

Properties of Difunctional Ionic Liquid Monomers and Their Polymers

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Abstract: *Ammonium based ionic liquid monomers based on ammonium-salt complexes have been synthesized and characterized. Photopolymerization of the ionic liquid monomers in the absence of solvent is fast and efficient. The resultant optically clear films have moderate hardness, absorb water from the atmosphere, and thermally decompose in a complex sequence of weight loss processes.*

Introduction

Ionic liquids are salts with melting temperatures below the boiling point of water. In general, they exhibit a wide variety of desirable properties including low or non-volatility, low flammability, high ion density, and extremely high ionic conductivity; however, those properties are not fully operational in all ionic liquids.¹

Ionic liquids have been used in free-radical, acid-catalyzed cationic, transition-metal catalyzed, Ziegler Natta, metathesis and living radical polymerizations as solvents, catalysts and plasticizers,¹⁻⁷ as well as for controlled processing of polymer materials. For instance, by introducing metal complexants in ionic liquid solutions, polymer composites with enhanced properties can be readily produced.⁸

Despite all of the extensive work on ionic liquids in recent years, the kinetics and coating properties of photocured ionic liquid monomers and their resultant polymer films have not been extensively investigated. As a consequence, we conducted an investigation of the photopolymerization of several ionic liquid monomers that are both monofunctional and *difunctional*. The *difunctional* monomers are actually held together by ionic salt complexes, and thus are not difunctional in the traditional sense. In this proceeding, we discuss only two types of *difunctional* ionic liquids as representative of an extensive investigation of ionic liquid monomers that includes other difunctional monomers as well as monofunctional ionic liquids. Herein, we report kinetic results obtained by thin-film calorimetry (TFC). Evaluation of the physical and mechanical properties of the resultant films was accomplished by thermogravimetric analysis, Persoz hardness, pencil hardness, Shore A hardness, and steel wool abrasion tests.

Experimental

Synthesis

Samples of (2-dimethylamino) ethyl acrylate (> 99 %), acrylic acid (> 99 %) and methacrylic acid (> 99 %) were purchased from Aldrich Chemical Company. Irgacure 651 was obtained from Ciba Specialty Chemicals. All reagents were used as received without further purification.

First, 7.20 mL of (2-dimethylamino)ethyl acrylate and 3.22 mL of acrylic acid were mixed with constant stirring for 15 minutes at room temperature. The structures of the ionic liquids were then confirmed by ^1H NMR and ^{13}C NMR. The same methodology was used to make the ionic liquid complex between methacrylic acid and (2-dimethylamino)ethyl acrylate.

Film Preparation

A sample of the ionic liquid with 1% of Irgacure 651 was coated (6 μm thick) onto a stainless steel plate. The film was then sealed in a chamber after being flushed with nitrogen to remove air from the sample. It was then cured by passing the chamber with the sample under a UV fusion line EPIQ 6000 (D bulb, 394.6 $\text{mJoule}/\text{cm}^2$) at a line speed of 10 m/min.

Characterization

A sample of the ionic liquid monomer with 1% of Irgacure 651 was prepared in order to study the kinetics of UV-induced polymerization by thin film calorimeter (TFC).⁹ A 25 μm film was placed between two glass plates and the exotherm recorded as a function of irradiation time. A medium pressure mercury lamp with an intensity of $\sim 32 \text{ mW}/\text{cm}^2$ was used as the lamp source.

A TA Thermogravimetric Analyzer Q500 was used to measure the thermal stability of the films (described above) over a temperature range of 35-500 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. Weight loss was recorded as a function of temperature.

Hardness properties for the films described above were obtained by using a PTC Instruments Type A Durometer, Derwent - Graphic technical graphite pencils, steel wool and a Persoz pendulum hardness tester. The steel wool test involved subjecting the sample to multiple rubs followed by a subjective evaluation. For the Persoz evaluation, the time taken for the amplitude of oscillation to decrease from 12 $^\circ$ to 4 $^\circ$ was measured.

Results and Discussion

Liquid monomer salt samples whose structures and accompanying acronyms are given in Figure 1 [(2-acrylate)ethyl dimethylammonium acrylate (2AEDMAA) and (2-acrylate) ethyl dimethylammonium methacrylate (2AEDMAM)] are yellowish liquids at room temperature with a slight odor. This is not totally unexpected since some ionic liquids, contrary to traditional expectations, have a very low vapor pressure at room temperature. We note that the ^1H and ^{13}C NMR spectra for both 2AEDMAA and 2AEDMAM are consistent with the structures in Figure 1. In the next sections, the basic photopolymerization results and a description of representative physical and mechanical properties will be given and discussed with reference to the monomer structures.

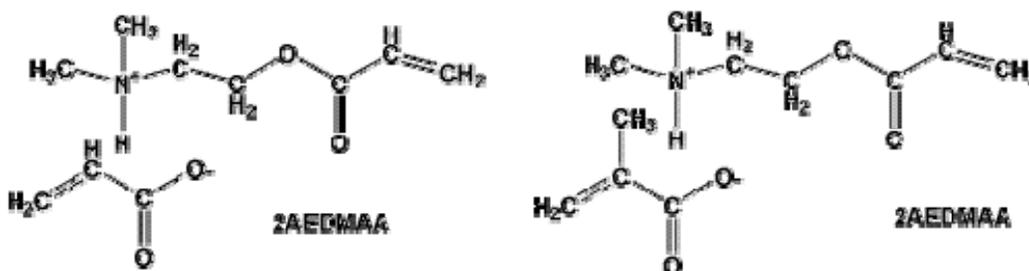


Figure 1. Ionic liquid difunctional monomers (2-acrylate)ethyl dimethylammonium acrylate [2AEDMAA] and (2-acrylate)ethyl dimethylammonium methacrylate [2AEDMAM].

Photo-Polymerization of Ionic Liquid Monomers

Figure 1 shows the photopolymerization exotherms of 2AEDMAA and 2AEDMAM: it is obvious that both readily polymerize, with the 2AEDMAM monomer attaining a lower peak maximum rate than 2AEDMAA. This is assuredly due to the combination of slower rates inherent to methacrylates as well as the lower enthalpy of reaction associated with the free-radical chain polymerization of a methacrylate functional group.¹⁰

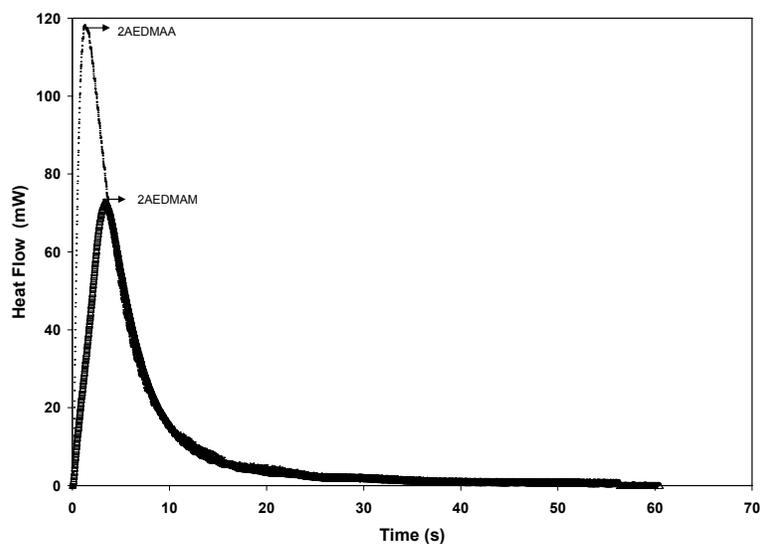


Figure 1. TFC polymerization exotherms of (2-acrylate)ethyl-dimethylammonium acrylate and methacrylate, 2AEDMAA and 2AEDMAM, respectively with a 25.5 μm of thickness. Samples with 1 % of Irgacure 651 were irradiated with a light intensity of 32 mW/cm^2 .

Film Characterization

Films were prepared in a nitrogen atmosphere to ensure that a rapid polymerization was achieved for all samples. Samples were passed for 10 times (AEDMAM) or 20 times (AEDMAA) under the Fusion lamp (see experimental) at a speed of 10 m/min to ensure that each sample was thoroughly cured and tack free. Each of the films was optically clear after photopolymerization; however, the film formed by photocuring 2AEDMAA absorbed water and became cloudy and tacky after exposure to the atmosphere for a few hours. The water could be removed by placing the sample in a vacuum. Interestingly, the photocured 2AEDMAM sample did not pick up an appreciable concentration of water presumably due to the methacrylic group, which is more hydrophobic than the acrylic group.

The films prepared as described above were subjected to a thermal scan on a conventional TGA at 10 °C/min in order to establish the degradation profile for the cured samples and any differences that may be found for the 2AEDMAA and 2AEDMAM samples. The results shown in Figure 3 for the cured 2AEDMAA and 2AEDMAM films indicate that they are not thermally stable. After losing water at approximately 100 °C, both samples show two decomposition temperature ranges with onsets of mass loss occurring at around 220 °C and 360 °C. Interestingly, the mass loss is almost complete by approximately 400 °C leaving little char for either sample. The presence of the two decomposition temperature ranges is different from traditional films formed by photocuring multifunctional polymers which exhibit only one decomposition temperature, i. e., photocured HDDA (1,6-hexanediol diacrylate) has an onset of decomposition beginning at around 350 °C under the same conditions.

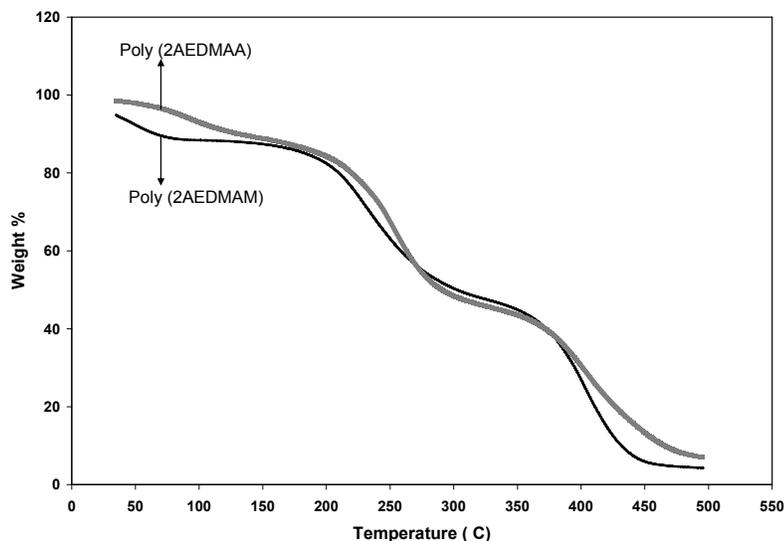


Figure 3. TGA of Poly[(2-acrylate)ethyl-dimethylammonium acrylate] and Poly[(2-acrylate)ethyl-dimethylammonium methacrylate], Poly(2AEDMAA) and Poly(2AEDMAM), respectively; at a heating rate of 10 °C/min.

Next, several tests were performed in order to attain information about the mechanical and physical properties of the photocured 2AEDMAA and 2AEDMAA films. All evaluations were

conducted on films immediately after photopolymerization in order to avoid any influence of water absorption on physical properties. The results for the Persoz hardness, Shore A hardness and pencil hardness indicate that the films were only moderately hard, and in order to be useful in many commercial applications as a cured film would need to be copolymerized with covalently linked multifunctional monomers. In accordance with the hardness tests, the films exhibited poor steel wool scratch resistance, again suggesting that commercially useful films would need to be crosslinked for many applications. However, we note that there are applications in which ion containing polymer films which can be readily removed after short service lives, and therefore it may not be necessary to add multifunctional covalent crosslinkers in all cases.

Hardness Test	Poly(2AEDMAA)	Poly(2AEDMAM)
Persoz (sec)	198	158
Shore A	92	81
Pencil	H	H
Steel Wood	1	1

Table 1. Summary of hardness tests for films obtained by photocuring 2AEDMAA and 2AEDMAM.

Conclusions

Optically clear films were produced by photopolymerization of two ionic liquid ammonium-based difunctional monomers. Potential use for ion containing polymer films as described herein and those obtained using added multifunctional monomers will be highlighted in the presentation. Also, the photoinduced frontal polymerization of ionic liquid monomers will be described.

Acknowledgements

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