Structure–Reactivity Relationships of Alkyl α-Hydroxymethacrylate Derivatives

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Received 18 February 2011; accepted 22 April 2011
DOI: 10.1002/pola.24743
Published online 16 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of alkyl α-hydroxymethacrylate derivatives with various secondary functionalities (ether, ester, carbonate, and carbamate) and terminal groups (alkyl, cyano, oxetane, cyclic carbonate, phenyl and morpholine) were synthesized to investigate the effect of intermolecular interactions, H-bonding, π–π interactions, and dipole moment on monomer reactivity. All of the monomers except one ester and one ether derivative are novel. The polymerization rates, determined by using photo-DSC, showed the average trend (aromatic carbamate > hydroxyl > ester > carbonate ~ aliphatic carbamate ~ ether), with several exceptions due to the differences in terminal groups. There is a correlation between the chemical shift differences of the double bond carbons, the calculated dipole moments, and the reactivities only for nonhydrogen bonded monomers. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3058–3068, 2011

KEYWORDS: dipole moment; methacrylates; photopolymerization; radical polymerization; structure–property relations

INTRODUCTION Acrylates and methacrylates are the most commonly used monomers in photoinitiated polymerizations due to their high reactivities and excellent polymer properties. They are used in dental materials, biomaterials, coatings, adhesives, and photolithography.[1–3] Because of the wide variety of application areas, extensive research has been conducted to understand the relationship between the monomer structure and reactivity and to develop monomers with enhanced reactivity.

In recent years, several factors leading to the enhanced reactivity of (meth)acrylates were hypothesized. These are hydrogen abstraction from labile hydrogens in monomers, hydrogen bonding, and electronic effects (dipole moment, secondary functionalities).

Decker and Bowman formulated new monoacrylate monomers with carbonate, cyclic carbonate, carbamate, and oxazolidone groups that react extremely rapidly despite one vinyl group and form crosslinked polymers. They mentioned that crosslinking due to hydrogen abstraction reactions causes an increase in viscosity, earlier gelation, and autoacceleration, which lead to high rate of polymerization.[4–11]

It was observed that the presence of secondary functionalities (carbamates, carbonates, cyclic carbonates, cyclic acetals, morpholine, oxazolidones, hydroxyl, and aromatic rings) enhances the reactivity by reducing the activation energies in both Michael addition and photopolymerizations as indicated by a monotonic correlation between reactivities of monomers with respect to both processes. The cyclic voltammetry experiments also proved a correlation between reduction potential of the monomers and Michael addition and photopolymerization reactivities.[5]

Andrzejewska reported that the presence of the heteroatom in the ester group led to enhanced reactivity due to the CH_2 group attached to the heteroatom donating hydrogen to give a crosslinked network. This reaction also leads to a reduction in oxygen inhibition and faster rates and higher conversions in air.[12]

Jansen et al. investigated the rate of polymerization of different acrylates as a function of hydrogen bonding capability for systems containing amide, urethane, and urea groups and found that the monomers capable of forming hydrogen bonds show three to six times higher polymerization rates compared with their nonhydrogen-bonded analogs possessing ester and carbonate groups.[13] The high reactivities were suggested to be due to preorganization via hydrogen bonding to bring the double bonds close to each other, enhancing propagation, although reduction in termination rate may also be involved or be the cause. Hoyle et al. showed that the degree of hydrogen bonding and the rate of polymerization of hydroxyalkyl acrylates are directly related and both decrease with increasing temperature. Although they could not find a quantitative relationship between hydrogen bonding and termination rate constants, they claimed that highly hydrogen-bonded systems behave as multifunctional monomers and have low termination constants.[14]

Jansen et al. also investigated the effect of monomer polarity on the rate of polymerization and found a direct correlation

Additional Supporting Information may be found in the online version of this article. Correspondence to: D. Avci (E-mail: avcid@boun.edu.tr)
Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3058–3068 (2011)

between the maximum rate of polymerization and the dipole moment for the monomers having dipole moments higher than 3.5 Debye. However, Kilambi et al. found no monotonic correlation between monomer reactivity and molecular dipole moment during bulk polymerization of various acrylate monomers.[7] They suggested that a low dipole moment conformation of some monomers may be more reactive due to intermolecular hydrogen bonding than a conformation with a higher dipole moment.

Monomers based on alkyl α-hydroxymethacrylates (RHMA) and their halide derivatives offer great versatility for functionalization. Conversion of the alcohol group to various ester, ether, and other derivatives has been demonstrated by us and others.[15–22] Although these derivatives have smaller k_p values than methyl methacrylate due to the steric effect of the α-substituent, they have good polymerizability due to their low k_t values, and this type of polymerization has been called "steric hindrance assisted polymerization" by Yamada et al.[23] Studies on the reactivities of several ester derivatives of ethyl α-hydroxymethacrylate indicated that aromatic esters are more reactive than nonaromatic ones, ether derivatives, and methyl methacrylate.[16,23]

In this work, we report the synthesis and photopolymerizations of ester, ether, carbonate, and carbamate derivatives of RHMA to evaluate the role of hydrogen bonding, dipole moment, and π–π interactions on the reactivity.

EXPERIMENTAL

Reagents

Ethyl α-hydroxymethacrylate (EHMA), *t*-butyl α-hydroxymethacrylate (TBHMA), *t*-butyl α-bromomethacrylate (TBBr), and ethyl α-bromomethacrylate (EBBr) were synthesized according to literature procedures.[24,25] 2-[2-(2-Methoxyethoxy)ethoxy]-acetic acid, 3-hydroxypropionitrile, 3-hydroxymethyl-3-methyloxetane, ethyl chloroformate, 4-(2-hydroxyethyl)morpholine, 4-(hydroxymethyl)-1,3-dioxolan-2-one, 2,6-di-*tert*-butyl-4-methyl phenol (BHT), trifluoroacetic acid, triethyl amine (TEA), 2-hydroxyethyl methacrylate (HEMA), butyl isocyanate, and phenyl isocyanate were obtained from Aldrich and Fluka and used as obtained.

Characterization

The monomer characterization involved ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 400 MHz) and Fourier transform infrared (FTIR) spectroscopy (T 380). The photopolymerizations were carried out on a TA Instruments (Q100) photodifferential scanning calorimeter (photo-DSC). Elemental analyses were obtained from Thermo Electron SpA FlashEA 1112 elemental analyser (CHNS separation column, PTFE; 2 m; 6 × 5 mm^2).

Synthesis of the Monomers

General Procedure for the Synthesis of Monomers 1–7

To a mixture of alcohol (10 mmol) and TEA (3.86 g, 38 mmol) in 5 mL THF in an ice bath, EBBr or TBBr (10 mmol) in 5-mL THF was added dropwise. The mixture was stirred at 60 °C for 24 h. After removal of the solvent, the mixture was diluted with CH_2Cl_2 and extracted with water (3 × 5 mL). The organic phase phase was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The crude products were purified by column chromatography (silica gel 0.063–0.200 mm) using hexane initially and gradually changing to CH_2Cl_2 as eluent.

Ethyl 2-((2-morpholinoethoxy)methyl)acrylate (Monomer 1). Monomer **1** was obtained as a colorless liquid in 62% yield (bp = 76–78 °C/1.2 × 10^{-2} mbar). Viscosity = 0.014 Pa s.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.3 (t, 3H, CH_3), 2.5 (t, 4H, CH_2—N), 2.6 (t, 2H, CH_2—N), 3.6 (t, 2H, CH_2—O), 3.7 (t, 4H, CH_2—O), 4.1 (m, 4H, CH_2—CH_3, CH_2—O), 5.8 (s, 1H, CH_2=C), 6.3 (s, 1H, CH_2=C). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.0 (CH_3), 53.9, 58.1 (CH_2—N), 60.5 (CH_2—CH_3), 66.8, 68.3, 69.1 (CH_2—O), 125.3 (CH_2=C), 137.3 (C=CH_2), 165.7 (C=O). FTIR (cm^{-1}): 2941 (C—H), 1713 (C=O), 1638 (C=C), 1108 (C—O). Elem. Anal., Calcd. for $C_{12}H_{21}NO_4$: C, 59.26%; H, 8.64%; N, 5.76%; O 26.34%. Found: C, 58.98%; H, 9.03%; N, 5.67%; O, 26.32%.

Characterization results of monomers **2–7** are given as Supporting Information.

General Procedure for the Synthesis of Monomers 8 and 9

Ethyl chloroformate (5.43 g, 50 mmol) in 10-mL CCl_4 was added dropwise to the mixture of RHMA (38 mmol) and pyridine (3.95 g, 50 mmol) in 20-mL CCl_4 under nitrogen. The mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the mixture was poured into ice water and neutralized with $NaHCO_3$ (5%). The mixture was extracted with CH_2Cl_2, dried with anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel 0.063–0.200 mm) using hexane initially and gradually changing to CH_2Cl_2 as eluent.

Tert-butyl 2-((ethoxycarbonyloxy)methyl)acrylate (Monomer 9). Monomer **9** was obtained as a light yellow liquid in 35% yield (bp = 67–68 °C/1.2 × 10^{-2} mbar). Viscosity = 0.006 Pa s.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.3 (t, 3H, CH_3—CH_2), 1.5 (s, 9H, CH_3—C), 4.2 (q, 2H, CH_2—CH_3), 4.8 (s, 2H, CH_2—O), 5.8 (s, 1H, CH_2=C), 6.3 (s, 1H, CH_2=C). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.2 (CH_3), 27.9 (CH_3—C), 65.6 (CH_2—CH_3), 68.9 (CH_2—O), 81.4 (C—CH_3), 126.3 (CH_2=C), 136.4 (C=CH_2), 154.7 (C=O), 164.1 (C=O). FTIR (cm^{-1}): 1706 (C=O), 1751 (C=O), 1640 (C=C).

Characterization results of monomer **8** are given as Supporting Information.

General Procedure for the Synthesis of Monomers 10–12

The acid (10 mmol), EBBr or TBBr (10 mmol), K_2CO_3 (1.38 g, 10 mmol), and methyl ethyl ketone (MEK; 25 mL) were added to a round-bottomed flask with a nitrogen inlet. The mixture was stirred at 60 °C for 24 h. After removal of the solvent, the mixture was diluted with CH_2Cl_2 and extracted with water (3 × 5 mL). The organic phase was separated, dried with anhydrous sodium sulfate, and evaporated under

reduced pressure. The crude products (**10** and **11**) were purified by column chromatography (silica gel 0.063–0.200 mm) using hexane initially and gradually changing to CH_2Cl_2 as eluent. Monomer **12** was purified by distillation.

Ethyl 2-((2-(2-(2-methoxyethoxy)ethoxy)acetoxy)methyl) acrylate (Monomer 10). Monomer **10** was obtained as a colorless liquid in 41% yield. Viscosity = 0.010 Pa s.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.3 (t, 3H, CH_3), 3.4 (s, 3H, CH_3—O), 3.55 (t, 2H, CH_2—O), 3.65 (t, 2H, CH_2—O), 3.69 (t, 2H, CH_2—O), 3.75 (t, 2H, CH_2—O), 4.2 (m, 4H, CH_2—O, CH_2—CH_3), 4.9 (s, 2H, CH_2—O), 5.9 (s, 1H, CH_2=C), 6.4 (s, 1H, CH_2=C). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.1 (CH_3), 58.9 (CH_3—O), 60.9 (CH_2—CH_3), 62.5, 68.5, 70.4, 70.5, 70.8 (CH_2—O), 127.6 (CH_2=C), 135.0 (C=CH_2), 164.9 (C=O), 169.8 (C=O). FTIR (cm^{-1}): 2878 (C—H), 1757 (C=O), 1717 (C=O), 1640 (C=C), 1106 (C—O). ELEM. ANAL., Calcd. for $C_{13}H_{22}O_7$: C, 53.79%; H, 7.59%; O, 38.62%. Found: C, 53.61%; H, 7.79%; O, 38.60%.

Characterization results of monomers **11** and **12** are given as Supporting Information.

General Procedure for the Synthesis of Monomers 13–16

The isocyanate (7.69 mmol) was added dropwise to a mixture of RHMA (7.69 mmol) and BHT (4 mg, 0.018 mmol) in an ice bath. After stirring (1.5 h for monomers **13** and **14** and 10 h for monomers **15** and **16**) at 60 °C, the mixture was washed with hexane.

Ethyl 2-((phenylcarbamoyloxy)methyl)acrylate (Monomer 13). Monomer **13** was obtained as a white solid after recrystallization from methanol in 79% yield (mp =58 °C).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.3 (t, 3H, CH_3), 4.3 (q, 2H, CH_2—CH_3), 4.9 (s, 2H, CH_2—O), 5.9 (s, 1H, CH_2=C), 6.4 (s, 1H, CH_2=C), 6.7 (s, 1H, NH—C), 7.1 (t, 1H, Ar-CH), 7.3–7.4 (m, 4H, Ar-CH). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 14.2 (CH_3), 61.0 (CH_2—CH_3), 63.2 (CH_2—O), 118.7, 123.6 (Ar-CH), 127.6 (CH_2=C), 129.1 (Ar-CH), 135.7 (C=CH_2), 137.6 (Ar-C), 152.8 (C=O), 165.3 (C=O). FTIR (cm^{-1}): 3349 (N—H), 2982 (C—H), 1728 (C=O), 1691 (C=O), 1637 (C=C), 1601 (C=C), 1540 (N—H). ELEM. ANAL., Calcd. for $C_{13}H_{15}NO_4$: C, 62.65%; H, 6.03%; N, 5.63%; O, 25.69%. Found: C, 62.35%; H, 6.26%; N, 5.81%; O, 25.58%.

Characterization results of monomers **14–16** are given as Supporting Information.

Photopolymerization

Approximately 3.0 or 4.0 mg of sample was placed in an aluminum DSC pan. The photoinitiator, which was dissolved in CH_2Cl_2, was added with a microsyringe to give a final concentration in the monomer of 2.0 mol % after the evaporation of the solvent. The sample and the reference pans were placed in the DSC chamber, the system was purged with nitrogen flow to remove air and CH_2Cl_2 for 10 min before polymerization and purging was continued during polymerization. Heats of photoreactions were measured using a DSC equipped with a mercury arc lamp. The samples were irradiated for 10 min at 40 °C with an incident light density of 20 mW/cm^2. The heat flux as a function of reaction time was monitored using DSC under isothermal conditions and both the rate of polymerization (R_p) and conversion were calculated as a function of time. The theoretical values used for the heats of reaction (ΔH_p) were 13.1 kcal/mol for methacrylate double bonds.[26,27] Rates of polymerization were calculated according to the following formula:

$$\text{Rate} = \frac{(Q/s)M}{n\Delta H_p\ m} \tag{1}$$

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

Calculation of Dipole Moments

Boltzman-averaged dipole moments were calculated with PM3 for all the monomers. For this purpose, all posible rotations around single bonds were considered for a given acrylate to generate all the conformations corresponding to stationary points. Minimization, followed by the calculation of the Boltzmann-averaged dipole moments for all the conformations was carried out with PM3 by using Spartan '06.[28] The unique structures were sorted in the order of increasing energy. The dipole moments of the first 100 conformers are Boltzmann averaged at 298.15 K according to the following formula:

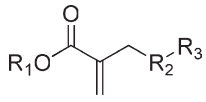
$$\langle \mu_{calc} \rangle = \sum_j D_j \frac{e^{\Delta H_j/RT}}{\sum_i e^{\Delta H_i/RT}} = \sum_j D_j p_j \tag{2}$$

where D_j is the dipole moment of the conformation j, ΔH_j is the heat of formation of conformation j, T is the absolute temperature, R is the Boltzmann constant, and p_j is the probability of finding the monomer in conformation j at the temperature T.[13]

RESULTS AND DISCUSSION

Synthesis of the Monomers

The general structure of the synthesized monomers can be given as



where R_1 is ethyl or *t*-butyl group due to methacrylate, R_2 is the secondary functionality, which displays the ester, ether, carbonate, and carbamate groups, and R_3 is the terminal group. The terminal groups were varied to incorporate highly polar or cyclic groups.

The synthesis of all the monomers is illustrated in Figure 1. The ether derivatives (**1–7**) were synthesized by the reaction of alcohols with EBBr and/or TBBr using TEA as catalyst in THF at 60 °C for 24 h: 4-(2-hydroxyethyl)morpholine with EBBr and TBBr gave **1** and **2**; 3-hydroxypropionitrile with

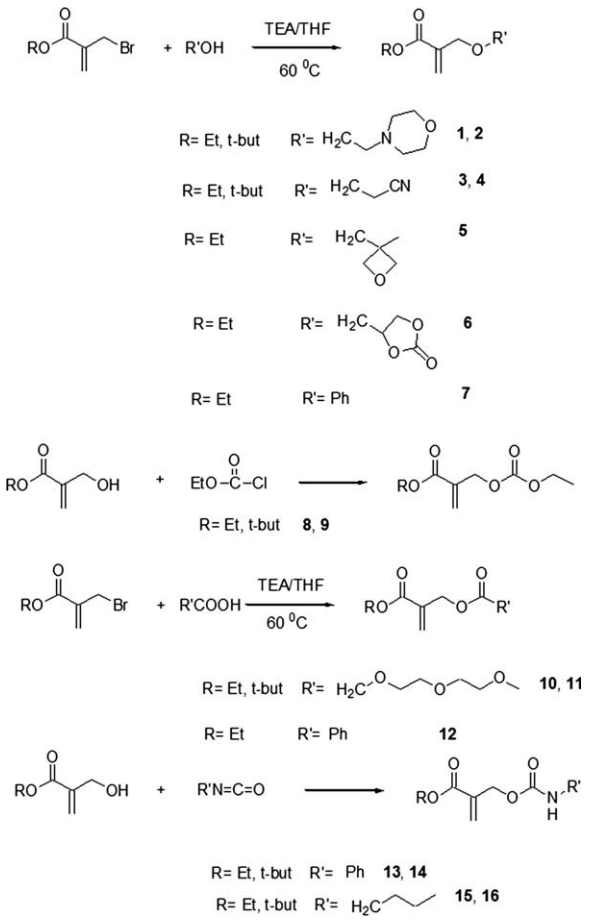


FIGURE 1 Synthesis of monomers.

EBBr and TBBr gave **3** and **4**; 3-hydroxymethyl-3-methyloxetane with EBBr gave **5**, 4-(hydroxymethyl)-1,3-dioxolan-2-one with EBBr gave **6** and phenol with EBBr gave **7**. Four of these (**1**, **2**, **5**, **6**) contain cyclic terminal groups, which were found to enhance the reactivities of acrylates and methacrylates.[5] The other two (**3** and **4**) contain a cyano group and are designed to assess the electron withdrawing effect of the substituent. Monomer **7** was synthesized to evaluate the importance of $\pi-\pi$ interactions. The reaction time for monomer **3** was decreased to 7 h due to unexpected polymerization in 24 h. This monomer polymerizes without an initiator to give a polymer with M_n and T_g values of 3200 and 45 °C during the synthesis; other indications and possible reasons for the high reactivity of this monomer are discussed later in this work.

The carbonate derivatives (**8** and **9**) were prepared from the reactions of EHMA and TBHMA with ethyl chloroformate using pyridine as the catalyst; the aim being to evaluate the enhancement of reactivity due to carbonates, as discussed above. Although the crude products were purified by column chromatography, monomer **8** quickly turned to dark red color after storage, even refrigerated. In the literature, the use of pyridine and dimethylaniline during the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate produced yellow and dark purple colors.[29] The color change during storage of monomer **8** may be explained by one of the two following mechanisms: (i) sorption of carbon dioxide released during storage of the monomer to residual pyridine and formation of protonated pyridine bicarbonates in the presence of water[30] and (ii) attack of residual pyridine to double bond of the monomer with the release of carbonate ion and forming a carbonate salt. Because we were not able to solve coloration problem, we did not further investigate this monomer.

The ester derivatives were synthesized from the reactions of EBBr and/or TBBr and 2-[2-(2-methoxyethoxy)ethoxy]acetic acid and benzoic acid to increase the dipole moment in an effort to investigate the electronic effect of high dipole moment (μ) and also $\pi-\pi$ interactions. Also, the monomers obtained from 2-[2-(2-methoxyethoxy)ethoxy]acetic acid will contain two ether linkages with abstractable hydrogens, which may reduce the oxygen inhibition.[31] The reaction was carried out at 60 °C in methyl ethyl ketone in the presence of the catalyst potassium carbonate and gave the ester derivatives **10**, **11**, and **12**.

To investigate the importance of hydrogen bonding and $\pi-\pi$ interactions in the polymerization rate, the carbamate derivatives **13**–**16** were prepared via a reaction of the isocyanates (phenyl and butyl isocyanates) with EHMA and TBHMA with catalyst (dibutyltin dilaurate) at room temperature or without catalyst at 60 °C. The reactions were monitored by following the disappearance of the isocyanate peak in the FTIR spectrum.

The synthesis of monomers gave the crude products in high yields (80–90%). All of the monomers were liquids except monomer **13**, which was a white solid (mp 58 °C) at room temperature. The monomers were purified by column chromatography, distillation, or recrystallization and characterized by using FTIR, ^{13}C NMR, and ^{1}H NMR spectra (Figs. 2 and 3). The ^{1}H NMR of monomer **1** showed methyl protons at 1.3 ppm, two methylene protons adjacent to nitrogen at 2.5 and 2.6 ppm, four methylene protons adjacent to oxygen at 3.6, 3.7, and 4.1 ppm and double bond protons at 5.8 and 6.3 ppm (Fig. 2). The ^{13}C NMR spectrum of monomer **6** showed characteristic peaks for methyl carbon at 14.1 ppm, methylene carbons at 60.8, 66.1, 69.6, and 74.9 ppm, a methine carbon at 69.8 ppm, double bond carbons at 126.3 and 136.4 ppm, and carbonyl carbons at 154.8 and 165.5 ppm (Fig. 3). The FTIR spectra of monomers **13** and **14** are shown in Figure 4.

Photopolymerizations

The reactivities of the synthesized monomers in photopolymerization were investigated with photodifferential scanning calorimetry and compared with those of EHMA, TBHMA, and HEMA. Photopolymerizations were carried out using 2,2-dimethoxy-2-phenylacetophenone (DMPA; 2 mol %) at 40 °C.

EHMA, TBHMA, and HEMA polymerizations behave in the same way in which a distinct shoulder at the onset of autoacceleration was observed (Fig. 5 and Table 1). This shoulder was observed earlier for EHMA and HEMA when compared with TBHMA. It is known that intermolecular

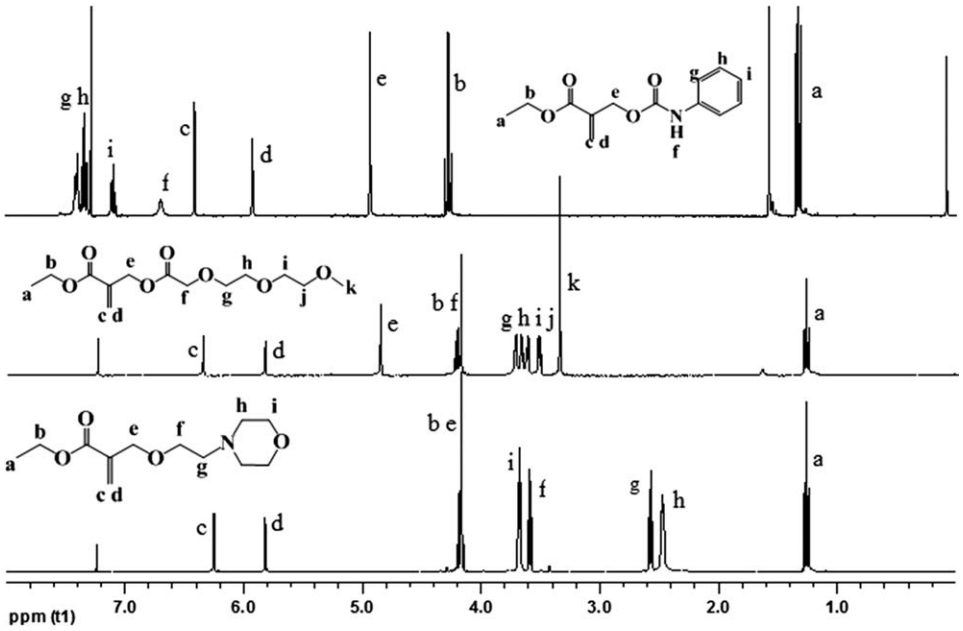


FIGURE 2 ^{1}H NMR spectra of monomers **1**, **10**, and **13**.

hydrogen bonding and/or chain transfer reactions leading to an increase in viscosity and a decrease in termination rate cause autoacceleration. The extent of autoacceleration was observed in the following order: HEMA > EHMA > TBHMA, this was also the order of their maximum rates of polymerization. Increasing the size of the ester group from ethyl to *t*-butyl decreased the polymerization rate due to steric effects. We observed this behavior in all of the synthesized monomers here.

The high reactivity of HEMA compared with EHMA was also observed by Buback et al.[32] They reported propagation rate coefficients for bulk polymerizations of EHMA and HEMA at 50 °C as 944 and 2563 L mol^{-1} s^{-1}. The activation energy of HEMA (21.9 kJ mol^{-1}) is not significantly different from the one of EHMA (20.4 kJ mol^{-1}) but the frequency factor (which reflects the steric effect) for HEMA (8.88×10^6 L mol^{-1} s^{-1}) is higher than that of EHMA (1.87×10^6 L mol^{-1} s^{-1}). Davis et al. also reported the activation energy and the frequency factor for EHMA as 14–17 kJ mol^{-1} and (3–8) $\times 10^6$ L mol^{-1} s^{-1}, respectively.[33,34] They also found an important solvent effect on k_p of EHMA that changes between 580 L mol^{-1} s^{-1} (THF) and 1860 L mol^{-1} s^{-1} (xylene) at 15 °C.[35]

In general, overall monomer conversion increases for systems that are polymerized at faster rates. As the polymerization

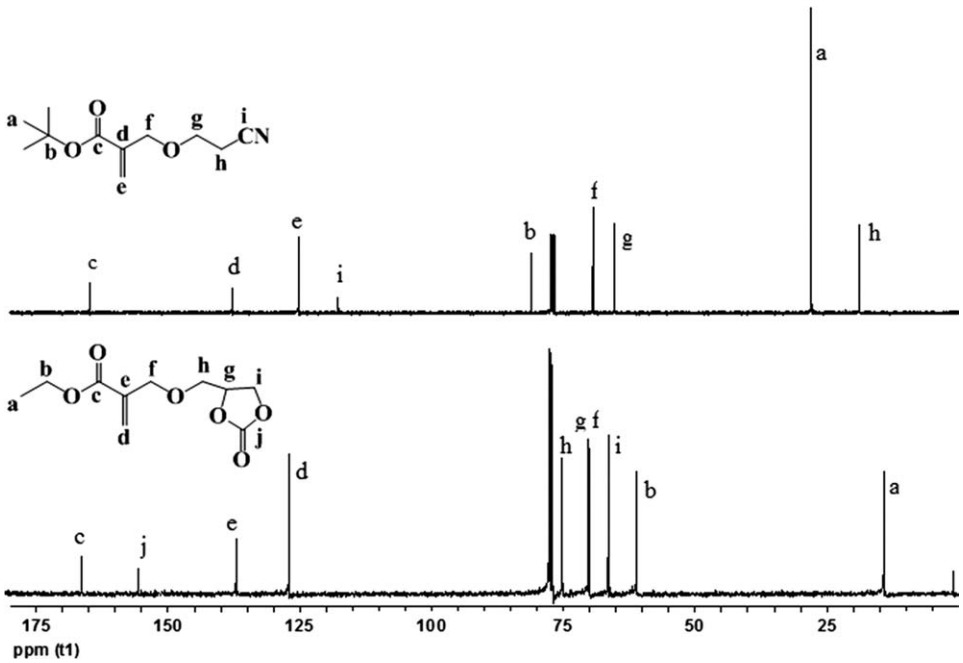


FIGURE 3 ^{13}C NMR spectra of monomers **4** and **6**.

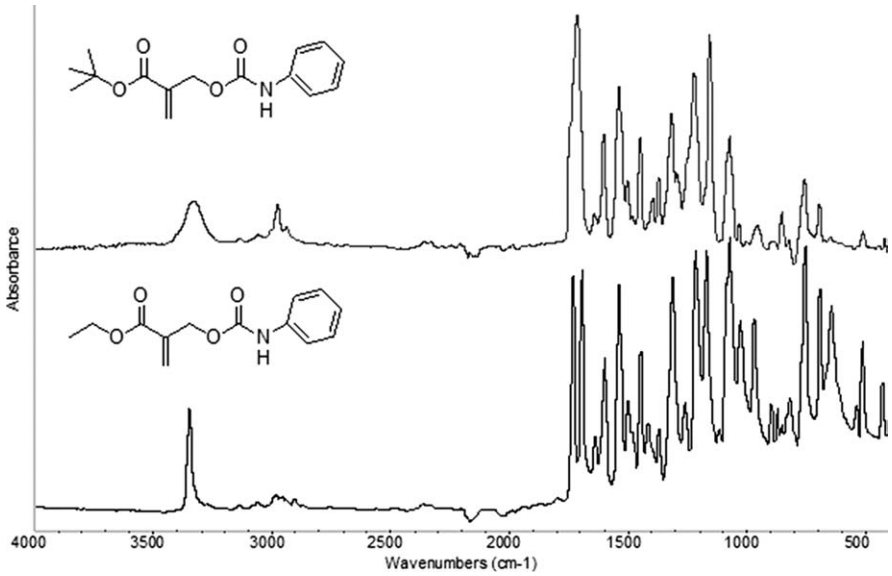


FIGURE 4 FTIR spectra of monomers **13** and **14**.

rate increases, the volume relaxation is unable to keep pace with conversion, leading to increased free volume formation. The free volume in excess of equilibrium values causes higher mobility, which results in increased conversion. Also, conversion depends on the polymerization temperature and the T_g of the system, which indicates its mobility. The T_g of a polymerization system depends on flexibility of monomers. For example, polar groups are responsible for intramolecular and intermolecular interactions and decrease flexibility of the system, increase T_g and decrease conversion.

The overall conversions were 90, 69, and 51% for HEMA, EHMA, and TBHMA. It was observed that the greater the extent of autoacceleration, the higher the conversion. The T_g values for poly-HEMA, poly-EHMA, and poly-TBHMA are 83–95, 64, and 120 °C.[25] Low conversion of TBHMA is due to a combination of high T_g of its polymer and low rate of polymerization.

It is known that hydrogen bonding decreases with increasing temperature, which tends to decrease the polymerization rate, whereas chain transfer increases with increasing temperature which tends to increase the polymerization rate. To investigate the effect of temperature change on polymerization rate, the monomers were polymerized at 25, 40, and 70 °C. We found that rate of polymerizations of these monomers increase roughly with temperature (Table 1). This can be explained by competing effects of activation, which occurs by increasing temperature and deactivation, which is due to decreased hydrogen bonding. The FTIR spectrum of HEMA clearly shows two carbonyl peak maxima at 1713 and 1699 cm^{-1} due to a hydrogen-bonded carbonyl and free carbonyl stretching bands. However, FTIR spectrum of EHMA and TBHMA shows one peak at 1704 and 1707 cm^{-1} corresponding more to a hydrogen-bonded carbonyl stretching band (Fig. 6). Additionally, thermal bulk polymerization of HEMA and EHMA gave crosslinked polymers, indicating the importance of chain transfer reactions.

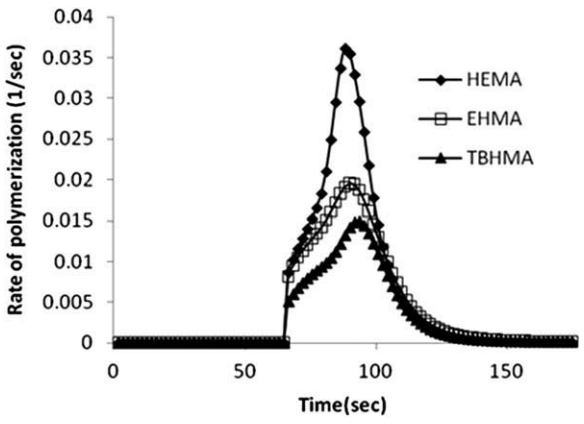
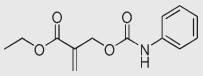
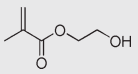
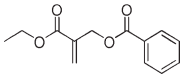
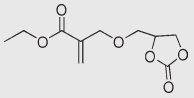
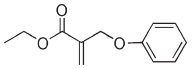
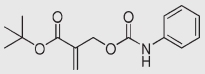
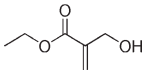
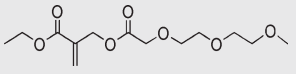
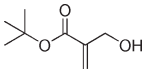
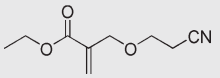
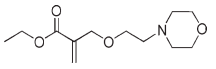
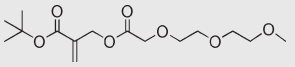
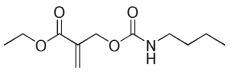
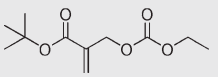
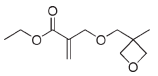
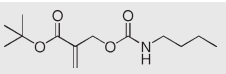


FIGURE 5 Rate of polymerization versus time for HEMA, EHMA, and TBHMA.

The rates of polymerization of the phenyl carbamate monomers (monomers **13** and **14**) were found to be significantly higher than those of the monomers with other functional groups (Fig. 7, Table 1); even higher than EHMA and TBHMA. The intermolecular interactions due to hydrogen bonding and/or π–π stacking are probably the reason for the high reactivity of monomers **13** and **14**.

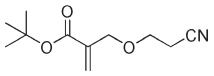
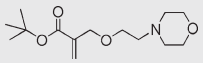
The different states of monomer **13** and **14** (solid vs. liquid) indicate their different extent of hydrogen bonding. The extent of hydrogen bonding was evaluated by NH and C=O stretching modes observed by FTIR spectra of monomers (Fig. 4). The locations of NH peaks were 3349 and 3331 cm^{-1} (monomers **13** and **14**), both correspond to hydrogen-bonded NH peaks.[36] The locations of C=O peaks were 1690 (carbamate) and 1728 cm^{-1} (ester) for monomer **13**. Because monomer **13** is crystalline and its C=O groups are completely bonded to NH, the peak at 1690 cm^{-1} is due to ordered carbamate C=O. The other C=O peak at 1728 cm^{-1} is due to the free ester C=O. However, monomer **14** is liquid and both C=O groups (carbamate and ester) can make

TABLE 1 Rates of Polymerization, Conversions, Calculated Boltzmann-Averaged Dipole Moments, and Differences in Chemical Shift Values of Monomers **1**–**16**, HEMA, EHMA, and TBHMA

Monomer	Monomer Structure	Rate (s^{-1})	Converison (%)	Dipole Moment (Debye)	$\Delta\delta$ (ppm)
13		0.038[b] 0.045[c]	44 63	2.99	8.1
HEMA		0.031[a] 0.036[b] 0.042[c]	81 90 83	3.55	10.0
12		0.033[b]	89	3.18	8.5
6		0.023[a] 0.026[b] 0.030[c]	64 56 74	3.99	10.1
7		0.024[b]	80	3.66	9.6
14		0.022[b]	62	2.67	10.6
EHMA		0.016[a] 0.019[b] 0.023[c]	61 69 71	3.19	14.0
10		0.015[b]	94	3.60	7.4
TBHMA		0.012[a] 0.015[b] 0.016[c]	49 51 61	2.76	16.4
3		0.012[b]	90	3.35	10.4
1		0.009[b]	78	2.73	12.0
11		0.008[b]	70	2.94	9.8
15		0.007[b]	77	2.93	13.1
9		0.006[b]	85	2.26	10.1
5		0.005[b]	82	2.54	11.8
16		0.005[b]	72	2.35	15.5

(Continued)

TABLE 1 (Continued)

Monomer	Monomer Structure	Rate (s^{-1})	Converison (%)	Dipole Moment (Debye)	$\Delta\delta$ (ppm)
4		0.004[b]	65	2.01	12.6
2		0.003[b]	66	2.21	14.3

[a] At 25 °C.
[b] At 40 °C.
[c] At 70 °C.

hydrogen bonding with NH. Therefore, carbamate C=O shifts to higher frequency and overlaps with hydrogen bonded ester C=O at 1710 cm^{-1}. No free ester C=O exists. All these results confirm a greater extent of hydrogen bonding in monomer **13**, which results in high rate of polymerization. Therefore, photopolymerization of this monomer was investigated in both crystalline (40 °C) and noncrystalline states (70 °C; Table 1). The results showed that polymerization occurs in both states and the rate increases with temperature. Also, higher conversions were obtained in noncrystalline state, as expected.

To investigate the effect of $\pi-\pi$ stacking on monomer reactivity, the aliphatic carbamate monomers (**15** and **16**) were polymerized. These monomers were found to be about four or five times less reactive than phenyl carbamate monomers (**13** and **14**; Fig. 7, Table 1). They have rates of polymerization comparable with ether derivatives. These monomers were liquids and the locations of NH (3344 cm^{-1}) and overlapping ester and carbamate C=O peaks (1710 cm^{-1}) in their FTIR spectra were similar to those of monomer **14**. Thus, we can say that the strength of hydrogen bonding of these monomers (**14**, **15**, and **16**) has no discernible effect on the polymerization rate. The relatively low reactivity of monomers **15** and **16** despite their ability to still make hydrogen bonding brings out the importance of π–π stacking. We observed a similar behavior in the literature.[37] For example, the maximum rate of polymerization of phenyl carbamate ethyl acrylate was 1.3 s^{-1} whereas *n*-butyl carbamate ethyl acrylate gave a much lower rate of polymerization of 0.38 s^{-1}. The conversions obtained for monomers **15** and **16** were higher than those of monomers **13** and **14** despite their lower rates of polymerization, indicating the enhanced mobility of these monomers.

Among the ester-linked monomers (**10**, **11**, and **12**), the aromatic ester monomer (**12**) capable of π–π interaction exhibited about twice the rate of polymerization of the aliphatic monomer (**10**), approaching even that of the most reactive carbamate monomer (**13**; Fig. 8, Table 1). This result was previously indicated with the evaluation of k_p and k_t of the benzoate derivative (990 and 2.9 $\times$ 10^{-6} L mol^{-1} s^{-1}) of EHMA and the acetate derivative (k_p = 350, k_t= 2.1 $\times$ 10^{-6} L mol^{-1} s^{-1}) of MHMA.[23,38] Also, Davis et al. indicated that when going from EHMA to its acetate derivative both E_{act} (12.4 kJ mol^{-1}) and the frequency factor (8 $\times$ 10^4 L mol^{-1} s^{-1}) decrease.[33] Monomer **10**, due to its very flexible structure and high rate of polymerization exhibits the highest conversion among the monomers studied in this work.

The carbonate derivative (**9**) was found to be less reactive than ester and aromatic carbamate derivatives, EHMA, TBHMA, and HEMA. It showed similar reactivity with TBHMA-ether and TBHMA-aliphatic carbamate derivatives.

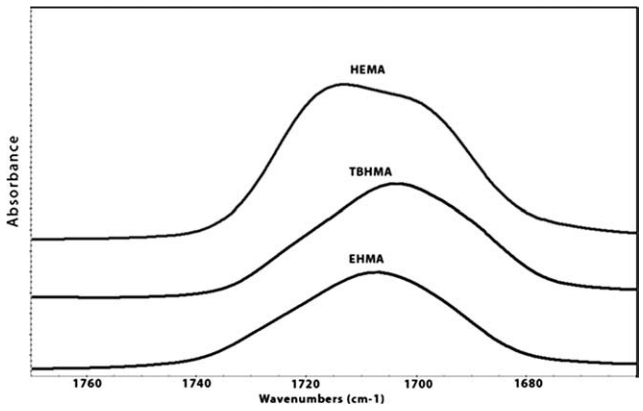


FIGURE 6 FTIR spectra of carbonyl stretching regions of HEMA, EHMA, and TBHMA.

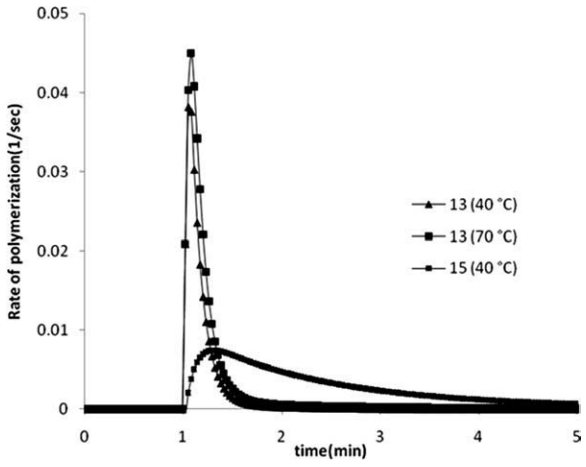


FIGURE 7 Rate of polymerization versus time for monomers **13** and **15**.

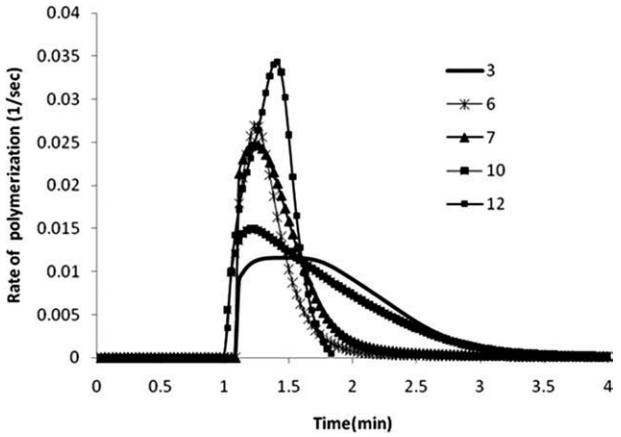


FIGURE 8 Rate of polymerization versus time for monomers **3**, **6**, **7**, **10**, and **12**.

On average, ether derivatives were found to be less reactive than ester derivatives (Table 1). Yamada et al. previously reported k_p and k_t values for the butyl ether derivative of MHMA as 298 and 8.0 $\times$ 10^{-6} L mol s^{-1}, respectively.[23,39] Although this k_p value is similar to that of the acetate derivative, the higher k_t value of the ether derivative is responsible for the lower rate of polymerization. However, we observed that rates of ether derivatives can be increased by modifications of the terminal groups. The maximum rate of polymerizations of EHMA ether derivatives (**1**–**7**) with different terminal groups showed the following trend: cyclic carbonate > phenyl > cyano > morpholine > oxetane, where $R_{p,max}$ (monomer **6**) = 1.08, $R_{p,max}$ (monomer **7**) = 1.83, $R_{p,max}$ (monomer **3**) = 2.44, $R_{p,max}$ (monomer **1**) = 4.4, and $R_{p,max}$ (monomer **5**; Fig. 8, Table 1). This trend was similar to that observed for acrylate monomers reported by Jansen et al. where $R_{p,max}$ (glycerol carbonate acrylate) = 2.16, $R_{p,max}$ (cyano ethyl acrylate) = 3.66 and $R_{p,max}$ (oxethane acrylate).[13] The high reactivity of monomer **6** may be due to hydrogen abstraction, ring stacking interactions, and relatively high dipole moment. However, monomers that also possess a heterocyclic ring (**1**, **2**, and **5**) did not exhibit such rate enhancement. To check the possibility of hydrogen abstraction, the photopolymerization of monomer **6** in the presence of benzophenone was tried; no polymerization was observed, indicating that there are no labile hydrogens under our photopolymerization conditions. Additionally, the polymers obtained from this monomer were totally soluble indicating that chain transfer is not important. The effect of temperature on photopolymerization of **6** was also investigated (Table 1). Monomer **6** exhibited small changes in polymerization rate over the 25–70 °C range, while the conversion was increased by about 25%. Although monomer **6** has the highest rate of polymerization among the ether derivatives, its conversion was lower, similar to cyclic carbonate-containing (meth)acrylates reported in the literature,[11] which may be attributed to early autoacceleration and/or high T_g of its polymer (85 °C). Among the ether derivatives, monomer **3** with a high rate of polymerization and flexible structure exhibited highest conversion.

The rate differences of ether derivatives can be explained by the differences in dipole moment as will discussed in the next section.

Dipole Moment

The synthesized monomers were evaluated in terms of dipole moment to find a relation between the monomer structure and the reactivity. The Boltzmann-averaged dipole moments of the monomers were calculated for their minimum energy conformers (Table 1). When we consider non-hydrogen bonding monomers (**1**–**12**), there seems to be a correlation except for monomers **7** and **12** (Table 1, Fig. 9). This exception may be due to an additional $\pi-\pi$ interaction, which increases the rate of polymerization. The high reactivity of monomer **6** can be explained by its high dipole moment.

When we consider all hydrogen-bonding monomers (**13**–**16**, HEMA, EHMA, and TBHMA), it was not possible to find a correlation between monomer reactivity and dipole moment. For example, monomers **13** and **15**, both having approximately similar dipole moments (2.99 and 2.93 Debye), showed completely different polymerization rates. Kilambi et al. have also investigated hydrogen-bonding monomers having high reactivity but low dipole moments. They said that a particular conformation with a low dipole moment may be energetically favored due to intermolecular hydrogen bonding.[7]

Chemical Shift Values

^{13}C NMR can be used to predict the free radical polymerizability of monomers. Vaidya et al. have reported that chemical shifts of the C=C double bonds ($C_\beta H_2{=}C_\alpha$) depend on the substituents. δC_β and δC_α shift to lower and higher fields, respectively, with an increase in electron withdrawing power of the substituents.[40] Therefore, $\Delta\delta$ (δC_β–δC_α) shows the effects of substituents on polymerizability. The stronger the electron-withdrawing power of the substituents the smaller the chemical shift difference and the higher the radical polymerizability.[40,41] Also, bulky substituents may cause differences in chemical shifts and/or lead to lower propagation enthalpy through steric hindrance.

To see a correlation between polymerizability and differences in chemical shift values ($\Delta\delta$), we evaluated the monomers in three categories. In the first category (HEMA, EHMA, and TBHMA), the reactivity trend was correlated to $\Delta\delta$

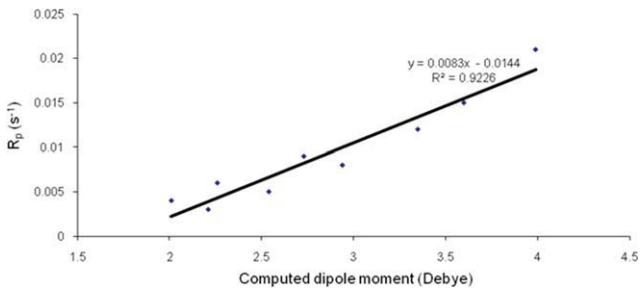


FIGURE 9 Rate of polymerization versus calculated dipole moment for monomers **1**–**11** (except for **7** and **12**).

values (Table 1). As expected, TBHMA was found to be the least reactive monomer due to steric effect. The second category involved ester, ether, and carbonate derivatives (**1**–**12**) of RHMA monomers. Here also, the reactivity of ester derivatives, compared with carbonate and ether derivatives was confirmed by low $\Delta\delta$ values. For example, the maximum rates of polymerization of TBHMA derivatives (**11**, **9**, **4**, and **2**) with the chemical shift values of 9.8, 10.1, 12.6, and 14.3 ppm were found to be 0.008, 0.006, 0.004, and 0.003 s^{-1}. Among the ether derivatives, monomers **3**, **6**, and **7** were expected to have the highest reactivity, comparable with those of the ester derivatives.

The last category involved carbamate derivatives (**13**–**16**) of RHMA monomers. The $\Delta\delta$ values were well correlated with the reactivities, indicating the low reactivities of monomers **15** and **16**.

CONCLUSIONS

Novel RHMA derivatives were prepared and evaluated using photopolymerization rates to understand the relation between the monomer structure and the reactivity. It was observed that the nature of both secondary functionalities (ester, ether, carbonate, and carbamate) and the terminal groups (phenyl, cyano, morpholine, butyl, etc.) have significant effects on polymerization kinetics. Depending on the type of the secondary functionality, the polymerization rate may increase up to five times by changing terminal groups. The $\pi-\pi$ interactions were found to be an important rate enhancing factor. Among the monomers studied here, aromatic carbamates capable of both $\pi-\pi$ interactions and hydrogen bonding were found to show highest rate of polymerization. Studies on the other aromatic carbamate derivatives of RHMA monomers are continuing. The high reactivity of cyclic carbonate-containing monomers was shown once more with a new derivative. The relationship between the polymerization and the dipole moment of monomers for nonhydrogen-bonded monomers seems to hold.

The computational resources used in this work were provided by the TUBITAK ULAKBIM High Performance Computing Center, and the National Center for High Performance Computing of Turkey (UYBHM) under the grant number 20792009.

REFERENCES AND NOTES

1 Kloosterboer, J. G. Adv Polym Sci 1988, 84, 1–61.

2 Decker, C. Prog Polym Sci 1996, 21, 593–650.

3 Anseth, K. S.; Newman, S. M.; Bowman, C. N. Adv Polym Sci 1995, 122, 177–217.

4 Moussa, K.; Decker, C. J Polym Sci Part A: Polym Chem 1993, 31, 2197–2203.

5 Kilambi, H.; Reddy, S. K.; Schneidewind, L.; Stansbury, J. W.; Bowman, N. C. J Polym Sci Part A: Polym Chem 2009, 47, 4859–4870.

6 Lu, H.; Stansbury, J. W.; Nie, J.; Berchtold, K. A.; Bowman, C. N. Biomaterials 2005, 26, 1329–1336.

7 Kilambi, H.; Beckel, E. R.; Berchtold, K. A.; Stansbury, J. W.; Bowman, N. C. Polymer 2005, 46, 4735–4742.

8 Berchtold, K. A.; Nie, J.; Stansbury, J. W.; Hacioglu, B.; Beckel, E. R.; Bowman, N. C. Macromolecules 2004, 37, 3165–3179.

9 Beckel, E. R.; Stansbury, J. W.; Bowman, N. C. Macromolecules 2005, 38, 9474–9481.

10 Beckel, E. R.; Nie, J.; Stansbury, J. W.; Bowman, N. C. Macromolecules 2004, 37, 4062–4069.

11 Berchtold, K. A.; Nie, J. N.; Stansbury, J. W.; Bowman, C. N. Macromolecules 2008, 41, 9035–9043.

12 Andrzejewska, E.; Andrzejesky, M. J Polym Sci Part A: Polym Chem 1998, 36, 665–673.

13 Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. Macromolecules 2003, 36, 3861–3873.

14 Lee, T. Y.; Roper, T. M.; Jonsson, S.; Guymon, C. A.; Hoyle, C. E. Macromolecules 2004, 37, 3659–3665.

15 Jariwala, P. C.; Mathias, L. J. Macromolecules 1993, 26, 5129–5136.

16 Avci, D.; Kusefoglu, S. H.; Thompson, R. D.; Mathias, L. J. Macromolecules 1994, 27, 1981–1982.

17 Mathias, L. J.; Thigpen, K.; Avci, D. Macromolecules 1995, 28, 8872–8874.

18 Thompson, R. D.; Barclay, T. B.; Basu, K. R.; Mathias, L. J. Polymer J 1995, 27, 325–338.

19 Avci, D.; Ziylan Albayrak, A. J Polym Sci Part A: Polym Chem 2003, 41, 2207–2217.

20 Avci, D.; Mathias, L. J. J Polym Sci Part A: Polym Chem 2002, 40, 3221–3231.

21 Avci, D.; Mathias, L. J. Polymer 2004, 45, 1763–1769.

22 Avci, D.; Kusefoglu, S. H. J Polym Sci Part A: Polym Chem 1993, 31, 2941–2949.

23 Yamada, B.; Kobatake, S. Prog Polym Sci 1994, 19, 1089–1131.

24 Warren, S. C.; Mathias, L. J. J Polym Sci Part A: Polym Chem 1990, 28, 1637–1648.

25 Mathias, L. J.; Warren, M. R.; Huang, S. Macromolecules 1991, 24, 2036–2042.

26 Anseth, K. S.; Wang, C. M.; Bowman, C. N. Macromolecules 1994, 27, 650–655.

27 Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd Ed.; Wiley-Interscience: New York, 1975; pp II-424.

28 Spartan version 4.0, 1995; Wavefunction, Inc.; Irvine, CA.

29 D'Alelio, G. F.; Huemmer, T. J Polym Sci Part A: Polym Chem 1967, 5, 307–321.

30 Burton, B. L. In Proceedings of Epoxy Resin Formulators' Meeting of the Society of the Plastics Industry, Baltimore, MD, July, 2001.

31 Lee, T. Y.; Guymon, C. A.; Jonsson, E. S.; Hoyle, C. E. Polymer 2004, 45, 6155–6162.

32 Beuermann, S.; Buback, M. Prog Polym Sci 2002, 27, 191–254.

33 Barner-Kowollik, C.; Vana, P.; Davis, T. P. In Handbook of Radical Polymerization; Matyjaszewski, K.; Davis, T. P., Eds.; Wiley: New York, 2002; Chapter 4, pp 197–198.

34 Davis, T. P.; Heuts, J. P. A.; Barner-Kowollik, Harrisson, S.; Morrison, D. A.; Yee, L. H.; Kapfenstein, H. M.; Coote, M. L. Macromol Symp 2002, 182, 131–148.

35 Morrison, D. A.; Davis, T. P. Macromol Chem Phys 2000, 201, 2128–2137.

36 Coleman, M. M., Lee, K. H.; Skrovanek, D. J.; Painter, P. C. Macromolecules 1986, 19, 2149–2157.

37 Kilambi, H.; Stansbury, J. W.; Bowman, C. H. Macromolecules 2007, 40, 47–54.

38 Sato, T.; Kamiya, I.; Tanaka, H.; Ota, T. Eur Polym J 1991, 27, 1087–1092.

39 Yamada, B.; Satake, M.; Otsu, T. Makromol Chem 1991, 192, 2713–2722.

40 Vaidya, R. A.; Mathias, L. J. J Polym Sci Polym Symp 1986, 74, 243–251.

41 Kodaira, T.; Fujisawa, T.; Liu, Q.-Q.; Urushisaki, M. Macromolecules 1996, 29, 484–485.