

Synthesis and photopolymerization kinetics of new flexible diacrylate and dimethacrylate crosslinkers based on C18 diacid

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Abstract

A series of new di(meth)acrylate monomers was synthesized from the reactions of methyl α -hydroxymethylacrylate (MHMA), ethyl α -hydroxymethylacrylate (EHMA), hydroxyethyl acrylate (HEA) and hydroxyethylmethacrylate (HEMA) with α,ω -C18 diacid chloride. The photopolymerization behavior and reaction kinetics of the synthesized monomers were investigated using photoinitiation with differential scanning calorimetry. The polymerization rates, conversions and kinetic constants for propagation and termination were determined for each of the monomers. The maximum rate of polymerizations of the diacrylate monomers was higher than that of the dimethacrylate monomers and followed the order: HDDA (1,6-hexanediol diacrylate) > HEA-C18 > EHMA-C18 \sim HEMA-C18 > MHMA-C18. The total conversions obtained were 78, 75, 72, 64 and 69% for MHMA-C18, EHMA-C18, HEMA-C18, HEA-C18 and HDDA, respectively, indicating comparable or higher conversions for methacrylates despite their lower rates of polymerization. Propagation and termination mechanisms of the monomers were investigated by plotting propagation and termination rate constants as a function of conversion.

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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 have many industrial applications, especially in areas such as coatings for flooring and furniture, dental restorative materials, optical fiber coatings, hard and soft contact lenses, and photolithography [1–7]. The monomers that are most widely used for photopolymerization are multifunctional acrylates and methacrylates [8–15]. Photopolymerizations of various multiacrylates and multimethacrylates have been studied using differential scanning calorimeter, dilatometry, dynamic mechanical testing, and real-time IR spectroscopy [10,11,14,16–18]. Polymerization of multifunctional monomers is complex due to autoacceleration, autodeceleration, incomplete conversion, trapping of radicals in networks,

physical inhomogeneities in networks, plus unequal reactivities of different functional groups [8,10,14,19–21].

For any real-world application, it is essential to understand the relationships between the polymer structure and reaction conditions with the properties of network materials formed. For example, the number of functional groups, plus the distance and flexibility between functional groups, combine to affect the crosslink density versus the primary and secondary cyclic structures that can form during polymerization [12,18,19,22]. Primary cyclization occurs when a pendant double bond reacts with the radical on the same propagating chain, leading to reduced crosslink density, and generation of microgels and heterogeneity in the polymer [23]. This heterogeneity causes reduction in physical properties such as mechanical strength, solvent resistance and glass transition temperature.

In this work, we investigate the polymerization behavior, and especially the kinetics, of a series of new multifunctional (meth)acrylate monomers. Due to their flexible linking units, it is possible to obtain materials having improved impact resistance and toughness. These will allow

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expanded application of these new materials in areas where bulk hardness (with accompanying brittle failure) is less important than nanoscopic uniformity, toughness and durability.

2. Experimental

2.1. Reagents

Methyl α -hydroxymethylacrylate (MHMA), ethyl α -hydroxymethylacrylate (EHMA) were a generous donation from Nippon Shokobai, while the C18 diacid was provided by Cognis Chemical Company. Hydroxyethyl acrylate, hydroxyethyl methacrylate and 1,6-hexanediol diacrylate (HDDA) were obtained from Aldrich Chemical Company and used as received. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651 or DMPA from Ciba-Geigy), was recrystallized from hexane before use. All other solvents and starting materials were reagent grade and used as received.

2.2. Characterization

Monomer characterization involved ^1H and ^{13}C NMR spectroscopy (Varian Gemini 200 MHz) and FT-IR spectroscopy on thin films on NaCl plates or as KBr pellets (Mattson 5000). Photopolymerizations were done in a Perkin Elmer differential photocalorimeter with a medium pressure mercury lamp.

2.3. Procedures for the synthesis of monomers

1,18-Octadecanoyl chloride (C18 diacid chloride) was synthesized from the reaction of commercial grade C-18 diacid (monomer grade provided by Cognis, 10.00 g) and thionyl chloride (19 ml) using one drop of DMF, (*N,N*-dimethylformamide). Essentially 100% conversion of diacid to diacid chloride was obtained, based on the purity of the crude product as determined by ^{13}C NMR spectroscopy (CDCl_3 solution).

2.3.1. MHMA-C18 (bisester of C18 diacid with MHMA)

MHMA (1.62 g, 0.014 m), C18 diacid chloride (2 g, 0.00626 m), *N,N*-dimethylaminopyridine (DMAP, 0.0074 g) and 14 ml tetrahydrofuran (THF) were added to a 100 ml round bottom flask and the mixture stirred at 60 °C for 24 h. THF was evaporated under reduced pressure and the product was purified by recrystallization from methanol to give a white solid with a melting point of 76–77 °C; monomer purity was confirmed by ^{13}C NMR spectroscopy (CDCl_3 solution). The other monomers investigated (EHMA-C18, HEMA-C18 and HEA-C18) were obtained with the same procedure. EHMA-C18 and HEA-C18 were purified by chromatography on silica gel using hexane/ethyl acetate (80:20) as eluent for EHMA-C18 and hexane/ethyl

acetate (70:30) as eluent for HEA-C18. EHMA-C18 and HEA-C18 were white solids with melting points of 45–46 and 42–43 °C, respectively. HEMA-C18 was a white oily solid, melting point around room temperature. The yields of products were 80–90% in all cases. Individual characterization data for each monomer are given below.

MHMA-C18. ^{13}C NMR (CDCl_3): 24.9, 29.1, 29.2, 29.4, 29.6, 34.2 (CH_2); 52.0 (CH_3); 62.2 (CH_2O); 127.4 ($\text{CH}_2=\text{C}$); 135.3 ($\text{H}_2\text{C}=\text{C}$); 165.7, 173.2 ($\text{C}=\text{O}$) ppm. Anal. calcd for $\text{C}_{28}\text{H}_{46}\text{O}_8$: C, 65.88; H, 9.02. Found: C, 65.93; H, 9.07.

EHMA-C18. ^{13}C NMR (CDCl_3): 14.0 (CH_3); 25.5, 29.1, 29.3, 29.5, 34.1 (CH_2); 60.8, 62.1 (CH_2O); 126.9 ($\text{CH}_2=\text{C}$), 135.5 ($\text{CH}_2=\text{C}$); 165.1, 173.1 ($\text{C}=\text{O}$) ppm. Anal. calcd for $\text{C}_{30}\text{H}_{50}\text{O}_8$: C, 66.91; H, 9.29. Found: C, 66.46; H, 9.60.

HEA-C18. ^{13}C NMR (CDCl_3): 24.8, 29.0, 29.2, 29.4, 29.6, 34.1 (CH_2); 61.8, 62.2 (CH_2O); 127.9 ($\text{CH}_2=\text{CH}$), 131.3 ($\text{CH}_2=\text{CH}$), 165.8, 173.6 ($\text{C}=\text{O}$) ppm. Anal. calcd for $\text{C}_{28}\text{H}_{46}\text{O}_8$: C, 65.88; H, 9.02. Found: C, 65.47; H, 9.50.

HEMA-C18: ^{13}C NMR (CDCl_3): 18.5 (CH_3); 25.0, 29.0–34.3 (CH_2); 62.2, 63.0 (CH_2O), 126.5 ($\text{CH}_2=\text{C}$), 136.2 ($\text{CH}_2=\text{C}$); 167.5, 174.0 ($\text{C}=\text{O}$) ppm.

2.4. Photopolymerization procedure

Typically, 3 mg of sample was placed in an uncovered aluminum DSC pan and a drop of a CH_2Cl_2 solution of photoinitiator (DMPA) was added. The initiator solution was added with a micro-syringe to give a final concentration in the monomer of 0.2 mol% after evaporation of the solvent. The chamber of the DSC was purged with nitrogen to remove air and CH_2Cl_2 for 10 min before polymerization and purging was continued during polymerization. The samples were photocured for 11 min at 80 °C. Monochromatic 365 nm ultraviolet light was used for all of the photopolymerizations, and the light intensity was 1.0 mW/cm². 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 [19,24]. The heats of reaction (ΔH_p) used were 13.1 kcal/mol for the methacrylate double bond and 20.6 kcal/mol for the acrylate double bond.

The rate formula used in evaluation of the photopolymerization data was:

$$R_p = \frac{Q/sM}{n\Delta H_p m}$$

where Q/s is heat flow per second during reaction, M the molar mass 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. The kinetic constants for propagation and termination were determined using two sets of experiments. First, $k_p/k_t^{1/2}$ values as a function of time were determined by

complete polymerization of monomers using steady-state analysis with the formula [24]:

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](\Theta I_0 \epsilon [A])^{1/2}}$$

where R_p is the rate of polymerization, $[M]$ the molar concentration of double bonds, Θ the initiator efficiency, I_0 the incident light intensity, ϵ the extinction coefficient of the initiator and $[A]$ the initiator concentration. For this study, Θ is assumed to be unity and ϵ was set equal to 124 l/mol cm.

Then, a second set of experiments were done by closing the lamp shutter to stop radical initiation at various time before complete polymerization, and then monitoring reaction rates as a function of 'dark' time. The kinetic constants were determined using non-steady-state analysis. It was assumed that the kinetic constants are constant over the time $t_1 - t_0$ where conversion changes are very small. Since the kinetic constants are changing most rapidly at the beginning and end of the overall polymerization, the data from these parts were not used. The relationship used was:

$$\frac{1}{R_p} \Big|_{t=t_1} = \frac{2k_t(t-t_0)}{k_p[M]} + \frac{1}{R_p} \Big|_{t=t_0}$$

where t_0 is the beginning of the dark period, and t_1 is some time later in the dark reaction. Thus, a plot of $1/R_p$ versus the time elapsed is linear with a slope of $2k_t/k_p[M]$. The values of k_p and k_t were determined from the two equations, $k_p/k_t^{1/2}$ values obtained using steady-state analysis and k_t/k_p values obtained from the slope of the equation above.

3. Results and discussion

3.1. Synthesis of monomers

The monomers were synthesized by the reaction of C18 diacid chloride with MHMA, EHMA, HEMA and HEA with *N,N*-dimethylaminopyridine as catalyst in THF at 60 °C (Fig. 1). Although pure monomers of MHMA-C18 and HEMA-C18 were obtained by recrystallization from methanol, purification of HEA-C18 and EHMA-C18

monomers required chromatography on silica gel using ethyl acetate/hexane mixtures. Monomer yields were 80–90% after purification. Monomers MHMA-C18, HEA-C18, and EHMA-C18 were white solids with melting points of 76–77, 42–43, and 45–46 °C respectively, whereas HEMA-C18 was an oily solid. Purity was confirmed by spectral characterization (below).

The ^{13}C NMR spectra of EHMA-C18 (Fig. 2) showed characteristic peaks for a methyl carbon at 14.0 ppm, methylene carbons of the C18 chain between 25.5 and 34.1 ppm; the methylene carbons attached to oxygen at 60.8 and 62.1 ppm, double bond carbons at 126.9 and 135.5 ppm, and carbonyl carbons at 165.1 and 173.1 ppm. The FT-IR spectrum of this monomer (Fig. 3) showed two different carbonyl peaks due to two different ester groups at 1735 and 1716 cm^{-1} plus the double bond peak at 1638 cm^{-1} .

3.2. Photopolymerizations

Photopolymerizations of the monomers were followed by DSC. All the polymerizations were performed under identical conditions of temperature, initiator concentration and light intensity (80 °C, 0.2 mol%, 1.0 mW/cm^2). Fig. 4 shows the time dependences of the polymerization rate R_p for each of the synthesized monomers. It is known that diacrylates have higher rates of polymerization than comparable dimethacrylates. Thus, it is not surprising that HEA-C18 displayed the highest rate of polymerization of the difunctional monomers evaluated here. Although MHMA-C18 and EHMA-C18 have similar chemical structures (only the ester group substituents are different), EHMA-C18 polymerized faster than MHMA-C18. The reason for this difference may be that the polymerization temperature (80 °C) was close to the melting point of MHMA-C18 monomer (76–77 °C) while far above that of the EHMA-C18 monomer.

On the other hand, EHMA-C18 and HEMA-C18 showed quite similar polymerization behavior in spite of large structural differences. Maximum rates of polymerizations for EHMA-C18 and HEMA-C18 were found to be 0.0193 and 0.0198 s^{-1} . For comparison with these monomers, commercial 1,6-hexanediol diacrylate (HDDA) monomer was polymerized under the same conditions. Fig. 5 shows

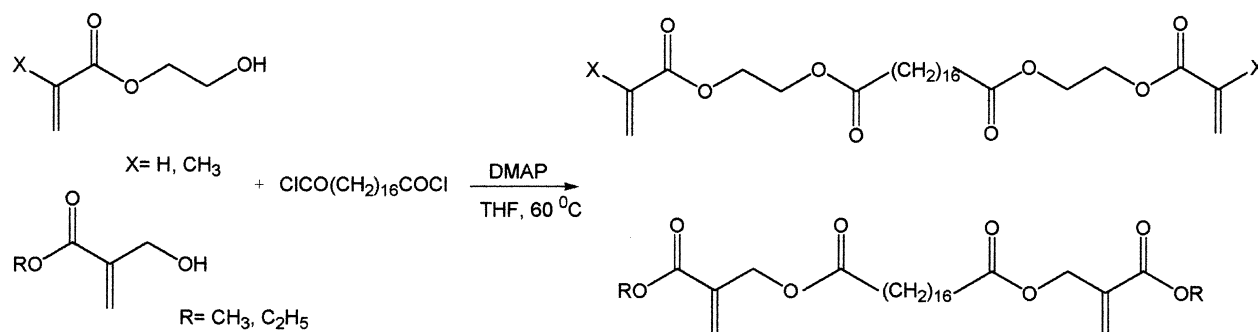
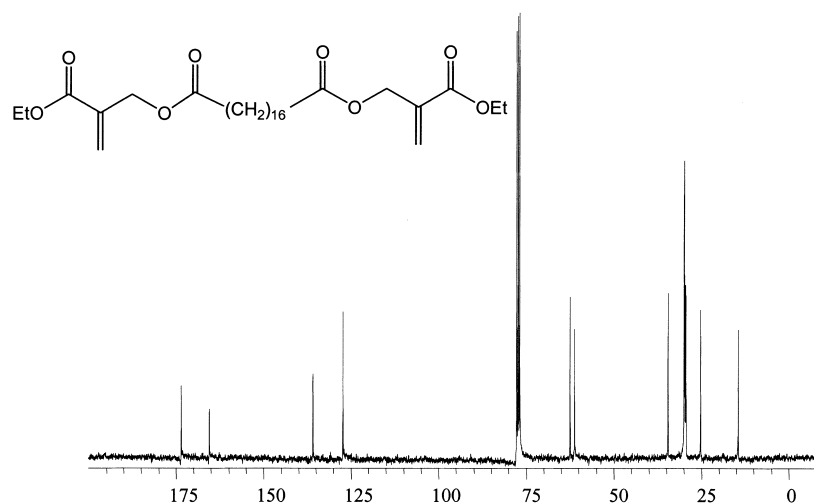


Fig. 1. General synthetic scheme for C18 monomers.

Fig. 2. ^{13}C NMR spectrum of EHMA-C18 monomer.

the rate of polymerization of some synthesized monomers and HDDA as a function of time. The data for HDDA shows a 1.2-fold higher value for the maximum rate compared to HEA-C18. Similar behavior was also reported for the photopolymerization of diethylene glycol dimethacrylate (DEGDMA), poly(ethylene glycol 200) dimethacrylate (PEG200DMA) and poly(ethylene glycol 600) dimethacrylate (PEG600DMA) [8]. When the rates of polymerization of DEGDMA, PEG200DMA, PEG600DMA were compared with respect to the increasing number of ethylene glycol units in the monomer, the maximum rate of polymerization was found to decrease. In summary, the maximum rates of the commercial and synthesized monomers follows the order: HDDA > HEA-C18 > EHMA-C18 ~ HEMA-C18 > MHMA-C18.

The conversion dependencies of the polymerization rate are given in Fig. 6. Several observations can be made from this data. First, the polymerization rate increased with conversion. This is known as ‘autoacceleration’ and results from a decrease in mobility of polymer radicals with an increase in viscosity, which causes a reduced termination

rate. The reduced rate of termination causes an increase in the radical concentration, which increases the polymerization rate. It has been reported that, instead of termination by translational and/or segmental diffusion of the radicals, reaction diffusion controls termination (i.e., radicals propagate through the unreacted double bonds in the system until they encounter another radical chain-end) [8]. After the polymerization reaches its maximum rate, it starts to decrease due to autodeceleration, where crosslinking restricts and stops the propagation reaction altogether, locking the reactive chain-ends into local domains where monomer diffusion diminishes and termination stops.

In general, it has been observed by many researchers that overall monomer conversion increases for systems that are polymerized at faster rates. As the polymerization 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. Although the rates of polymerization of HDDA and HEA-C18 diacrylates are higher than the dimethacrylates, conversions

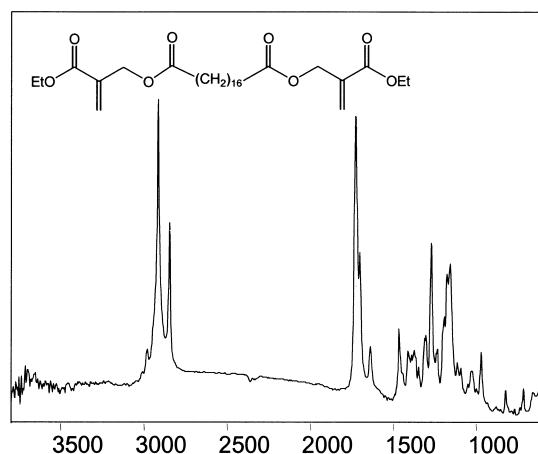
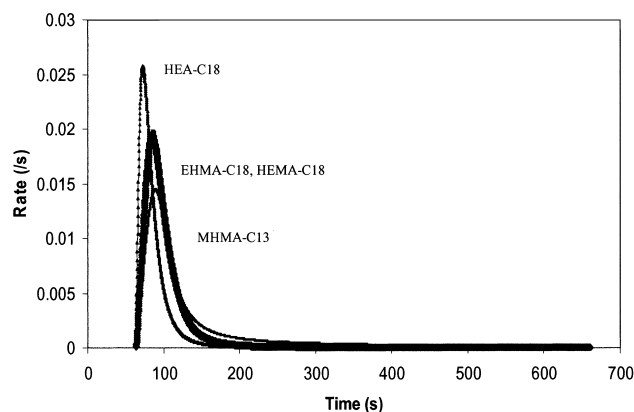


Fig. 3. FT-IR spectrum of EHMA-C18 monomer.

Fig. 4. Rate of polymerization of MHMA-C18, HEA-C18, EHMA-C18 and HEMA-C18 as a function of time at 80 °C. Photopolymerizations were initiated with 0.2 mol% DMPA and $I_0 = 1 \text{ mW/cm}^2$.

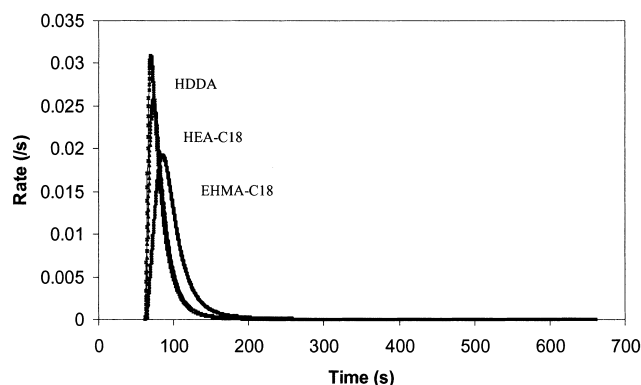


Fig. 5. Rate of polymerization of HEA-C18, EHMA-C18 and HDDA as a function of time at 80 °C. Photopolymerizations were initiated with 0.2 mol% DMPA and $I_0 = 1 \text{ mW/cm}^2$.

at maximum rates and overall conversions were lower. Conversion at maximum rates were 12.6 and 16% for HDDA and HEA-C18, respectively.

The monomer structure also affects the conversion. As the distance and flexibility between functional groups increases, the conversion at maximum rate of polymerization increases, and maximum double bond conversion increases. The reason for increased conversion at maximum rate is a delayed gel effect (autoacceleration). For example, the enhanced mobility of PEG600 DMA leads to nearly 100% conversion of the double bonds [8]. Apparently, as the mobility of the system is increased from HDDA to the monomers synthesized here, autoacceleration is delayed and conversions reached at the point of maximum rate both increased. The result is a shift in the conversion at the maximum rate of polymerization from 12.6% for HDDA to 16% for HEA-C18, 21% for MHMA-C18, 23% for EHMA-C18, and 22.4% for HEMA-C18. The magnitude of the gel effect is highest in HDDA. In EHMA-C18, MHMA-C18 and HEMA-C18, autoacceleration is spread over an extended conversion range. Overall conversions were 78, 75, 72 and 64% for MHMA-C18, EHMA-C18, HEMA-C18 and HEA-C18 compared to 69% for HDDA.

The individual kinetic constants were determined from dark reactions using photo-DSC results. In Figs. 7 and 8, the propagation and termination kinetic constants are plotted

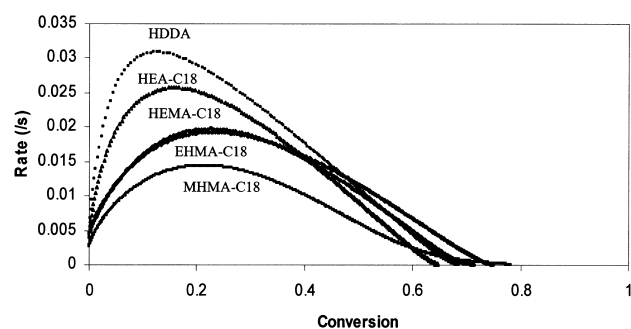


Fig. 6. Rate of polymerization as a function of conversion for MHMA-C18, EHMA-C18, HEMA-C18, HEA-C18 and HDDA 80 °C. Photopolymerizations were initiated with 0.2 mol% DMPA and $I_0 = 1 \text{ mW/cm}^2$.

versus double bond conversion for each of the monomers. It is seen in Fig. 7 that the propagation constants remain relatively unchanged as the monomer molecules and pendent vinyl groups remain mobile at low conversions. In this region, chemical reaction controls the propagation mechanism, which is typical behavior of multifunctional monomers [19]. At higher conversions (>40%), diffusion of the monomer was significantly decreased, so k_p began to decrease. The k_p values for all the synthesized monomers were of the same order of magnitude. The k_p value for HDDA was significantly higher than those of the synthesized monomers. In general, termination constants of multifunctional (meth)acrylate monomers decrease up to a certain conversion. At this point, termination changes from segmental diffusion to reaction diffusion and k_t reaches a plateau. It has been reported that during the polymerization of methyl methacrylate, the plateau in k_t is observed after 40–50% conversion. Whereas during polymerization of multifunctional monomers, the plateau in k_t is seen as early as 5–10% conversion [19]. For our monomers the initial decrease in termination rate constants were not obvious. A long plateau region was observed in the termination kinetic constants, starting from around 5–10% conversion and continuing up to 40–50% conversion (Fig. 8). It was reported that when the termination is reaction diffusion controlled, k_t/k_p ratio becomes constant [19]. When the ratio k_t/k_p as a function of conversion was calculated for all the monomers, the ratio appeared to change between 1300 and 4000. The conversion where the reaction diffusion became the major termination mechanism was not obvious.

In general, acrylates have greater values of both the propagation and the termination rate constants compared to methacrylates due to their higher reactivities. Thus, it is not surprising that HDDA showed the highest k_p value. The k_p values of HEA-C18 was slightly higher than the methacrylate monomers. The high value of $k_p/k_t^{1/2}$ compared to methacrylate monomers may explain high reactivity of this monomer. For example, the maximum $k_p/k_t^{1/2}$ values of

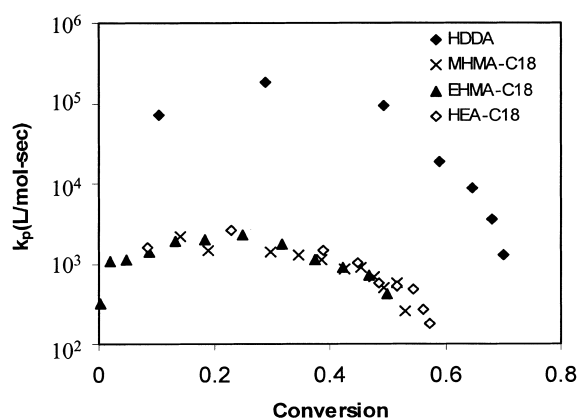


Fig. 7. Propagation kinetic constants, k_p , as a function of conversion for MHMA-C18, HEMA-C18, EHMA-C18, HEA-C18 and HDDA 80 °C. Photopolymerizations were initiated with 0.2 mol% DMPA and $I_0 = 1 \text{ mW/cm}^2$.

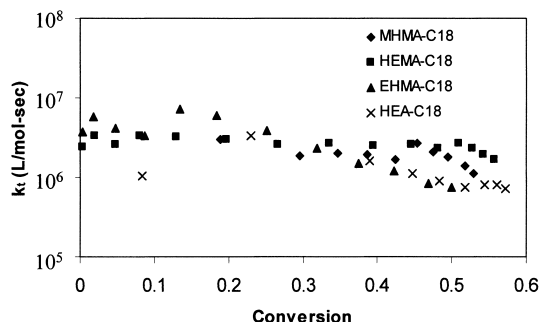


Fig. 8. Termination kinetic constants, k_t , as a function of conversion for MHMA-C18, HEMA-C18, EHMA-C18 and HEA-C18 80 °C. Photopolymerizations were initiated with 0.2 mol% DMPA and $I_0 = 1 \text{ mW/cm}^2$.

HEA-C18 and EHMA-C18 were around 1.56 and 1.15, consistent with the differences in maximum rates. The maximum $k_p/k_t^{1/2}$ values for the monomers followed the order: HDDA > HEA-C18 > EHMA-C18 > HEMA-C18 > MHMA-C18. This trend was consistent with the behavior observed in the rate of polymerization versus conversion plots. For example, MHMA-C18 monomer with the lowest $k_p/k_t^{1/2}$ value showed the lowest maximum rate of polymerization.

4. Conclusions

Four novel multifunctional monomers were synthesized and photopolymerizations of these monomers were investigated with respect to rates of polymerization, conversion and the propagation and termination kinetic constants. The maximum rate of polymerizations of the diacrylate monomers was higher than that of the dimethacrylate monomers. It was found for all C18 dimethacrylate monomers the maximum conversions were approximately 72–78%, independent of the structural differences of the monomers. These values were slightly higher than the diacrylate monomers. The propagation and termination rate constants were nearly constant up to about 40–50% conversion. The $k_p/k_t^{1/2}$ values for the di(meth)acrylate monomers were significantly lower than that of HDDA.

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