Cholinium Lactate Methacrylate: Ionic Liquid Monomer for Cellulose Composites and Biocompatible Ion Gels

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Summary: Cholinium, a quaternary ammonium cation, trimethylethanol ammonium, is an essential micronutrient which supports several biological functions. In this work, a new cholinium based ionic liquid methacrylate monomer was used to process cellulose and produce optically transparent coatings through a simple photopolymerization procedure. The same monomer was also employed to manufacture biocompatible ion gels. Simply, the methacrylic monomer was photopolymerized within the ionic liquid matrix to form a gel type material.

Keywords: cellulose composites; ion-gel; ionic liquid

Introduction

Incorporation of renewable sources either as a reactive component or as a filler into polymeric systems gathered attention due to environmental concerns.[1–3] For this reason, a general trend is to develop new types of ionic liquids from renewable sources, which are also known as, bioionic liquids. It is well known that cellulose is one of the most important raw materials on earth being the structural component of plant cell walls.[1] Therefore, it is necessary to take advantage of this material by using it for different applications other than just using as a raw material for paper industry. It is well known from literature that some ionic liquids can efficiently dissolve cellulose.[4,5] Among these ionic liquids, imidazolium based ionic liquids are commonly employed due to their ability to dissolve cellulose efficiently.[4] The major drawback for these ionic liquids is their low biocompatibility and biodegradability.[6,7] Therefore, In this study, we focused on the preparation of cellulose-poly(ionic liquid) composites by using a new bioionic liquid monomer to process cellulose and subsequent photopolymerization.[8] The monomer of choice was 2-cholinium lactate methacrylate since cholinium moiety is known to have low toxicity and to be biocompatible.[9] Another potential application of this monomer consists in producing biocompatible ion gels. There are many examples in literature for the fabrication of ion gels containing different ionic liquids.[10] The ionic liquid of choice is determined by taking into account the application and the miscibility of the ionic liquid with the matrix material to have a homogeneous material in the end. Ion gels can simply be categorized into three major classes; organic gels containing polymers and gelators,[11] inorganic gels made of ceramics, carbon nanotubes or sol-gel chemistry[12] and hybrid organic-inorganic ion gels containing both organic and inorganic parts to have materials with hybrid properties.[13] The common feature of these materials is that they have an ionic liquid which is immobilized in a solid matrix. By this way, dimensional stability is given to the ionic liquid.

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Experimental Part

Ionic liquid monomer was synthesized through quaternization of commercially available 2-dimethylaminoethylmethacrylate monomer. Stoichiometrically excess 2-bromoethanol was reacted with the monomer at room temperature for 24 hours in bulk. The resulting crude product was washed with ethylacetate. The yield of quaternization was over 90%. Anion exchange reaction was performed with silver lactate to obtain the final 2-cholinium lactate methacrylate monomer. Silver bromide byproduct was removed by filtration. The desired monomer was clear viscous liquid at room temperature. The yield of the anion exchange reaction was calculated as 86%. ^{1}HNMR was used to confirm the formation of the monomers (Figure 1). Photopolymerization was conducted on a Dymax UV conveyor belt system having an iron halide lamp with a power of 900 mW/cm^2. ATR-FTIR spectra were recorded on a Nicolet iS10 FTIR Spectrometer using photopolymerized films on diamond crystal with an incident angle of 42°. 32 scans with a resolution of 4 cm^{-1} were averaged for each spectrum. The ^{1}HNMR measurement was carried out on a Bruker AC-500 instrument in deuterium oxide as the solvent.

Polymerized Ionic Liquid (PIL)-Cellulose Composites

In order to prepare the cellulose composites, different amounts (1–10 wt %) of cellulose were mixed with 2-cholinium lactate methacrylate monomer at room temperature. The resulting viscous cellulose/ionic liquid monomer solutions were formulated with a small amount of 2,2-dimethoxy-2-phenylacetophenone photoinitiator and applied onto a glass substrate by using doctor blade method. Photopolymerization was performed on the conveyor belt system. The monomer photopolymerized and led to a thin solid polymeric coating on the substrate. The

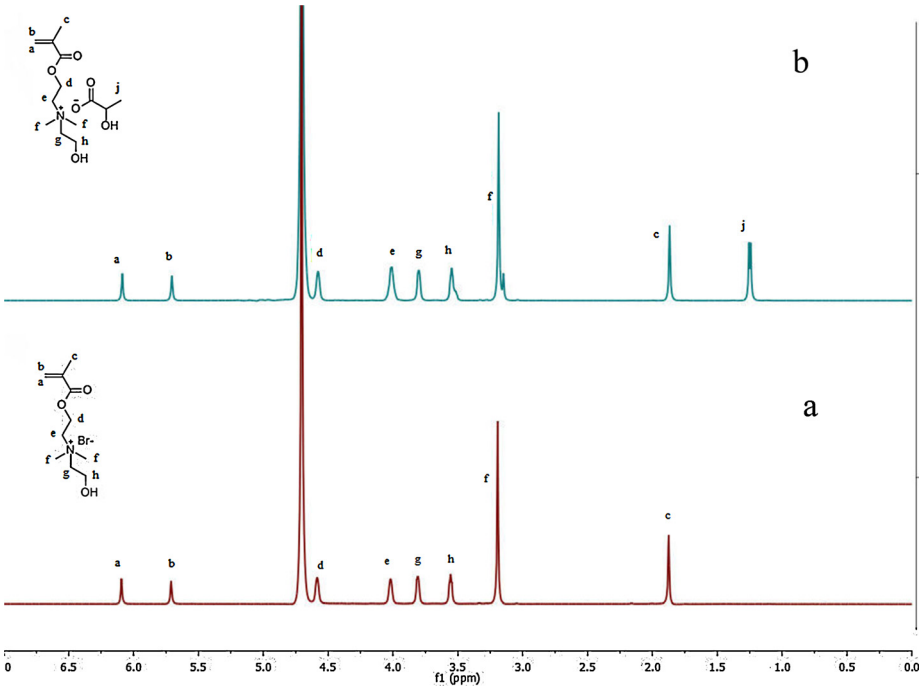

Figure 1.
^{1}HNMR spectra of ionic liquid monomers (a) before and (b) after anion exchange reactions.

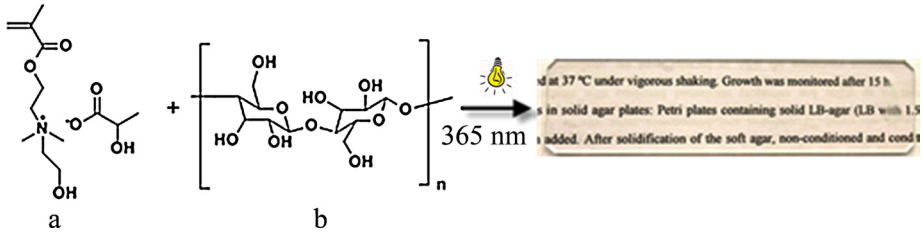

Figure 2.
2-cholinium lactate methacrylate ionic liquid monomer (a) – 5 wt% cellulose (b) and picture of the resulting composite coating produced through photopolymerization.

resulting coating with 5 wt% of cellulose is displayed in Figure 2. As it can be seen from the image, a transparent coating was obtained as a result of facile and straightforward photopolymerization process. The transparency of the coating decreased as the amount of cellulose exceeded 5 wt%.

Cholinium Based Ion Gels

In order to produce the ion gels, cholinium lactate ionic liquid was blended with the ionic liquid monomer which afterwards photopolymerized in the presence of the photoinitiator. The ion gels were designed to contain 60 wt% free ionic liquid and

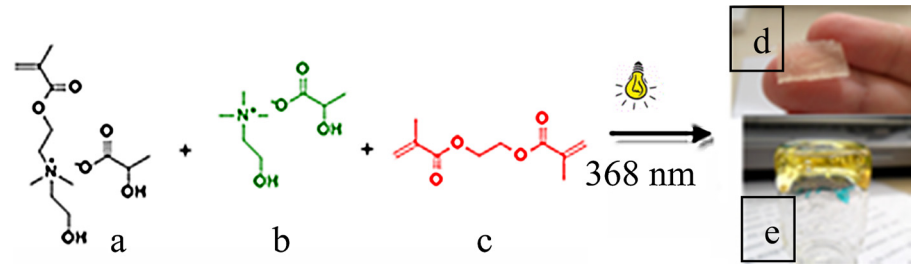

Figure 3.
Schematic representation of ion gels produced (d-with crosslinker, e-without crosslinker) with ionic liquid monomer (a), cholinium lactate ionic liquid (b) and difunctional crosslinker (c) through photopolymerization.

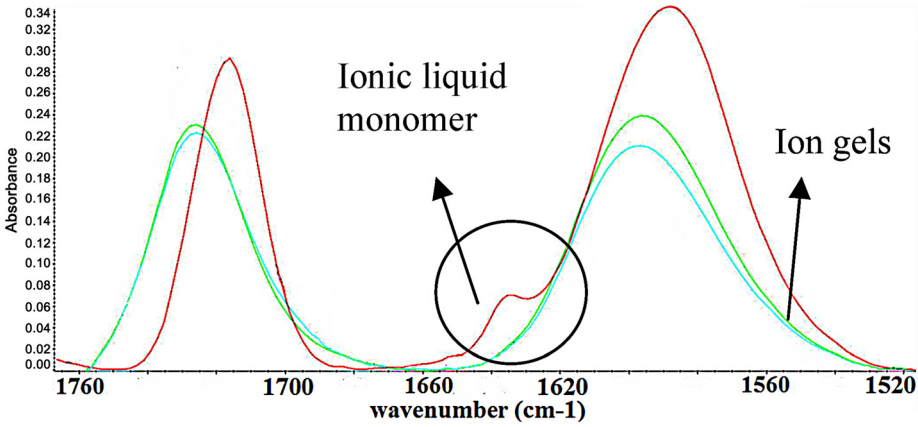

Figure 4.
ATR-FTIR spectra of the ion gels and the ionic liquid monomer (red line) in 1520–1760 cm^{-1} region.

40 wt% monomer. 4 wt% difunctional crosslinker monomer was introduced (Figure 3) to increase the integrity of the final material. The mixture of ionic liquid and monomer was adjusted as 1 gr and casted into a mold to give a film having a thickness around 0.5 mm. ATR-FTIR was used to determine the extent of photopolymerization by following the dissappearance of C=C stretching band which should be present in the monomer but not in the polymeric form. The dissappearance of C=C stretching band around 1640 cm^{-1} confirmed the conversion of the monomer to polymeric form (Figure 4).

All the ion gels produced were homogeneous, meaning that there was no phase separation between the polymer matrix and the ionic liquid after photopolymerization. While the ion- gel that is produced without the crosslinker was soft and jelly-like, the ion gel with 4 wt% difunctional crosslinker displayed better integrity as it can be seen from the Figure 4d. Ion-gels are important materials for emerging technologies and this work presents ion gels based in low toxicity cholinium ionic liquids[9] which may open their application in fields like bioelectronics.

Conclusion

A new cholinium based ionic liquid monomer was designed and used for the preparation of cellulose composites and biocompatible ion gels through fast and simple photopolymerization method. The coatings that were obtained were transparent indicating good processability of cellulose in the ionic liquid monomer. Cholinium based homogeneous ion gels were produced with the combination of cholinium lactate ionic liquid and 2-cholinium lactate methacrylate ionic liquid monomer.

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