The Effect of Water on the Photopolymerization of Tributylmethylammonium-based (Meth)acrylate Ionic Liquids

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Abstract: *Ionic liquid photopolymerization in applications that have biological and environmental implications is important. Herein, polymerizable ionic liquids were synthesized from the neutralization reaction between tributylmethylammonium hydroxide and acrylic acid and their photopolymerization kinetics determined. The acrylate monomer polymerization rate exhibited a profound dependence on the water content: the monomer viscosity was a strong function of the water content, increasing substantially as the water content increased. For the tributylmethylammounium 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.*

Introduction

Ionic liquids are salts with melting temperatures below the boiling point of water. They often possess important and unusual properties such as non-volatility, non-flammability, 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, $[PF_6]^-$, tetrafluoroborate, $[BF_4]^-$, bis(trifyl)imide, $[NTF_2]^-$, and Cl^-.[2]

The synthesis, characterization and polymerization of ionic liquid monomers was first reported in 1973.[3] 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 compared to typical non ionic acrylate analogues. The ionic liquids formed from (meth)acrylic acid 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.

In this work we investigated the kinetics of photo-induced polymerization for different ionic liquid monomers based on the tributylmethylammonium moiety and the surprising effect of water on the rate of polymerization of the acrylate-based ionic liquid monomers.

Experimental

Materials

Methanol-d_4 (99.8%), tributylmethylammonium hydroxide (20.0%; Solution in water), and acrylic acid (>99%), were obtained from Aldrich and used as received. 2,2-dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemicals Corporation 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 approximately 20 μm. Photopolymerizations were conducted upon exposure to the UV light at intensities of 18.7 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 [2,2-dimethoxy-2-phenylacetophenone (DMPA)] was used in each formulation. 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}), tributylmethylammonium acrylate ionic liquid (990 cm^{-1}).

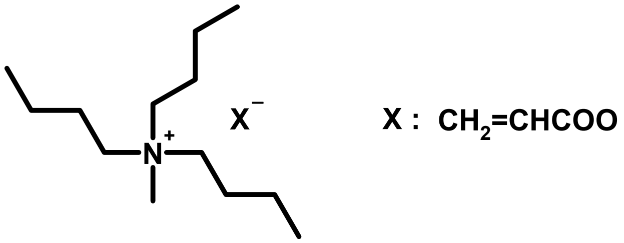
All polymerizations were conducted at least twice. All initial ionic liquid monomer samples were dried under vacuum at room temperature for several weeks and had less than 5 wt% water, except for samples that were used to investigate the kinetics during the drying process in Figures 3 (First sample, **a**, was taken after most of the water in tributylmethylammonium acrylate sample had been removed; the second sample, **b**, was taken after 3 days vacuum drying at room temperature; the last sample, **c**, was taken after 2 weeks vacuum drying at room temperature). The reactant conversions, as calculated from the change in the peak area over time, have an approximate error of ±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 in order to extract the ionic liquid, which was dried at room temperature under vacuum. A colorless, viscous liquid was obtained. The monomer structure is shown in Scheme 1. The ionic liquid was characterized by ^{1}H and ^{13}C NMR.

Results and discussion

Scheme 1 shows an ionic liquid monomer which was synthesized by simple addition of acrylic acid and tributylmethylammonium hydroxide in water.



Scheme 1. Ionic liquids from acrylic acid and tributylmethylammonium hydroxide.

Figures 1 and 2 show RTIR conversion versus time plots, the rate of polymerization for the tributylmethylammonium acrylate ionic liquid is much lower than the rate of photopolymerization for acrylic acid. This is due to the presence of hydrogen bonding between acrylic acid molecules, which is thought to increase the polymerization rate.[10-12] It is very interesting to note that in Figure 2b, at higher temperature the rate of polymerization for acrylate ionic liquid increases significantly; in contrast, the rate of polymerization for acrylic acid does not change significantly (shown in Figures 2a). This is also in agreement with previous studies: Due to hydrogen bonding, as temperature increases, the polymerization rate actually decreases (acrylic acid) with respect to what might be expected for a monomer without the capability of hydrogen bonding.[12]

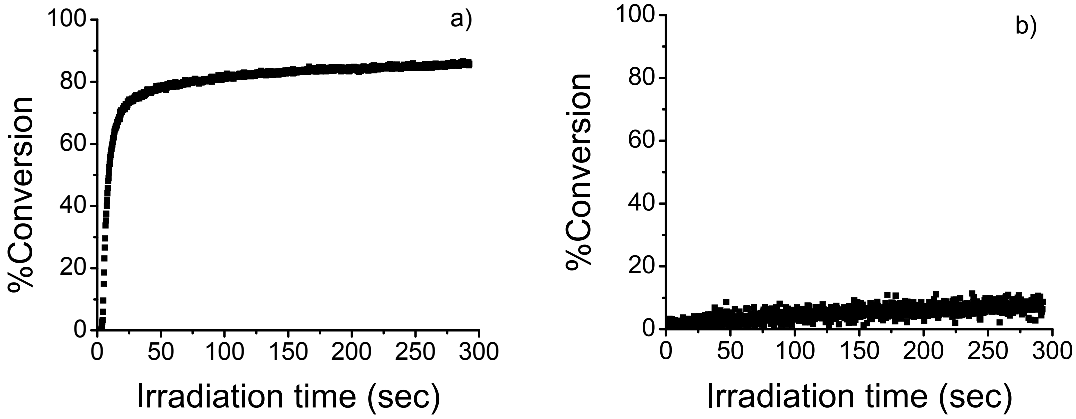


Figure 1. Conversion vs. time as determined via real-time FT-IR: (a) acrylic acid and (b) tributylmethylammonium acrylate at 25 °C. Light intensity: 18.7 mW/cm^{-2} with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator.

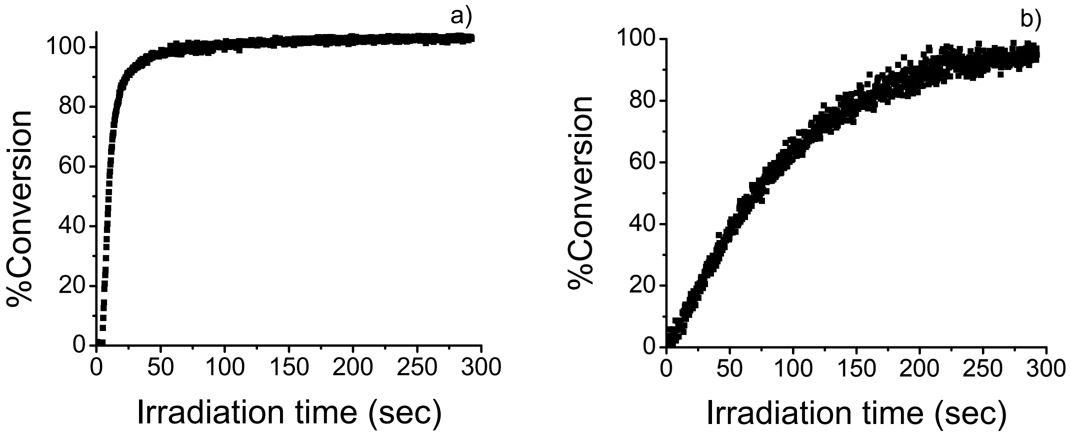


Figure 2. Conversion vs. time as determined via RTIR for acrylic (a) acid and (b) tributylmethylammonium acrylate at 80 °C. Light intensity: 18.7 mW/cm^{-2} with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator

Since the synthesis of the ionic liquid monomers was carried out in aqueous solution, the final products 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.

The rate of polymerization for the tributylmethylammonium acrylate was dramatically decreased by the removal of water (shown in Figure 3). The effect of water is reversible.

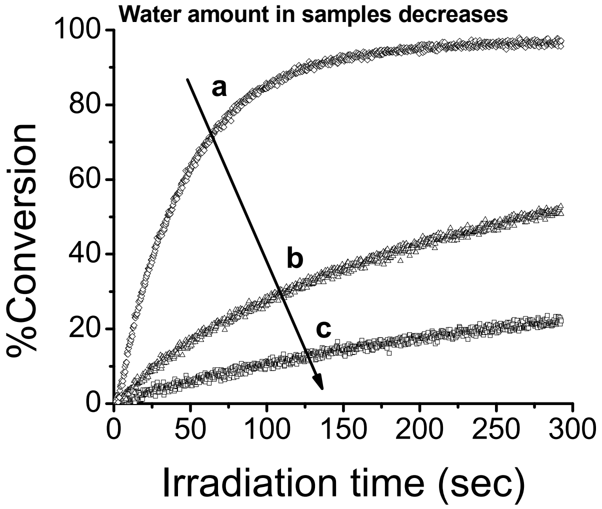


Figure 3. Conversion vs. time as determined via RTIR for tributylmethylammonium acrylate at 25 °C for samples with different amounts of water. Light intensity: 18.7 mW/cm^{-2} with 1 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator

The polymerization rate is apparently very slow for the acrylate when it has low water content because the viscosities are so high (see Figure 1b). As the water content increases, the viscosities decrease.

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] These monomers did not exhibit a strong sensitivity to the water content because their viscosities were orders of magnitude lower than the ones in the current study.

Conclusions

The significance of this work is two fold: First, for hygroscopic and viscous ionic liquid monomers, it is essential to control water content. Second, an acrylate ionic liquid monomer may polymerize readily in a wet environment, but slowly in a dry environment. The results for the methacrylic analog of the acrylic ionic liquid will be given in the presentation for comparison. Implications of ionic liquids for application in radiation curing applications will be discussed in the presentation.

Acknowledgements

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