

Photopolymerization Kinetics of Tributylmethylammonium-Based (Meth)acrylate Ionic Liquids and the Effect of Water

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ABSTRACT: Polymerizable ionic liquids were synthesized from the neutralization reaction between tributylmethylammonium hydroxide and methacrylic or acrylic acid, and their photopolymerization kinetics have been determined. The acrylate monomer polymerization rate exhibited a profound dependence on the water content as follows: the monomer viscosity was a strong function of the water content, increasing substantially as the water content increased from less than 5 to 30%. For the tributylmethylammonium acrylate with less than 5% water, the viscosity was 2000 times greater than that of butyl acrylate. The high viscosity is proposed to reduce both the propagation and termination steps. Both monomers exhibited an increase in rate with temperature. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 3766–3773, 2008

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INTRODUCTION

Ionic liquids are salts with melting temperatures below the boiling point of water. They typically possess important and unusual properties such as nonvolatility, nonflammability, high ion density, and high ionic conductivity.¹ The most commonly studied systems contain ammonium, phosphonium, pyridinium, or imidazolium cations. Anions that yield useful ionic liquids include hexafluorophosphate, $[\text{PF}_6]^-$, tetrafluoroborate, $[\text{BF}_4]^-$, bis(triflyl)imide, $[\text{NTF}_2]^-$, and Cl^- .²

The synthesis, characterization, and polymerization of ionic liquid monomers was first reported in 1973.³ Since then, ionic liquids have been most commonly used in free-radical, acid-catalyzed cationic, transition-metal catalyzed, Ziegler-Natta, metathesis, and living radical polymerizations as solvents, catalysts, and plasticizers.^{1,4–8} Jiménez et al. recently examined the photopolymerization of ionic liquid monomers synthesized by the neutralization reaction between trialkylamines and (meth)acrylic acid and 2-(dimethylamino)ethylmethacrylate.⁹ They found that the ionic liquids formed from acrylic acid and methacrylic acid with trialkylamines showed only moderate increases in rate when compared with typical nonionic acrylate analogs. The ionic liquids formed from (meth)acrylic acid

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and a tertiary amine with a pendant acrylate exhibited rates typical of traditional di(meth)acrylates although the (meth)acrylates were not covalently attached to the same molecule. All of the phosphate-based ionic liquids exhibited very rapid polymerization rates and a strong dependence on the initial viscosity.

Herein, we report the synthesis, characterization, and photopolymerization kinetics of methacrylate and acrylate ionic liquid monomers based on the tributylmethylammonium moiety. A profound effect of water on the rate of polymerization of the acrylate-based ionic liquid monomer is reported.

EXPERIMENTAL

Materials

Methanol- d_4 (99.8%), tributylmethylammonium hydroxide (20.0%; solution in water), acrylic acid (>99%), methacrylic acid (>99%), butyl acrylate (>99%), and butyl methacrylate (99%) were obtained from Aldrich and used as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) were obtained from Ciba Specialty Chemicals and used as received.

Characterization

NMR spectra were recorded in methanol- d_4 on a Spectrospin-Bruker 300 MHz spectrometer. Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200-W high-pressure mercury-xenon bulb was channeled through an electric shutter and fiber optic cable in the sample chamber filled with dry air. The photopolymerizations were conducted in a cell prepared by sandwiching the samples between two sodium chloride salt plates with a thickness of $\sim 20 \mu\text{m}$. Photopolymerizations were conducted upon exposure to the UV light at intensities of 18.7 and 187 mW cm^{-2} (the light intensity was measured with an IL-1400 calibrated radiometer from International Light). Infrared absorption spectra were obtained under continuous UV irradiation at a scanning rate of 5 scans per second. 1 wt % photoinitiator (DMPA) or 2 wt % 2-hydroxy-1-4-(hydroxyethoxy)phenyl-2-

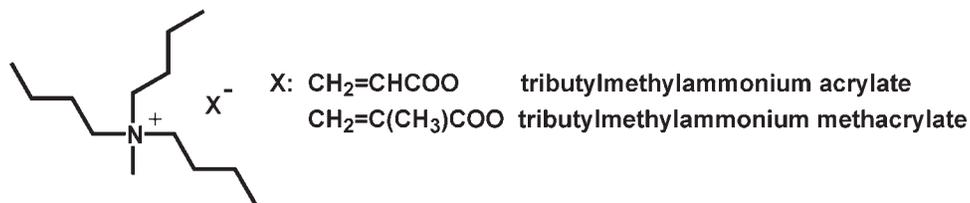
methyl-1-propanone (Irgacure 2959) were used. The characteristic infrared absorbance bands used to monitor the disappearance of the monomers during the photoreactions were as follows: acrylates (1636 and/or 812 cm^{-1}); methacrylates (1636 and/or 1007, 816 cm^{-1}); tributylmethylammonium methacrylate ionic liquid (835 cm^{-1}); tributylmethylammonium acrylate ionic liquid (990 cm^{-1}).

All polymerizations were conducted at least twice. Both ionic liquid monomer samples used in the initial polymerization were dried under vacuum at room temperature for several weeks and had less than 5 wt % water; for samples used to investigate the kinetics during drying process in Figures 3 and 4, the following scenario was used to prepare samples: the first sample, a, was not subjected to any vacuum and thus had the most water present; the second sample, b, was vacuum-dried for 1 day at room temperature; the third sample, c, was vacuum-dried for 3 days at room temperature; the fourth sample, d, was vacuum-dried for 8 days at room temperature; the final sample, e, was vacuum-dried for 2 weeks at room temperature. The wet sample in Figure 5 was dried under vacuum until it contained 12.5 wt % water based on thermogravimetric analysis, whereas the dry sample with less than 5 wt % water had been placed under vacuum at room temperature for several weeks. The reactant conversions, as calculated from the change in the peak area over time, have an approximate error of $\pm 2\%$.

Monomer Synthesis

Typically, the acid was dissolved in an equal molar amount of tributylmethylammonium hydroxide solution with stirring until the pH value of the solution reached 7.0. Diethyl ether was added to extract the ionic liquid, which was dried at room temperature under vacuum. A colorless viscous liquid was obtained. The monomer structures are shown in Scheme 1.

The characterization of each ionic liquid is given later. Additional peaks that appear in the spectra around 4.7 (1) ppm, 3.1 (5) in ^1H NMR and 48–49 (7) ppm in ^{13}C NMR correspond to the solvent (methanol- d_4). The following abbreviations are used to indicate the peak multiplicity: s, singlet; d, doublet; dd, double doublet; t, triplet; and m, multiplet.



Scheme 1. Ionic liquids from the reaction of acrylic and methacrylic acid with tributylmethylammonium hydroxide.

Tributylmethylammonium Acrylate

^1H NMR (CD_3OD , δ) 6.13 (1H, dd, $\text{H}_2\text{C}=\text{C}-\text{CO}$), 5.99 (1H, dd, $\text{H}_2\text{C}=\text{C}-\text{CO}$), 5.45 (1H, dd, $\text{C}=\text{CH}-\text{CO}$), 3.20 (6H, m, $\text{N}^+(\text{CH}_2-\text{C})_3$), 2.95 (3H, s, N^+-CH_3), 1.63 (6H, m, $\text{N}^+(\text{C}-\text{CH}_2-\text{C})_3$), 1.33 (6H, m, $\text{N}^+(\text{C}-\text{C}-\text{CH}_2-\text{C})_3$), 0.954 (9H, m, $\text{N}^+(\text{C}-\text{C}-\text{C}-\text{CH}_3)_3$). ^{13}C NMR (CD_3OD , δ) 173.2 ($-\text{O}-\text{CO}-\text{C}$), 135.8 ($\text{O}=\text{C}-\text{CH}=\text{C}$), 123.5 ($\text{O}=\text{C}-\text{CH}=\text{CH}_2$), 60.89 ($\text{N}^+(\text{CH}_2-\text{C})_3$), 47.64 (N^+-CH_3), 23.44 ($\text{N}^+(\text{C}-\text{CH}_2-\text{C})_3$), 19.15 ($\text{N}^+(\text{C}-\text{C}-\text{CH}_2-\text{C})_3$), 12.42 ($\text{N}^+(\text{C}-\text{C}-\text{C}-\text{CH}_3)_3$).

Tributylmethylammonium Methacrylate

^1H NMR (CD_3OD , δ) 5.66 (1H, m, $\text{H}_2\text{C}=\text{C}-\text{CO}$), 5.14 (1H, m, $\text{H}_2\text{C}=\text{C}-\text{CO}$), 3.21 (6H, m, $\text{N}^+(\text{CH}_2-\text{C})_3$), 2.95 (3H, s, N^+-CH_3), 1.84 (3H, t, $\text{O}=\text{C}-\text{C}-\text{CH}_3$), 1.63 (6H, m, $\text{N}^+(\text{C}-\text{CH}_2-\text{C})_3$), 1.36 (6H, m, $\text{N}^+(\text{C}-\text{C}-\text{CH}_2-\text{C})_3$), 0.957 (9H, m, $\text{N}^+(\text{C}-\text{C}-\text{C}-\text{CH}_3)_3$). ^{13}C NMR (CD_3OD , δ) 174.1 ($-\text{O}-\text{CO}-\text{C}$), 142.3 ($\text{O}=\text{C}-\text{C}=\text{C}$), 117.1 ($\text{O}=\text{C}-\text{C}=\text{CH}_2$), 59.27 ($\text{N}^+(\text{CH}_2-\text{C})_3$), 47.20 (N^+-CH_3), 22.1 ($\text{N}^+(\text{C}-\text{CH}_2-\text{C})_3$), 17.66 ($\text{N}^+(\text{C}-\text{C}-\text{CH}_2-\text{C})_3$), 17.40 ($\text{O}=\text{C}-\text{C}-\text{CH}_3$), 10.92 ($\text{N}^+(\text{C}-\text{C}-\text{C}-\text{CH}_3)_3$).

RESULTS AND DISCUSSION

Scheme 1 shows the two ionic liquid monomers synthesized by simple addition of acrylic or methacrylic acid and tributylmethylammonium hydroxide in water. Both monomers, whose NMR characterization is given in the Experimental section, were liquid at room temperature. In the next two sections, the photopolymerization rate characteristics of each ionic liquid monomer are presented. In the first section, the

basic kinetics of thoroughly dried samples are compared with the kinetics of (meth)acrylic acid and butyl ester counterparts to provide a basis for the basic interpretation of the polymerization processes of the two ionic liquid monomers. Since the synthesis of the ionic liquid monomers was carried out in aqueous solution, the final products for the initial kinetic evaluation were obtained by removing water in a vacuum oven at room temperature for several weeks. It was difficult to remove the water because we could not heat the materials lest they polymerize. In the second section, the important role of water on the polymerization rate of the ionic liquid acrylate monomer is described by measuring rates under a variety of water conditions.

Basic Photopolymerization Kinetics of Tributylmethylammonium Methacrylate and Tributylmethylammonium Acrylate

To characterize the basic polymerization kinetics of each ionic liquid monomer, photopolymerization results in Figures 1 and 2 for samples dried extensively under vacuum for several weeks were obtained at 25 and 80 °C and compared with the results obtained for the methacrylic and acrylic acid monomers from when they were synthesized. Results for the uncharged analogous monomers, butyl methacrylate and butyl acrylate photopolymerized under identical conditions are also included in Figures 1 and 2 for comparison with traditional uncharged (meth)acrylates. Examination of the polymerization rates in Table 1 taken from the initial slopes of the plots in Figures 1 and 2 indicate several important points. First, the polymerization rate for the extensively dried tributylmethylammonium acrylate ionic liquid is much lower (either at 25 or 80 °C) than the photopolymerization rate for both acrylic acid and butyl acrylate. As discussed extensively previously, the very rapid polymerization rate

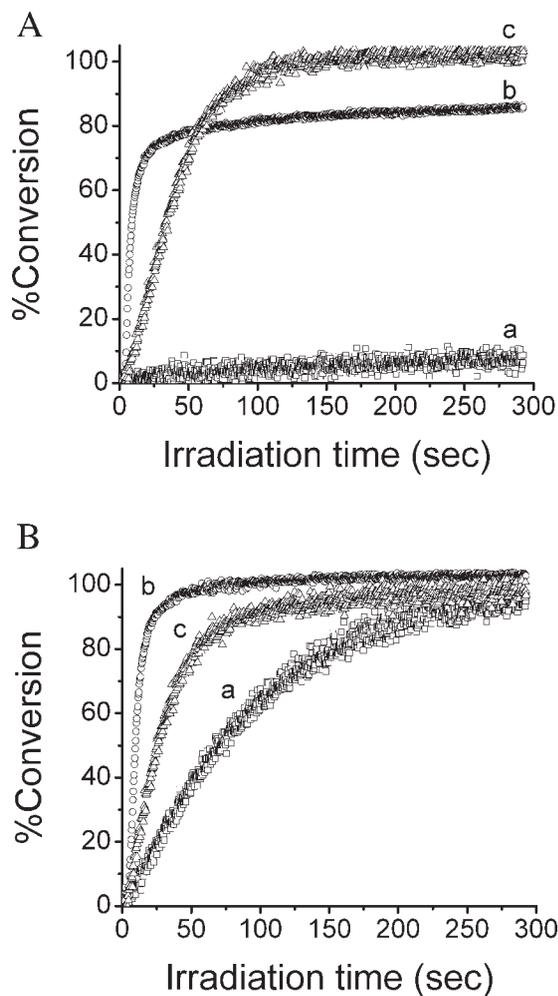


Figure 1. (A) Conversion versus time as determined via RTIR: (a) ionic liquid acrylate, (b) acrylic acid, and (c) butyl acrylate at 25 °C. Light intensity: 18.7 mW cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator. (B) Conversion versus time as determined via RTIR for (a) ionic liquid acrylate, (b) acrylic acid, and (c) butyl acrylate at 80 °C. Light intensity: 18.7 mW cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator.

for acrylic acid, which is about an order of magnitude greater than butyl acrylate and two orders of magnitude greater than tributylmethylammonium acrylate at 25 °C, is a result of extensive hydrogen bonding resulting in acrylates polymerizing as pseudo-multifunctional monomers.^{10–12} It is noted that at higher temperature, the rates of polymerization for both ionic monomers increase significantly. In contrast, the rates of polymerization for acrylic and methacrylic acid decrease or increase modestly, respec-

tively, with temperature due to reduction in hydrogen bonding as temperature increases.¹² It is speculated that the rate of polymerization of the dried tributylmethylammonium acrylate ionic liquid, which is much lower than for butyl acrylate, may result from a decrease in the propagation rate constant when compared with butyl acrylate, since tributylmethylammonium acrylate has a viscosity (2.71 Pa s) that is more than 2000 times greater than the viscosity for butyl acrylate (0.00,125 Pa s). For free-radical polymerization, we normally associate high viscosity with a high rate of polymerization

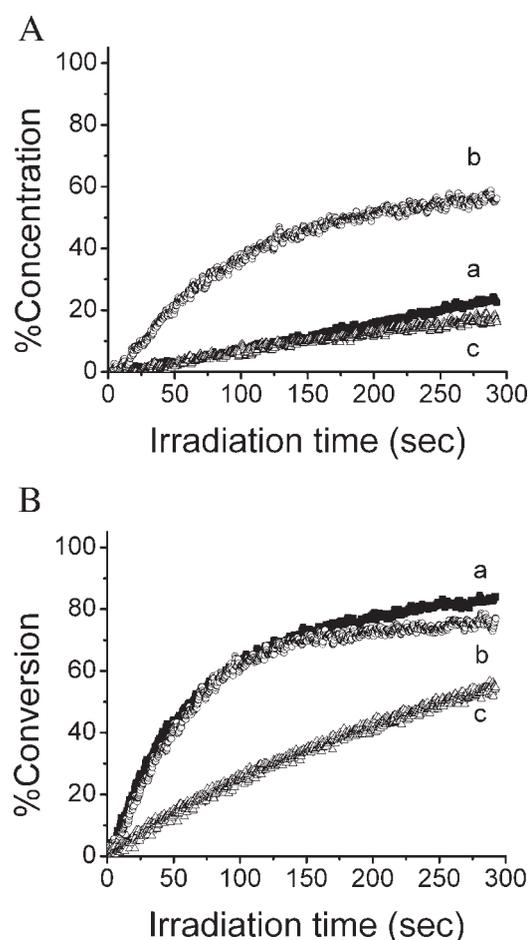


Figure 2. (A) Conversion versus time as determined via RTIR for (a) ionic liquid methacrylate, (b) methacrylic acid, and (c) butyl methacrylate at 25 °C. Light intensity: 18.7 mW cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator. (B) Conversion versus time as determined via RTIR for (a) ionic liquid methacrylate, (b) methacrylic acid, and (c) butyl methacrylate at 80 °C. Light intensity: 18.7 mW cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator.

Table 1. Maximum Photopolymerization Rates of Tributylmethylammonium (Meth)acrylates and (Meth)acrylic Acids at Different Temperatures

Compounds	Temperature (°C)	Maximum Photopolymerization Rate (s ⁻¹)
Acrylic acid	25	13.5 ± 0.5
	80	9.9 ± 0.1
Tributylmethylammonium acrylate	25	0.052 ± 0.002
	80	0.85 ± 0.09
Methacrylic acid	25	0.48 ± 0.01
	80	0.87 ± 0.03
Tributylmethylammonium methacrylate	25	0.1 ± 0.02
	80	0.87 ± 0.04
Butyl acrylate	25	1.65 ± 0.05
	80	2.25 ± 0.06
Butyl methacrylate	25	0.075 ± 0.01
	80	0.31 ± 0.03

Light intensity: 18.7 mW cm⁻² with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

because of the Norris-Trommsdorff (gel) effect.^{13,14} High viscosity reduces the rate of termination, and if the rate of the propagation reaction is also not significantly decreased, the overall rate will increase. However, if the viscosity is high enough, it is possible that the propagation step will also become diffusion controlled instead of chemically controlled. Indeed, it has been reported that the propagation rate constant for acrylate polymerization, which have rate constants about four orders of magnitude greater than traditional methacrylates, can indeed be reduced at moderately high viscosities,¹⁵ whereas for similarly structured methacrylates, the viscosity of the medium must be extremely high to result in diffusion-controlled propagation rate constants. Consequently, the rate constants for tributylmethylammonium methacrylate and butyl methacrylate at 25 and 80 °C are comparable, and in fact the rate constants for tributylmethylammonium methacrylate when consideration is given to the differences in the double bond concentration are measurably larger than for butyl methacrylate. Finally, it is also possible that the rate for the dry acrylate ionic liquid may be low due to phase separation of the polymer from the monomer. The presence of an increasing concentration of water would then result in providing a medium in which both monomer and polymer are in the same phase and hence a greater polymerization rate.

Water Effect on the Photopolymerization of Tributylmethylammonium Methacrylate and Tributylmethylammonium Acrylate

In the previous section, it was shown that the rate of polymerization for an extensively dried sample of tributylmethylammonium acrylate had a very low rate of polymerization when compared with either their acid analogs or the traditional noncharged butyl acrylate. In fact, the dry tributylmethylammonium acrylate and tributylmethylammonium methacrylate monomers exhibited essentially the same polymerization rates, quite different from results for butyl acrylate which polymerizes much faster than butyl methacrylate. One of the two explanations for these results proposed was a diffusion-controlled propagation rate constant for the highly viscous tributylmethylammonium acrylate monomer. Since ionic liquid monomers, unless extensively dried, will naturally have extensive concentrations of water present since they are highly hygroscopic, evaluation of the effect of water on both tributylmethylammonium acrylate and tributylmethylammonium methacrylate is important. Since the presence of water will lower the viscosity of ionic liquids, it might be expected that if indeed the acrylate propagation rate constant is diffusion controlled the polymerization rate of tributylmethylammonium acrylate might be expected to increase with water concentration. Tributylmethylammonium methacry-

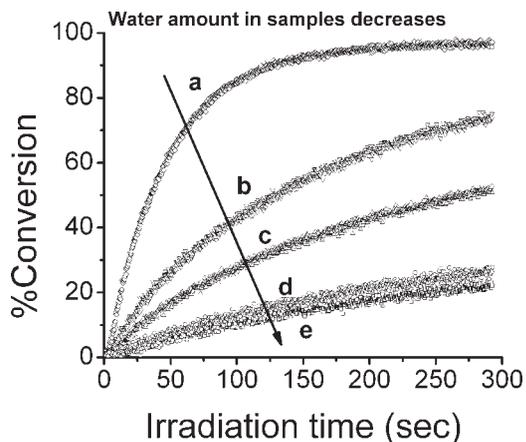


Figure 3. Conversion versus time as determined via RTIR for tributylmethylammonium acrylate at 25 °C for samples with different amounts of water. Light intensity: 18.7 mW/cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

late, with a much lower inherent chemically controlled propagation rate constant, would not be expected to show the same dependency on water. The RTIR results in Figures 3 and 4 for tributylmethylammonium acrylate clearly show that as water is removed by increasing vacuum time up to 2 weeks (see Experimental section for description of each sample), the rate decreases significantly: clearly the presence of water results in much faster rates of polymerization both at 25 and 80 °C, although the effect is most pronounced at 25 °C. The effect of water is reversible, that is, if the dried samples are

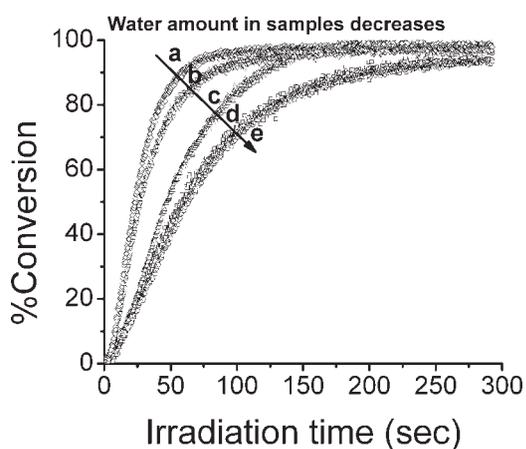


Figure 4. Conversion versus time as determined via RTIR for tributylmethylammonium acrylate at 80 °C for samples with different amounts of water. Light intensity: 18.7 mW cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

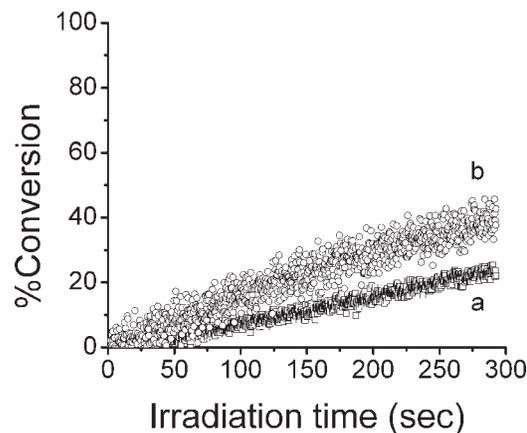


Figure 5. Conversion versus time as determined via RTIR for tributylmethylammonium methacrylate at 25 °C: (a) dry sample with less than 5 wt % and (b) wet sample with 12.5 wt % water. Light intensity: 18.7 mW/cm^{-2} with 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator.

removed from the desiccator and left for several days at ambient conditions (high humidity), the polymerization rates increase. By contrast to the results for tributylmethylammonium acrylate, tributylmethylammonium methacrylate does not show any significant effect of an increase in water concentration (Fig. 5). This is consistent with the lower inherent propagation rate constants of methacrylates, which require much higher viscosities than in the present case to render diffusion controlled propagation kinetics. It may be due to the fact that the chemically controlled propagation rate constant is almost identical to the diffusion-controlled propagation rate constant in the present system; in this case, one would not expect much effect of viscosity on the propagation rate constant.

To provide additional quantification of the effect of water on the polymerization kinetics of tributylmethylammonium acrylate, and to determine whether there is any effect of water on the photoinitiator's solubility, the polymerization rate of a tributylmethylammonium acrylate system with a more hydrophilic photoinitiator (2-hydroxy-1-4-(hydroxyethoxy)phenyl-2-methyl-1-propanone) was measured as a function of water content. As shown by the results in Figure 6 for the initial polymerization rate (determined from the initial slope of RTIR conversion time plots), upon addition of water, the rate of polymerization increased dramatically (from 0.03 s^{-1} for a sample with 5 wt % water to 4.4 s^{-1} for a sample with 25 wt % water). The polymerization

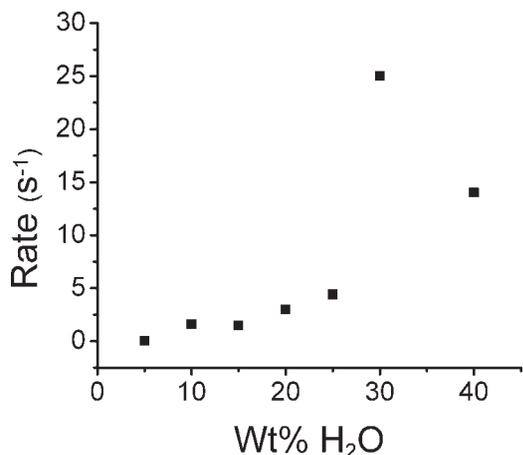


Figure 6. The rates of polymerization for tributylmethylammonium acrylate as a function of water content (error is $\pm 5\%$). Light intensity: 187 mW cm^{-2} with 2 wt % 2-hydroxy-1-4-(hydroxyethoxy)phenyl-2-methyl-1-propanone (Irgacure 2959) photoinitiator.

rate exhibits a maximum as a function of water content (Fig. 6) due to a continual decrease in the monomer concentration with increasing water concentration, which eventually reduces the inherent rate accelerating effect of water on the polymerization process. The results in Figure 6 clearly confirm the effect of water in Table 1 on enhancing the polymerization rate of tributylmethylammonium acrylate rate, and are certainly consistent with the argument for a diffusion-controlled propagation rate constant. However, it is mentioned again that the effect of water generating a media where the polymer is not phase separated is also consistent with the data.

CONCLUSIONS

Polymerizable ionic liquids were synthesized from the neutralization reaction between tributylmethylammonium hydroxide and methacrylic or acrylic acid and the polymerization kinetics is reported. The acrylate monomer polymerization rate exhibited a profound dependence on the water content, presumably due to either a diffusion-controlled propagation rate constant or a reduction in phase separation of the forming polymer. For the tributylmethylammonium acrylate with less than 5 wt % water, the viscosity was 2000 times greater than butyl acrylate. This high viscosity may reduce not only the ter-

mination rate constant, but also the propagation rate constant. Both tributylmethylammonium acrylate and tributylmethylammonium methacrylate monomers exhibited an increase in rate with temperature. The only other kinetic study for ionic liquid monomers was performed by Jiménez et al., for monomers derived from the neutralization reaction between tertiary amines and acrylic or methacrylic acid.⁹ The acrylate monomers in this report did not exhibit strong sensitivity to water content, which might be due to the fact that their viscosities were orders of magnitude lower than for tributylmethylammonium acrylate. Regardless of the exact reason for the rate increase in water, the significance of the work reported herein is then twofold. First, for hygroscopic and highly viscous ionic liquid monomers, it is essential to take into account the presence of water content when performing kinetic measurements. Because it is very difficult to dry the monomers and control the water content, the polymerization rates may appear to be irreproducible. As we have already stated, the acrylate ionic liquid monomer in this investigation polymerizes readily in a wet environment but in a very dry environment, polymerizes very slowly. This could be a problem when trying to polymerize such ionic liquid monomers in a dry climate or in a space environment where the humidity is 0%.

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