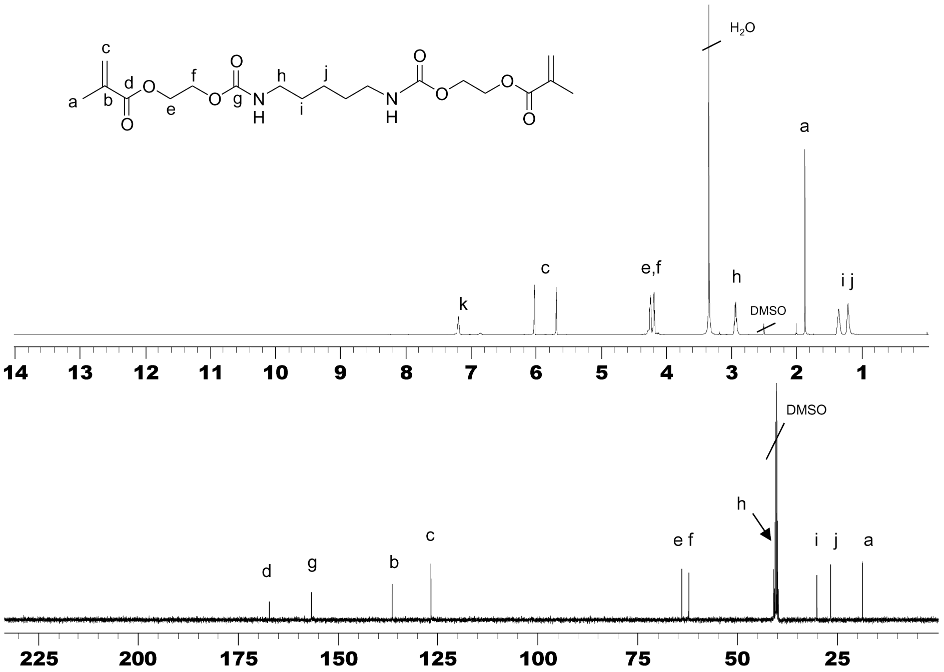


Fig. 3. ^1H and ^{13}C NMR spectra (500 MHz, DMSO-d_6, 25 °C) of UDMA 1, urethane dimethacrylate, where $R = (CH_2)_6$.

respectively. The overall conversion for UDMA 3 was lower than UDMA 1 and 2. The reason for this may be that, after the maximum polymerization rate is reached (after 4.2 s for UDMA 3, 4.6 s for UDMA 1 and 5.1 s for UDMA 2), solidification (vitrification) starts with transformation of the network from the rubbery to the glassy state [1,15]. Therefore, the rate starts to decrease due to autodeceleration. Rigidity of the system restricts and stop the propagation reaction altogether, locking the reactive chain ends into local domains where termination stops and monomer diffusion diminishes, consequently lower conversion of double bonds is achieved. Although the structures of UDMA 1 and 2 are significantly different, only small differences were observed in their photopolymerization behavior.

4. Conclusion

Urethane dimethacrylates were synthesized via a route that is safer and more environmentally friendly than those involving isocyanates and phosgene. The photopolymerizations of these bifunctional monomers were investigated with respect to polymerization rates and conversions. High rates were obtained for UDMA 1 and 2 ($0.09\ s^{-1}$) compared to $0.07\ s^{-1}$ for HDDMA. The photopolymerization behavior

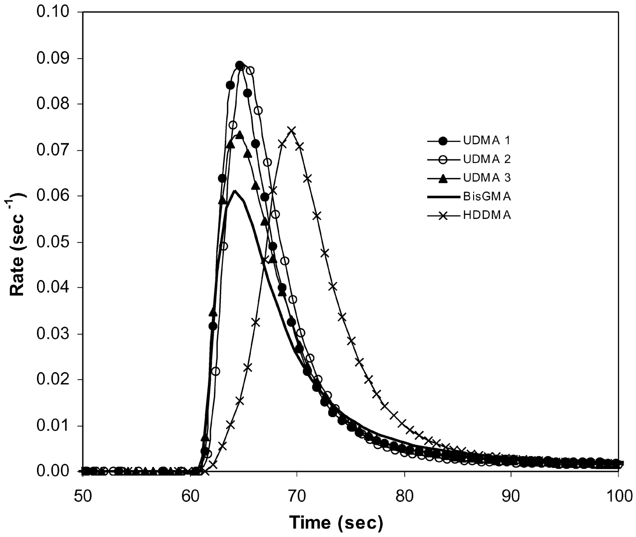


Fig. 4. Photo-DSC rate versus time plots for UDMA 1–3, bis-GMA and HDDMA. Light shutter opened at 60 s.

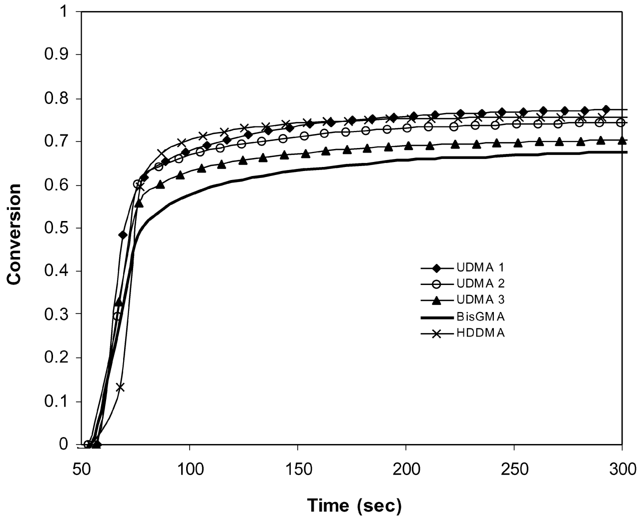


Fig. 5. Photo-DSC conversion versus time plots for UDMA 1–3, bis-GMA and HDDMA. Light shutter opened at 60 s.

was similar for UDMA 3 and bis-GMA, both of which are highly viscous monomers. The high rates observed for all these monomers can be attributed to pre-association of the molecules through strong hydrogen bonding. Conversions were higher for UDMA 1, UDMA 2 and HDDMA than those obtained for UDMA 3 and bis-GMA.

The methodology developed here is ideally suited for use with a wide range of readily available building blocks, such as diamines and amino-alcohols that are commercially available. The variety of possible structures allows synthetic flexibility in obtaining new urethane dimethacrylates with desirable properties that can enhance both cure rates and ultimate product behavior in commercial and biomedical applications.

Acknowledgements

The authors wish to gratefully acknowledge Dr Duygu Avci and Bianca Shemper for assistance during the photopolymerization studies and Dr Louis Somlai for continued interest and invaluable contributions through many discussions. We would also like to acknowledge Sasol Technology Research and Development for financial support and permission to pursue this research.

References

[1] Sideridou I, Tserki V, Papanastasiou G. Biomaterials 2002;23:1819–29.
[2] Moszner N, Völkel T, Fischer UK, Klester A, Rheinberger V. Die Angewandte Makromolekulare Chemie 1999;265:31–5.
[3] Avci D, Nobles J, Mathias LJ. Polymer 2003;44:963–8.
[4] Kammer S, Keomara K, Sandner B, Schreiber R. Macromol Mater Eng 2001;286:276–84.
[5] Kalachandra S, Wilson TW. Biomaterials 1992;13:103.
[6] Sankarapandian M, Shobba HK, Kalachandra S, Mc Grath JE, Taylor DF. J Mater Sci, Mater Med 1997;8:465–8.
[7] Labella R, Braden M, Clarke RL, Davy KWM. Biomaterials 1996;17:431–6.
[8] Uriz P, Serra M, Salagre P, Castillon S, Claver C, Fernandez E. Tetrahedron Lett 2002;43:1673–6.
[9] Rokicki G, Piotrowska A. Polymer 2002;43:2927–35.
[10] Anseth KS, Wang CM, Bowman CN. Macromolecules 1994;27:650–5.
[11] Miyazaki K, Horiba T. J Biomed Mater Res 1988;22:1011–22.
[12] Horie K, Otagawa A, Muraoka M, Mita I. J Polym Sci: Polym Chem 1975;13:445–54.
[13] Neffgen S, Keul H, Höcker H. Macromol Rapid Commun 1996;17:373.
[14] Jansen JFGA, Dias AA, Dorschu M, Coussens B. Macromolecules 2003;36:3861–73.
[15] Decker C. Macromol Rapid Commun 2002;23:1067–93.