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Crosslinking kinetics of methyl and ethyl (α-hydroxymethyl)acrylates: effect of crosslinker type and functionality

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Abstract

Photopolymerizations were carried out using monofunctional monomers methyl or ethyl-(α-hydroxymethyl)acrylate (MHMA and EHMA, respectively) with multifunctional crosslinkers. The effect of crosslinker type (acrylate versus methacrylate) and functionality (di-, tri-, tetra- and penta/hexaacrylates) on polymerization rates and conversions were investigated. RHMA systems (monomer plus crosslinker) reached very high conversions (70–83%) for all systems with the exception of dipentaerythritol penta/hexaacrylate systems. Network T_g played an important role in final conversions with dipentaerythritol penta/hexaacrylate and pentaerythritol tetraacrylate, while EHMA (with a lower T_g) went to higher conversions than MHMA.

Keywords: Crosslinking photopolymerizations; R-(α-hydroxymethyl)acrylates; Pentaerythritol-based acrylates

1. Introduction

Photopolymerization of multifunctional monomers is a commonly used process to produce highly crosslinked networks in rapid-cure coatings, stereolithography, and restorative materials. During crosslinking photopolymerizations, microgelation can occur very early in the reaction [1]. Further reaction leads to macrogelation and autoacceleration. This heterogeneous network formation may adversely effect mechanical properties [2,3].

In addition, conversion is often limited by the entrapment of pendant double bonds and monomer in microgel regions. Many factors have been shown to influence final conversion including glass transition temperature (T_g) of the forming network [4], polymerization temperature [5], crosslinker type (acrylate versus methacrylate) [5,6], and degree of functionality [3,6,7]. Also, vitrification and topological factors limit the final conversion to well below 100% unless a flexible spacer between vinyl groups is used [6].

While high conversions to homogeneous networks are desirable, polymerization rates cannot be compromised due to the advantages of crosslinkers for rapid cure systems. Incorporation of pendent heterocyclic groups into methacrylates has been shown to provide rate enhancements comparable to network forming systems with increases in polymerization rates due to reduced termination and perhaps increased chain transfer [8]. Similarly, the presence of a heteroatom linkage in diacrylate systems greatly enhanced polymerization rates in both argon and air [9]. Recently, dipole moment and hydrogen bonding capability have been shown to influence photopolymerization rates, possibly through pre-association or a template effect [10, 11].

We have been pursuing the chemistry of α-(hydroxymethyl)acrylate (HMA) derivatives for several years, and many ester monomers (RHMA where R is the ester group) are now available commercially [12]. These monomers show fast photopolymerization rates both alone, and in the presence of acrylate or methacrylate crosslinkers. In this work, we present the effect of crosslinker type and functionality on bulk conversions and rates of the methyl and ethyl (α-hydroxymethyl)acrylates (Fig. 1).

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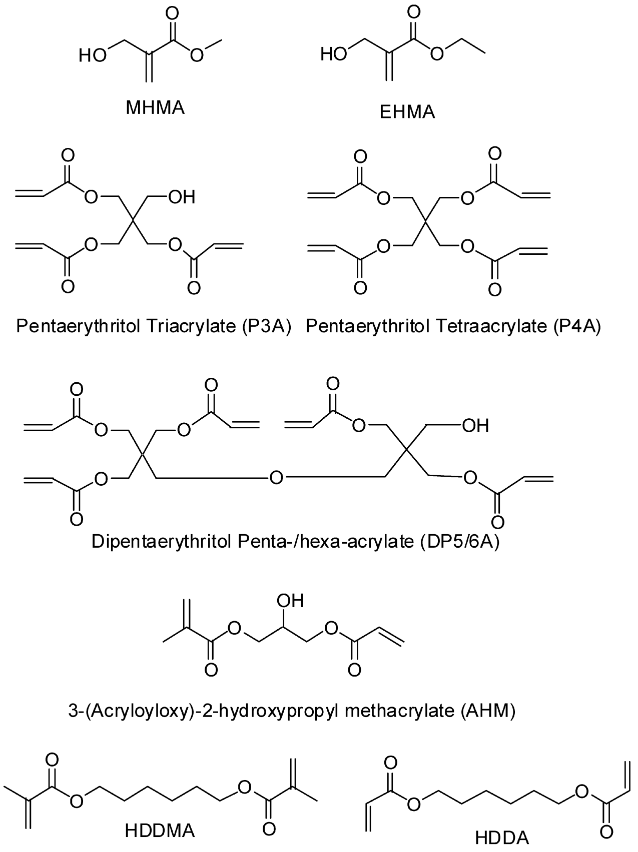

Fig. 1. Monofunctional RHMA monomers and multifunctional acrylate and/or methacrylate crosslinkers.

2. Experimental

2.1. Materials

Alkyl (α-hydroxylmethyl)acrylate (R = methyl, MHMA and R = ethyl, EHMA) were donated by Nippon Shokubai Co., Tokyo, Japan. Multifunctional acrylates and methacrylates were purchased from Aldrich, Milwaukee, WI. All the monomers were used as received, without further purification. Irgacure 651® was donated by Ciba Specialty Chemicals Inc., Basel, Switzerland and used as received.

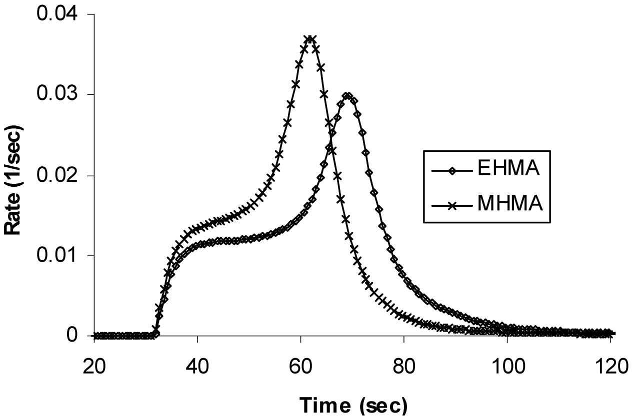

Fig. 2. Rate versus time of MHMA and EHMA photopolymerizations at 30 °C.

2.2. Photopolymerizations

For a typical photopolymerization, pentaerythritol triacrylate (1.0×10^{-2} g, 3.4×10^{-5} mol), and Irgacure 651® (8.9×10^{-3} g, 3.5×10^{-5} mol) were dissolved in MHMA (0.5 g, 3.4×10^{-3} mol). Approximately 3.0 mg of the mixture was placed in a bottom impressed and flattened aluminum DSC pan (approximately 200 μm thickness). Heats of photoreactions were measured using a TA Instruments 930 differential photocalorimeter (DPC) equipped with a high-pressure mercury arc lamp. This unit emits radiation predominantly in the 220–400 nm range, and provides light intensity of 31 mW/cm^2 as measured by a UV radiometer capable of broad UV range coverage (UV Process Supply, Inc., Chicago, IL). The chamber of the DPC was purged with nitrogen for 10 min before irradiation and a nitrogen blanket was maintained throughout the reaction. All the experiments were carried out sequentially so the light intensity during a given series of experiments would be as constant as possible. The sample was irradiated for 6 min at 30 °C with the light shutter opening at 30 s after the beginning of data acquisition; i.e. onset of photocure occurred at 30 s. The enthalpy value $\Delta H_{\text{theor}} = 13.1$ kcal/mol was used as the theoretical heat evolved for methacrylate double bonds, and for acrylate double bonds, the value of $\Delta H_{\text{theor}} = 20.6$ kcal/mol was used [13]. Instantaneous rates of polymerization were calculated according to Eq. (1) [14,15], where ΔH_{pol} is the heat released per mole of double bonds reacted, Q/s is the heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule, and mass being the mass of monomer in the sample. In this work we chose to base our calculations for the polymerization rates of methyl α-hydroxymethylacrylate (MHMA) systems using the theoretical heat of polymerization value of methyl methacrylate mentioned earlier. However, for the acrylate–methacrylate monomer, ΔH_{theor} was calculated using a weighted average of ΔH_{theor} for acrylates and methacrylates.

$$\text{Rate} = \frac{(Q/s)M}{n\Delta H_{\text{pol}}\,\text{mass}} \tag{1}$$

3. Results and discussion

RHMA derivatives have previously been shown to give faster photopolymerization rates than typical methacrylates [16]. Two RHMA derivatives were investigated here, MHMA and EHMA (Fig. 1). Poly(EHMA) has a reported density of 1.24 g/cm^3 and T_g of 64 °C, while poly(MHMA) has a density of 1.39 g/cm^3 and T_g of 146 °C [17]. MHMA and EHMA were found to have fast photopolymerization rates under the conditions used here (Fig. 2). EHMA has a plateau region (which is not as severe for MHMA) before the onset of autoacceleration, and this may be due to the lower density and T_g of poly(EHMA) which slows the onset of autoacceleration. Although different rate profiles were observed for MHMA and EHMA, overall conversions are high for both, 81% (±2) and 79% (±6), respectively.

To investigate the effect that the crosslinker type (acrylate or methacrylate) had on rate and conversion, photopolymerizations were carried out using hexanediol diacrylate (HDDA), hexanediol dimethacrylate (HDDMA), and 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) (see Fig. 1). To investigate the effect that the degree of functionality had on rate and conversion, various multifunctional acrylates based on pentaerythritol were also used (Fig. 1). Initially, the rates for bulk crosslinkers (no RHMA) were determined and found to be similar with the exception of HDDMA. Fig. 3 shows the rates versus time plots for four crosslinkers in bulk reactions; additional experimental data for well-known systems were included only to provide qualitative and quantitative comparison with the multifunctional acrylate and the mixed acrylate/methacrylate crosslinkers discussed in our work. Plots for P3A and DP5/6A not shown were similar to P4A. Not surprisingly, AHM was slightly slower than the pentaerythritol-based acrylates (P4A shown) because it possesses a methacrylate group. It was, however, significantly faster than HDDMA.

Conversions ranged from 35 to 45% for the pentaerythritol-based acrylates. HDDA and HDDMA had much higher overall conversions (>60%) although HDDMA was much slower than HDDA (Table 1). To calculate AHM conversions, a weighted average of ΔH_{theor} for acrylates and methacrylates was used. This assumes that an equal number of acrylates and methacrylates react, which may not be true given differences in reactivity; therefore, AHM conversions are only semi-quantitative. The conversion value of 41% is similar to the pentaerythritol derivatives, and lower than HDDA and HDDMA.

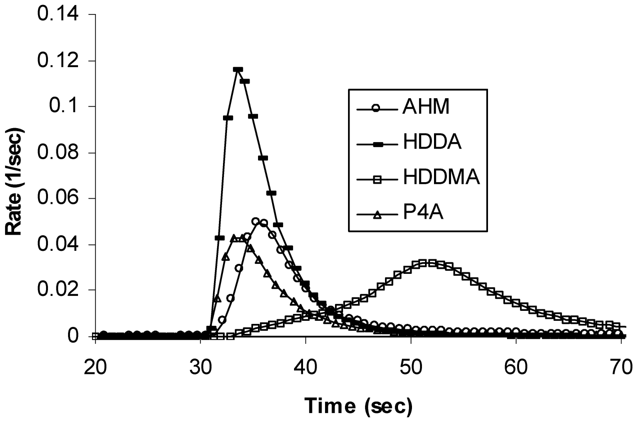

Fig. 3. Rate versus time of bulk crosslinkers at 30 °C.

Table 1
Final conversions for bulk crosslinkers

Crosslinker	Overall conversion (%)[a]
HDDA	68(4)
HDDMA	63(3)
AHM	41(7)
P3A	46(5)
P4A	35(10)
DP5/6A	42(2)

[a] Values are the average of three trials with standard deviations given in parentheses.

3.1. Effect of crosslinker type (acrylate versus methacrylate) on RHMA photopolymerizations

MHMA and EHMA were then photopolymerized in the presence of 1 and 2 mol% difunctional acrylates and methacrylates. For all polymerizations, initial rates were very similar. Slight differences were observed in the onset and extent of the autoacceleration peak (Fig. 4(B)). Faster onset of autoacceleration was seen for EHMA with crosslinkers than for MHMA, which showed small change in the overall rate plots compared to pure MHMA. This could be due to formation of a less dense network and reaction temperatures being closer to the T_g of poly(EHMA), or to

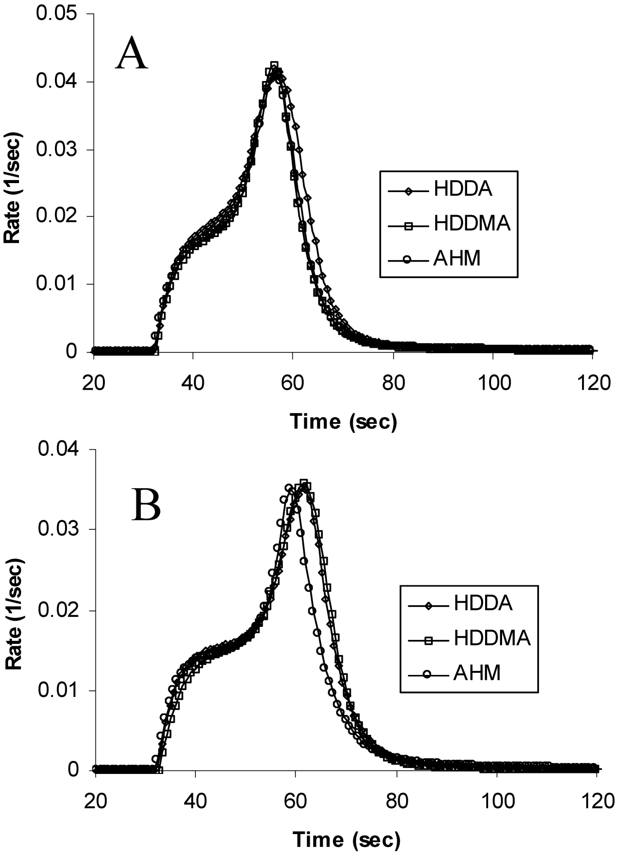

Fig. 4. Rate versus time plots with 1 mol% difunctional crosslinkers at 30 °C (A) MHMA and (B) EHMA.

Table 2
Overall conversions of MHMA and EHMA with difunctional crosslinkers

Crosslinker	Conversion (%)[a]			
	MHMA		EHMA	
	1 mol% Crosslinker	2 mol% Crosslinker	1 mol% Crosslinker	2 mol% Crosslinker
AHM	75(3)	78(3)	75(5)	81(9)
HDDA	82(2)	76(7)	79(3)	75(11)
HDDMA	83(3)	70(5)	78(7)	73(17)

[a] Values are the average of three trials with standard deviations given in parentheses.

the fact that MHMA reaction is already fast, so crosslinkers did not have as great an effect.

Conversion was high for all crosslinking systems, ranging from 70 to 83% (Table 2). Compared to neat monomers, it appears that the crosslinker is actually reducing overall conversions in some cases. This could be due to rapid microgelation that traps monomer and pendent double bonds, consequently limiting conversion.

3.2. Effect of degree of functionality (di-, tri-, tetra-, penta/hexa-) on MHMA photopolymerizations

MHMA was photopolymerized with 1 and 2 mol% of hexanediol diacrylate (HDDA), pentaerythritol triacrylate (P3A), pentaerythritol tetraacrylate (P4A), and dipentaerythritol penta/hexaacrylate (DP5/6A) in order to determine the effect that crosslinker functionality had on rates and final conversions. For all of these crosslinkers, initial rates were essentially equal with differences arising in the position and height of the autoacceleration peak (Fig. 5).

HDDA gave the highest final conversion for both 1 and 2 mol% crosslinkers while DP5/6A gave the lowest conversion (Fig. 6). With DP5/6A, network formation and gelation can occur very rapidly, trapping more pendent double bonds and monomer, thus limiting conversion. This effect can be seen more clearly with 2 mol% DP5/6A. Although the initial rate is equivalent to P3A and P4A, the rate decreases quickly after onset of autoacceleration. This indicates rapid gelation in systems with high degrees of acrylate functionality (DP5/6A) that limits final conversion

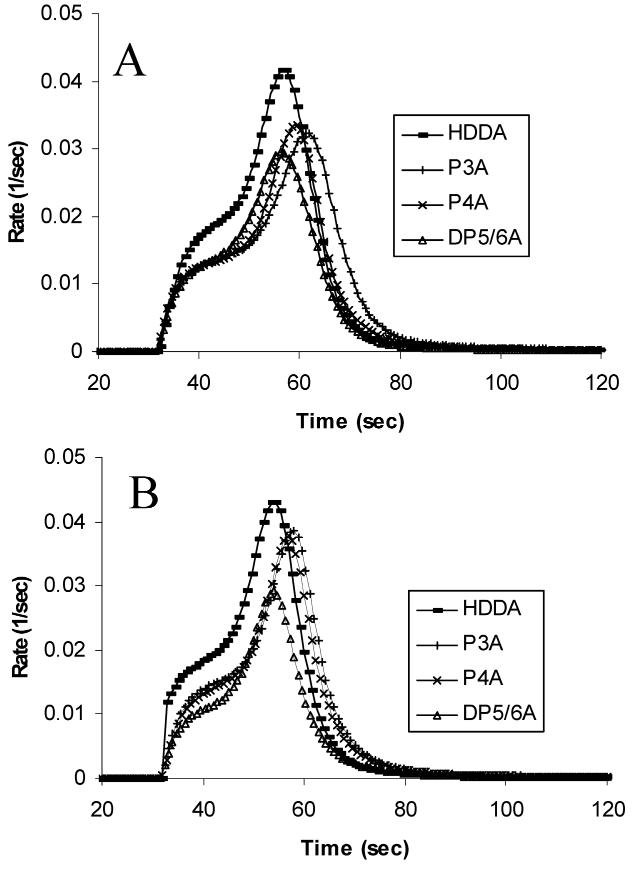

Fig. 5. Rate versus time of MHMA with multifunctional crosslinkers at 30 °C (A) 1 mol% and (B) 2 mol% concentration.

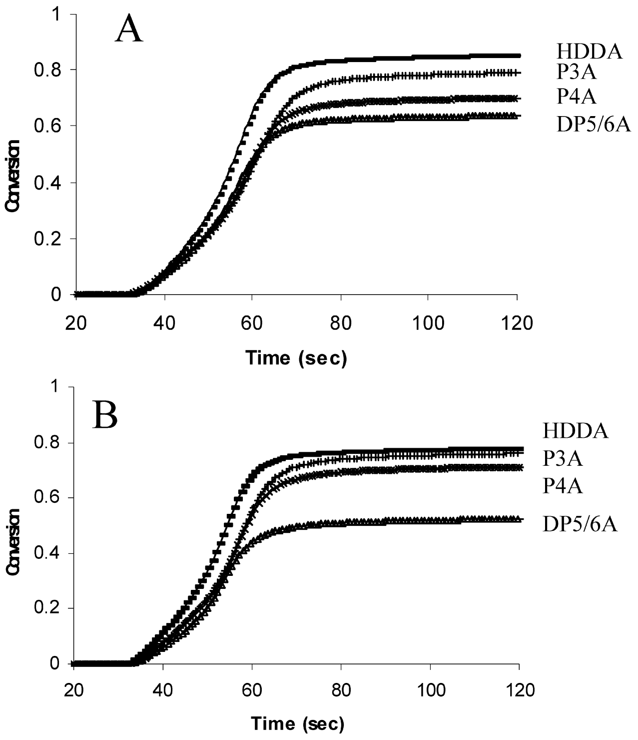

Fig. 6. Conversion versus time of MHMA with multifunctional crosslinkers at (A) 1 mol% and (B) 2 mol% concentration.

Table 3
Overall conversions of RHMA photopolymerizations with multifunctional acrylates

Crosslinker	Conversion (%)[a]			
	MHMA		EHMA	
	1 mol% Crosslinker	2 mol% Crosslinker	1 mol% Crosslinker	2 mol% Crosslinker
HDDA	82(2)	76(7)	79(3)	75(11)
P3A	80(1)	83(5)	79(6)	80(1)
P4A	71(1)	68(5)	78(5)	70(4)
DP5/6A	61(4)	58(5)	72(1)	58(3)

[a] Values are the average of three trials with standard deviations given in parentheses.

(Fig. 6). This effect is enhanced when a greater mole percentage of multifunctional acrylate is used.

3.3. Effect of degree of functionality (di-, tri-, tetra-, penta/hexa-) on EHMA photopolymerizations

Multifunctional acrylates have a somewhat larger effect on EHMA polymerizations than on MHMA (Fig. 7). DP5/6A showed an earlier onset of autoacceleration; however, due to faster gelation, the rate quickly decreased. This effect is accentuated at 2 mol% crosslinker. Although gelation occurs rapidly in the DP5/6A systems, final conversion was nearly 60% (Table 3). Both 1 mol% P3A and P4A gave final conversions >80%, while 1 mol% HDDA showed a slightly higher conversion than other multifunctional acrylates.

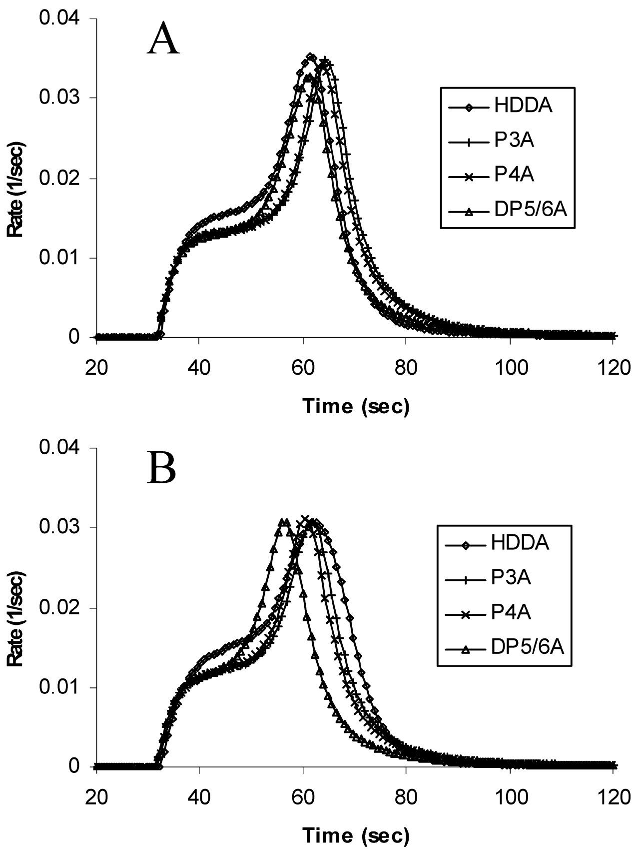

Fig. 7. Rate versus time of EHMA with multifunctional crosslinkers at 30 °C (A) 1 mol% and (B) 2 mol% concentration.

With increasing crosslinker functionality, EHMA reached slightly higher overall conversions compared to MHMA (Table 3). For example, EHMA with 1 mol% DP5/6A reached 72% conversion while MHMA with 1 mol% DP5/6A only attained 61% conversion. It may be that crosslinkers with higher functionality (DP5/6A) have a more dramatic effect on MHMA polymerizations compared to EHMA, most likely due to the higher density and T_g of poly(MHMA). This would lead to a more rigid polymerizing system, enhancing the gelation effects of DP5/6A.

4. Conclusions

RHMA derivatives are monomers showing fast photopolymerization rates and high bulk conversions without added crosslinker. Addition of multifunctional acrylates or methacrylates has little effect on rates, but reduces conversions slightly compared to bulk monomer. Overall conversions are still high (>70%) with the exception of DP5/6A systems. Generally, increasing crosslinker concentration lowered final conversions. Finally, significant differences were not observed in overall conversions between diacrylate and dimethacrylates, or the mixed acrylate/methacrylate crosslinker.

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