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Synthesis and photopolymerizations of phosphate-containing acrylate/(di)methacrylate monomers from 3-(acryloyloxy)-2-hydroxypropyl methacrylate

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Summary

Novel phosphorus-containing acrylate/(di)methacrylate monomers based on 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) were prepared by two different methods. The first method involved reaction of AHM with diethylchlorophosphate to produce a phosphate-containing acrylate/methacrylate monomer followed by Michael addition of this monomer with dihexyl amine. In the second method, a hydroxyl-containing dimethacrylate monomer was prepared via Michael addition of ethanol amine to AHM followed by its reaction with diethylchlorophosphate. The photopolymerization kinetics of the synthesized monomers were investigated using a differential scanning calorimeter. It was shown that changing the monomer structure allows control of polymerization reactivity and new phosphorus-containing polymers can be obtained.

Introduction

Phosphorous-containing polymers have attracted considerable attention because of their broad application areas. Generally, polyphosphonates and polyphosphates are known as flame retardants and are used in the electrical, transportation, and construction industries.[1,2] Besides their flame-retardant properties, phosphorus derivatives are used for their adhesive properties to metals, bone and dentin.[3,4] Polymers with selective metal-binding capacity have been reported.[5,6] Phosphorus-containing monomers with phosphonic acid groups have been synthesized and used as dentin adhesives.[7,8]

Photoinitiated free radical polymerization of multifunctional monomers produces highly crosslinked networks with high thermal stability, mechanical strength and resistance to solvent absorption. Monomers that are widely used for photopolymerization are multifunctional acrylates and methacrylates.[9-20] With new monomer systems, it is important to understand the effect of monomer structure on the photopolymerization reactivities. For example, type and number of functional group, the distance and flexibility between functional groups, hydrogen bonding ability, liquid crystallinity, and the presence of heteroatoms have drastic effects on reactivities

of monomers. Various acrylates containing chlorine, oxetane, dioxolane, oxazolidone and carbonate have been evaluated in photopolymerization by Decker et al.[10] Jansen et al. investigated rate of polymerization of different acrylates in terms of hydrogen bonding capability (pendent amides, urethane and ureas) and found that such monomers exhibit polymerization rates 3-6 times higher than non-hydrogen bonding analogues (esters and carbonates).[17,18] It was suggested that the high reactivities are due to pre-organization via hydrogen bonding which brings the double bonds close to each other reducing entropy loss and increasing rates of polymerization. They also investigated the effect of monomer polarity on rates of polymerization and found a direct correlation between the maximum rate and the dipole moment of the monomer (above a certain value).[18]
In our previous articles, synthesis, polymerization and copolymerization of new phosphorus-containing monomers were investigated.[21,22] The purpose of the present research is to develop a new synthetic route to a new family of phosphate-containing crosslinkers based on commercially available AHM. The ability to incorporate multiple pendant groups suggests applications in adhesives and flame retardant formulations where high local concentrations of active groups are desired. The influence of monomer structure of these new multiphosphate-containing acrylate/(di)methacrylate on their photopolymerization behavior is described.

Experimental

3-(acryloyloxy)-2-hydroxypropylmethacrylate (AHM) was 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.
Monomer characterization involved ^{1}H and ^{13}C NMR spectroscopy (Varian Gemini 200 MHz) and FT-IR spectroscopy on thin films (Mattson 5000). Photopolymerizations were done with a TA Instruments differential photocalorimeter (DPC) with a medium pressure mercury lamp.

Synthesis of monomers

*Monomer **1***

To a mixture of AHM (1.0182 g, 4.75 mmol) and triethylamine (3.7074 g, 36.6 mmol) in 18 ml benzene in an ice bath, diethylchlorophosphate (4.9176 g, 28.5 mmol) was added dropwise under nitrogen, and the mixture was stirred at room temperature for 24 h. The solution was filtered and benzene was evaporated under reduced pressure to give a clear yellow viscous liquid. The liquid was extracted with hexane to remove unreacted diethylchlorophosphate to give crude product in 70% yield. The product was further purified by chromatography through silica and eluted with 2:1 ethyl acetate-hexane, to give pure product as a colorless liquid in 20% yield.
^{13}C NMR ($CDCl_3$): 15.96 (CH_3), 18.04 (CH_3), 61.7 (CH_2-O), 63.95 (O$\underline{C}H_2CH_3$), 64.85 (CH_2-O), 69.68 (CH-O), 126.22 ($\underline{C}H_2$=C), 127.55 ($\underline{C}H_2$=CH), 131.83 (CH_2=$\underline{C}$H), 135.46 (CH_2=$\underline{C}$), 165.30 (C=O), 166.52 (C=O) ppm.
^{1}H-NMR ($CDCl_3$): 1.29 (CH_3, 6H, t), 1.89 (CH_3, 3H, m), 4.04-4.38 (CH_2-O, CH-O, 9H, m), 5.56-6.4 (CH_2=, CH=, 5H, m) ppm.
FT-IR (neat): 2987 (C-H), 1729 (C=O), 1637 (C=C), 1295 (P=O), 1033 (P-O-Et) cm^{-1}.

*Monomer **2***

Equimolar amounts of monomer **1** (0.0987g, 0.282 mmol) and dihexyl amine (0.052 g, 0.282 mmol) were added to a small round bottom flask and the mixture was stirred at room temperature for 6 h. ^{13}C NMR spectroscopy was used to follow disappearance of acrylate peak by sampling at 2h and 6 h.

^{13}C NMR ($CDCl_3$): 13.84 (CH_3), 15.81 (CH_3), 18.01 (CH_3), 22.46 (CH_2), 26.79 (CH_2), 31.60 (CH_2, CH_2-C=O), 48.99 (CH_2-N), 53.70 (CH_2-N), 63.4 (CH_2-O), 63.5 (CH_2-O), 63.78 ($CH_3\underline{C}H_2$-O), 73.14 (CH-O), 126.25 ($\underline{C}H_2$=C), 135.44 (CH_2=$\underline{C}$), 166.4 (C=O), 172.07 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): 0.81 (CH_3, 6H, t), 1.20 (CH_2, CH_3, 22 H, m), 1.89 (CH_3, 3H, s), 2.31 (CH_2-N, 6H, m), 2.71 ($\underline{C}H_2$-C=O, 2H, t), 4.0-4.3 (CH_2-O, 9H, m), 5.56 (CH_2=, 1H, s), 6.11 (CH_2=, 1H, s) ppm.

*Monomer **3***

AHM (8.569 g, 40 mmol) and ethanol amine (1.2216 g, 20 mmol) were added to a 50 ml round bottom flask and the mixture was stirred at room temperature for 24 h using magnetic stirring. The product, ethanol amine adduct of AHM, was a colorless, clear, viscous liquid.

^{13}C NMR ($CDCl_3$): 18.16 (CH_3), 32.70 ($\underline{C}H_2$-C=O), 49.02 (CH_2-N), 55.49 (CH_2-N), 58.74 (CH_2-OH), 65.11 (CH_2-O), 65.62 (CH_2-O), 67.51 (CH-OH), 126.20 (C=$\underline{C}H_2$), 135.69 ($\underline{C}$=CH_2), 167.19 (C=O), 172.84 (C=O) ppm.

^{1}H NMR ($CDCl_3$): 1.90 (s, 6H, CH_3), 2.2- 2.9 (O=C-CH_2, N-CH_2, 10H, m), 3.5-4.3 (CH_2OH, OH, CH_2-O, 12H, m), 5.56 (s, 2H, CH_2), 6.10 (s, 2H, CH_2) ppm.

To a mixture of ethanol amine adduct of AHM (1.5496 g, 3.169 mmol) and triethylamine (6.184 g, 61.11 mmol) in 14 ml benzene in an ice bath, was added dropwise diethylchlorophosphate (8.176 g, 0.0474 mol), and the mixture was stirred at room temperature for 24 h. The solution was filtered and benzene was evaporated under reduced pressure to give a clear yellow, viscous liquid. The liquid was extracted with hexane to remove unreacted diethylchlorophosphate. The product was further purified by chromatography through silica and eluted with ethyl acetate:methanol mixtures at different concentrations to give product as a clear yellow viscous liquid in low yield (<20%).

^{13}C NMR ($CDCl_3$): 15.79 (CH_3), 18.04 (CH_3), 28.5 ($\underline{C}H_2$-C=O), 49.96 (CH_2-$\underline{C}H_2$-N), 54.02 (CH_2-N), 62.99 (CH_2-O), 64.78 ($CH_3\underline{C}H_2$O), 66.82 (CH_2-O), 73.25 (CH-O), 126.51 ($\underline{C}H_2$=C), 135.34 (CH_2=$\underline{C}$), 166.57 (C=O), 169.66 (C=O).

FT-IR (neat): 2985 (C-H), 1724 (C=O), 1637 (C=C), 1276 (P=O), 1031 (P-O-Et) cm^{-1}.

Photopolymerization

For a typical photopolymerization kinetics evaluation, approximately 3.0 mg of monomer was placed in a aluminium DSC pan. The initiator solution (Irgacure 651 in CH_2Cl_2) was added with a micro-syringe to give a final concentration of 2 mol% initiator in the monomer after evaporation of the solvent. The DSC chamber was purged with nitrogen to remove air and CH_2Cl_2 for 10 min before polymerization and purging was continued during polymerization. The sample was irradiated for 10 min at room temperature. The heat flux as a function of reaction time was monitored using DSC under isothermal conditions, and both the rate of polymerization and conversion were then calculated as a function of time. The enthalpy value of ΔH_{theor}= 13.1

kcal/mol was used as the theoretical heat evolved for methacrylate double bonds.[23] Rates of polymerization were calculated according to the following formula:

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

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

Results and Discussion

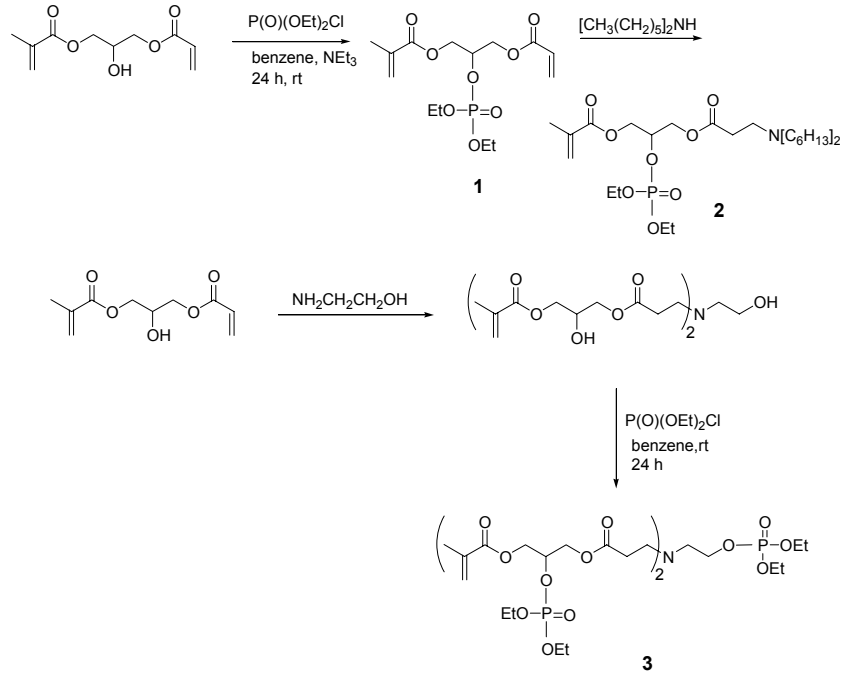
AHM is a mixed acrylate/methacrylate crosslinker containing a centered hydroxyl group. It shows faster photopolymerization rates than commercial dimethacrylate monomers, and is almost as fast as typical diacrylates. Amine Michael addition to this monomer allows us to develop new monomers and crosslinkers with different reactivities which contain a variety of additional functional groups. It is also possible to functionalize AHM and its derivatives through the pendant hydroxyl group, giving ester and ether derivatives.

The diethylphosphate derivative of AHM, monomer **1**, was synthesized by the reaction of AHM with diethylchlorophosphate in the presence of TEA as catalyst (Scheme 1). The crude product yield was 70% and purification of the monomer required chromatography. AHM consists of a mixture of two isomers in different ratios. These isomers are formed from 1,2 or 1,3 substitution reactions on glycerol (presumably acrylic acid adding to glycidyl methacrylate) giving one isomer with primary hydroxyl group (unsymmetrical glycerol substitution) and the other with a secondary hydroxyl group (symmetrical glycerol diester). Therefore, the phosphate monomer was also obtained as a mixture of two isomers in different ratios.

Figure 1 shows the ^{13}C NMR spectrum of monomer **1** together with that of AHM. The peaks at 61.04, 62.42 and 72.25 ppm in the AHM spectrum indicate the presence of a very small amount of the 1,2-glycerol diester. After the reaction, the main CH-OH peak of AHM at 68.00 ppm completely diasappeared and a new CH-O-P peak appeared at 69.68 ppm along with methyl and methylene peaks characteristic for the phosphate ester are seen at 15.96 and 63.95 ppm. The FT-IR spectrum of monomer **1** (Figure 2) showed no hydroxyl peak, confirming complete reaction of the alcohol groups.

New multifunctional materials have been reported from Michael addition of 3-aminopropyltriethoxysilane (APTES) to the acrylate functionalities of bisacrylates and mixed acrylate methacrylates such as 1,2-ethylene glycol diacrylate, ethylene glycol acrylate methacrylate, and 2-acyloyloxyethyl methacrylate.[24,25] We have synthesized a series of new hydroxylated monomers from Michael addition of ethanolamine, diethyleneglycolamine, triethyleneglycolamine, tetradecylamine, and adamantanamine with AHM.[26] Using the same approach, a new tertiary amine derivative of monomer **1** was synthesized via Michael addition of dihexyl amine to the acrylate group of monomer **1** at room temperature without any solvent and catalyst. Monomer **2** was obtained as clear, light yellow liquid. Reaction was monitored with ^{13}C NMR spectroscopy (Figure 1). The disapearance of the acrylate double bond at 127.55 and 131.83 ppm confirms clean formation of the product without any byproduct. New methylene carbon peaks at 48.99 and 53.70 ppm, a new carbonyl peak at 172.07 ppm and the methyl and methylene carbon peaks of the hexyl group at

13.84, 15.81, 22.46, 26.79, 31.60 ppm were observed in the adduct. Since both isomers in monomer **1** were present throughout the reactions and underwent Michael addition monomer **2** was also obtained as a mixture of the two isomers in different ratios. Using this method with different amine structures led to new secondary or tertiary amine and phosphate containing methacrylates (monomer **1**-**3**).



Scheme 1. Synthesis of monomers

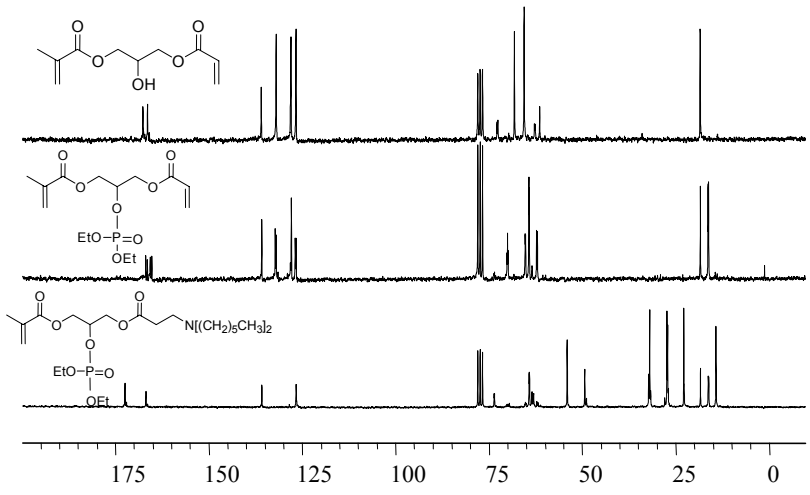


Figure 1. ^{13}C NMR spectra of AHM, monomer **1** and monomer **2**

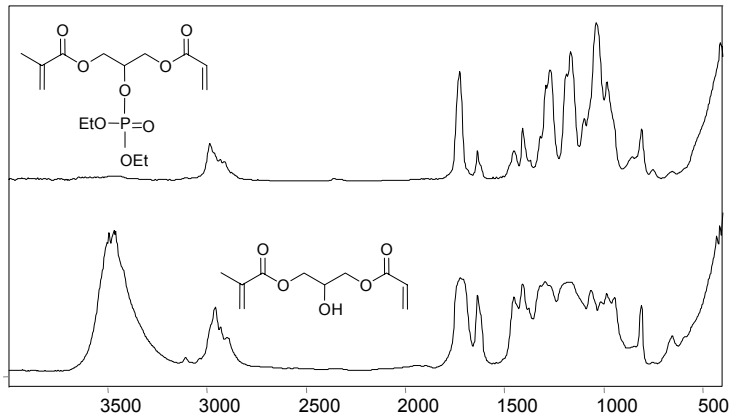


Figure 2. FTIR spectra of AHM and monomer **1**

The synthesis of monomer **3** first involved the preparation of the ethanol amine derivative of AHM as intermediate followed by its reaction with diethylchloro phosphate (Scheme 1). The intermediate dimethacrylate is a tertiary amine synthesized by the reaction between two molecules of AHM for each ethanol amine. This reaction is easy and clean, giving high yields of pure product as a clear, viscous liquid. Reaction of this intermediate with diethylchlorophosphate gave monomer **3** as viscous, yellow liquid. The advantage of this overall method is that a dimethacrylate monomer with three phosphate groups is readily obtained. The ^{13}C-NMR spectrum of this monomer shows loss of CH-OH (67.51 ppm) and CH_2OH (58.74 ppm) peaks of the intermediate and appearance of new CH-O (73.25 ppm) and phosphate ester peaks (15.79 and 64.78 ppm). The FTIR spectrum of monomer **3** (Figure 3) shows complete disappearance of the hydroxyl groups of the intermediate.

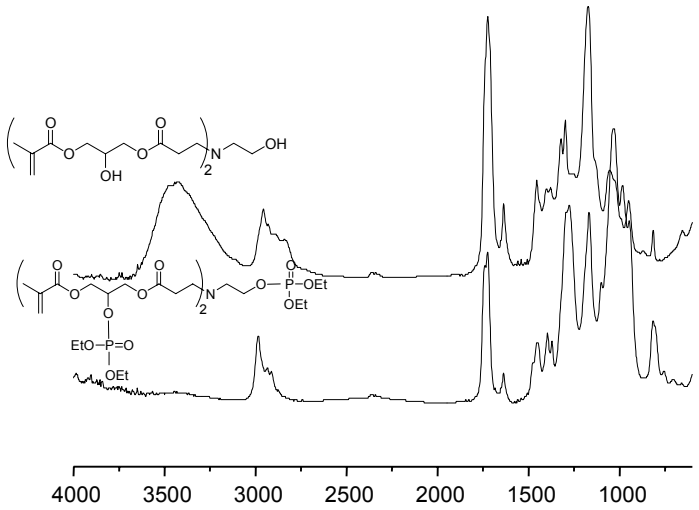


Figure 3. FTIR spectra of ethanol amine derivative of AHM and monomer **3**

Photopolymerizations of the synthesized monomers were investigated by photo DSC at room temperature using 2.0 mol-% DMPA as initiator. Figure 4 shows the polymerization rate versus time curves for monomers **1**, **2** and AHM. Monomer **1** and AHM showed similar polymerization behavior in spite of large structural differences, with the maximum rate of polymerizations of 0.061 and 0.053 s^{-1} for AHM and monomer **1**. These monomers also gave similar conversions with the values of 58 and 57%, respectively (Figure 4). Figure 4 also shows the rate and conversion versus time plots for monomer **2**. It is known that diacrylates, acrylate/methacrylates, and dimethacrylates have higher rates of polymerization than comparable monoacrylates. Thus, it is not surprising that AHM and monomer **1** also have higher rates than monomer **2**. The maximum rate of polymerization for monomer **2** was found to be 0.0144 s^{-1}. On the other hand, conversion for monomer **2** was much higher (80-82%) than those of AHM and monomer **1**. As expected, higher monomer mobility of monomethacrylate system leads to more nearly complete conversion.

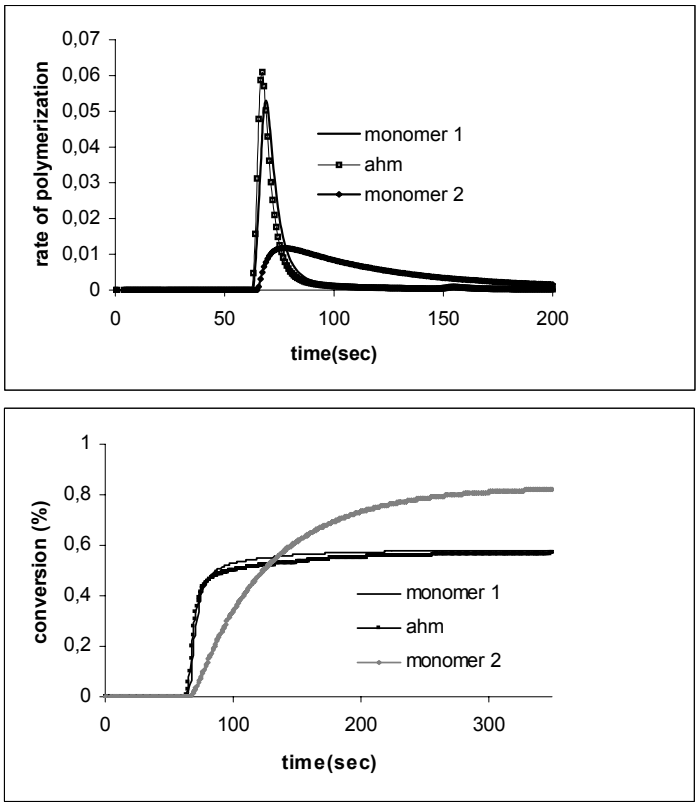


Figure 4. Rate of polymerization of AHM, monomer **1**, monomer **2** (top) and conversion-time plots of AHM, monomer **1**, monomer **2** (bottom)

Figure 5 shows rate of polymerization versus time and conversion versus time plots of the ethanol amine derivative of AHM and monomer **3**. Although the intermediate containing three hydroxyl groups is expected to have higher reactivity than non-hydrogen bonding monomer **3,** both monomers displayed the similar reactivity. The

reason for this similar reactivity is not understood at this time, but may be related to both high group polarity in both monomers. Polarity of monomer **3** (with three phosphate groups) probably compensate for the loss of hydrogen bonding character present in the intermediate (with three hydroxyl groups).
Although rates of polymerizations for monomer **3** and the intermediate are similar, a conversion of only 50% was reached for monomer **3**, whereas for the intermediate, conversion was 70%. Clearly, monomer structure also affects conversion. As the distance and flexibility between functional groups increases, the conversion increases. The reason for increased conversion may be delayed gelation. The distance between double bonds is the same for both monomer **3** and the intermediate, so the difference in flexibility between double bonds is probably not responsible for this behavior, since AHM and monomer **1** (with the same functional groups between double bonds) showed similar conversions. The hydrogen bonding capability of the intermediate may result in higher conversion versus monomer **3**. We have previously reported that the conversions of hydroxylated monomers were significantly higher (80-87%) than commercial dimethacrylate monomers such as hexanediol dimethacrylate (HDDMA) and diacrylates such as hexanediol diacrylate (HDDA) (63 and 68%), respectively. But this seems not to be the reason since AHM and monomer **1** behaved identically. The viscosity may also influence the rate of polymerization and conversion. The low conversion of monomer **3** may be due to the decreased mobility resulting from the size of the pendant phosphate groups.

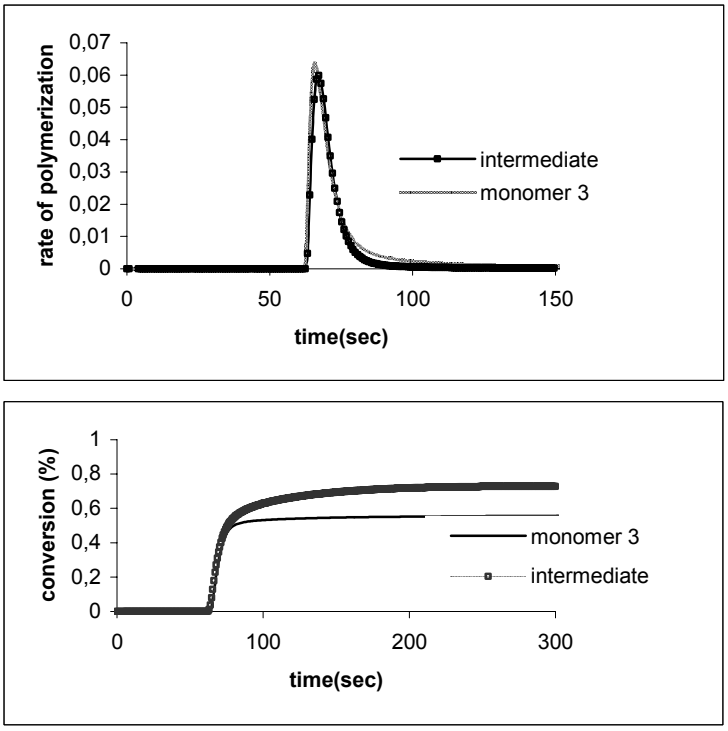


Figure 5. Rate of polymerization of the intermediate, monomer **3** (top) and conversion-time plots of the intermediate, monomer **3** (bottom)

Conclusion

It is generally known that diacrylates have higher rates of polymerization than comparable dimethacrylates. Thus, it is expected that AHM and monomer **1**, both with acrylate and methacrylate groups, should have higher reactivities than monomer **3** and the intermediate monomer containing two methacrylate double bonds. Surprisingly, the rates of polymerization of these dimethacrylates were found to be similar to acrylate/methacrylate monomers described here. Thus, we have developed a synthetic route to a new family of phosphate-containing crosslinkers based on commercially available AHM. The ability to incorporate multiple pendant groups (up to three here but more possible) suggests applications in adhesives and flame retardant formulations where high local concentrations of active groups are desired.

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