Cholinium-Based Poly(ionic liquid)s: Synthesis, Characterization, and Application as Biocompatible Ion Gels and Cellulose Coatings

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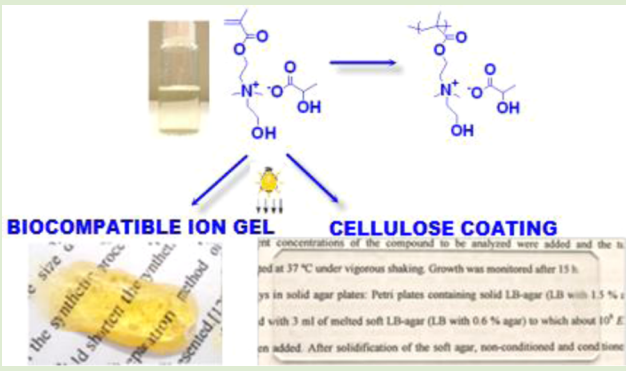[†]POLYMAT, University of the Basque Country UPV/EHU, Avda. Tolosa 72, 20018, San Sebastian, Spain
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S *Supporting Information*

ABSTRACT: Cholinium-based ionic liquid methacrylic monomers having halide, lactate and acetate counter-anions were synthesized and polymerized by using conventional free radical polymerization. The polymer properties were characterized by NMR, SEC/GPC, TGA, and DSC and compared among eight different cationic polymethacrylic analogs. Polycations with different methacrylic alkylammonium backbones having lactate anion displayed comparatively better thermal stability than those having the acetate counter-anions and they also exhibited lower glass transition temperatures than their counterparts having acetate and halide counteranions. As an application, cholinium lactate methacrylate ionic liquid monomer was used to prepare ion gels by photopolymerization. Interestingly, these are the first examples of ion gels which are fully composed of low toxicity and biocompatible cholinium ionic liquids. Furthermore, the same ionic liquid monomer, cholinium lactate methacrylate, showed the ability to dissolve cellulose. This facilitated the preparation of transparent poly(ionic liquid)/cellulose composite coatings by photopolymerization.

The properties and applications of polyelectrolytes are being extended through the introduction of new ionic moieties (cations and anions) into the polymeric backbone. These ionic moieties are easily accessible due to the enormous scientific and technological interest in the field of ionic liquids. For this reason, some of these new polyelectrolytes are being named poly(ionic liquid)s or polymeric ionic liquids (PILs).[1,2] Poly(ionic liquid)s have been finding a wide range of applications in different technological fields such as polymer electrolytes for batteries,[3] CO_2 separation membranes,[4] smart materials and functional colloids,[5,6] cellulose processing,[7] gene delivery,[8] or catalysis.[9]

Although ionic liquids were initially defined as green solvents, one of the most actual concerns regarding ionic liquids is their toxicology. It is widely accepted that among all the different types of ionic liquids some of them are toxic and some others not. As a general rule even though there is a certain contribution from the anion,[10] the toxicity of the ionic liquid is largely determined by the headgroup of the cation.[11,12] In particular, cholinium cation based ionic liquids are considered as low toxic ones and known also as bioionic liquids.[12,13] Cholinium, a quaternary ammonium cation, trimethylethanol ammonium, is an essential micronutrient

which supports several biological functions. Due to their particular features, such as biocompatibility, excellent biodegradability, and low toxicity, ionic liquids combining cholinium cation with nonhazardous anions have been used in several applications as diverse as solvents in benign extraction schemes as aqueous biphasic systems, agents for collagen-based materials, or in the pretreatment or the dissolution of biomass.[14] Taking into account all the benefits of cholinium-based ionic liquids, we propose here for the first time the synthesis of cholinium-based poly(ionic liquid)s and two examples of their potential applications.
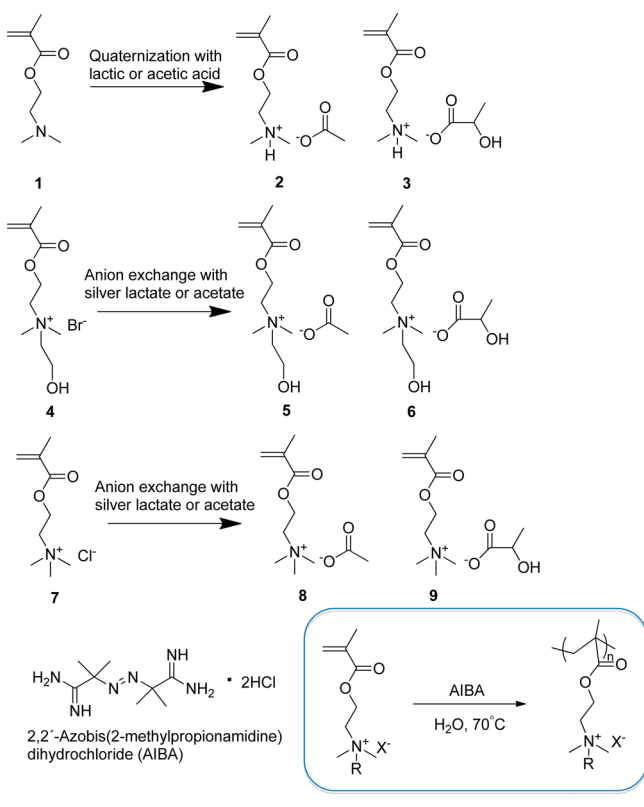
For that purpose, a series of eight different methacrylic ionic monomers were synthesized (see Supporting Information for further details). The basic chemical structure is similar to that of 2-dimethylaminoethyl methacrylate monomer (compound **1**, Scheme 1), from which after the quaternization reaction using 2-bromoethanol, the corresponding 2-cholinium bromide methacrylate was obtained (compound **4**, Scheme 1). Afterward, the 2-cholinium acetate methacrylate (compound **5**,

Scheme 1. Chemical Structures of the Monomers and the Synthetic Pathway for Their Polymerization

Table 1. Molecular and Thermal Properties of the Polymers Synthesized in This Work

polymer code	$M_n{}^a$ (kDa)	$M_w{}^b$ (kDa)	$T_{onset}{}^c$ (°C)	$T_{dec}{}^d$ (°C)	$T_g{}^e$ (°C)
1	nd^h	nd^h	138.6	387.2	19.0^f
2	405.4	485.9	163.3	327.4	9.0
3	140.8	191.8	173.8	252.4	−36.0
4	62.2	100.6	240.0	300.0	80.0
5	70.6	80.9	163.9	218.5	−26.0
6	38.8	42.3	183.9	253.7	−52.0
7	224.3	306.5	243.6	307.5	88.0
8	463.6	701.0	160.4	212.5	31.0^g
9	36.6	57.1	180.4	240.7	−50.0

^{a}Number average. ^{b}Weight average molecular weights measured by light scattering detector. ^{c}The temperature value at the point where a sharp decrease in the weight percent starts. ^{d}The temperature value at which 50% of the weight is lost. ^{e}The glass transition temperatures are taken as the temperature at the middle point of the glass transition region. ^{f}The value is taken from literature. ^{g}The glass temperature for this polymer is obtained from modulated DSC scan (Figure S15). ^{h}Not determined. Predetermined amounts of monomer, solvent (10% solid) and initiator (1 wt % wrt monomer) were mixed in the reactor and dry nitrogen was let to pass for 20 min. Then, the polymerization was conducted for 24 h at 70 °C.

Scheme 1) and the 2-cholinium lactate methacrylate (compound **6**, Scheme 1) monomers were synthesized by simple anion exchange reactions. In order to compare the properties of the prepared cholinium-based poly(ionic liquid)s with similar methacrylic ionic liquid polymers, protic ionic liquid monomers of 2-dimethylaminoethyl methacrylate having acetate and lactate counteranions were also synthesized (compounds **2** and **3**, Scheme 1), as well as the ionic monomers of 2-trimethylammoniumethyl methacrylate combining chloride, acetate, and lactate as counteranions (compounds **7**–**9**, Scheme 1). All the prepared monomers were polymerized in water to full conversions by free radical polymerization using 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (AIBA) as the radical initiator. Table 1 summarizes the molecular and thermal properties of the synthesized polymers. In all the cases, high molecular weights (50−400.000 g/mol) and polydispersity indexes (1.5−2.5) were obtained as expected by the uncontrolled solution free radical process, which provided sufficient molecular weight to characterize and compare their properties such as T_g and degradation temperature (Table 1). Although some trends can be observed among the different counteranions, such as the acetate polymers, showed higher molecular weights than the halide and lactate ones, further experiments need to be made to analyze the effect of the anion in the "free" radical polymerization process.

Thermal stabilities of the polymers were determined by thermogravimetric analysis (TGA). The resulting curves are shown in Figure 1 and the extracted data is presented in Table 1.

A three-step degradation profile was recorded for all the prepared polymers. It is well described in literature that quaternary ammonium salts decompose through Hofmann

elimination, which results in the formation of unsaturated groups and free amine.[15] Therefore, the first steps of the TGA signals can be attributed to the degradation of pendant groups on the polymer backbone. On the other hand, a thermal stability trend of poly(ionic liquid)s with different anions was observed in the order of T_{dec} halide > T_{dec} lactate > T_{dec} acetate, except for poly(2-dimethylaminoethyl methacrylate) and the quaternized analogs of the same polymer. This fact may be associated to the self-catalyzed nucleophilic attack of the anions to form the corresponding S_N2 products at high temperatures.[16] For all the polymers having lactate and acetate counteranions, similar onset, and decomposition temperatures were recorded, the decomposition temperature of poly(2-dimethylammoniumethyl acetate methacrylate) at 327 °C being the only exception.

The thermal properties of the poly(ionic liquid)s were further studied using differential scanning calorimetry (DSC; see Figure S14). All the polymers were found to be amorphous and displayed glass transition temperatures (T_g). As it can be seen from Table 1, T_gs of 80, −26, and −52 °C were obtained for poly(2-cholinium bromide methacrylate), poly(2-cholinium acetate methacrylate), and poly(2-cholinium lactate methacrylate), respectively. For 2-trimethylammonium ethyl methacrylate and 2-dimethylaminoethyl methacrylate based polymers, similar trends in the glass transition temperatures were also observed in the order of T_g chloride > T_g acetate > T_g lactate. The lowest T_gs were recorded for the polymers combining lactate as counteranions. Indeed, the lactate has the highest H-bonding ability, which weakens the electrostatic interactions between the cation and the anion, and consequently lowers the T_g of the polymer. The same explanation is also valid for poly(2-cholinium lactate methacrylate) and poly(2-cholinium acetate methacrylate), which displayed the lowest glass transition temperatures among their analogs.

As a potential application of the new poly(ionic liquid)s, we proposed the preparation of biocompatible ion gels. Ion gels are a class of gels similar to hydrogels where the ionic liquid is stabilized in a matrix instead of water.[17] In the past few years,

Figure 1. Thermogravimetric analysis (TGA) signals of the polymers showing the temperature values at 20, 50, and 90 wt % losses.

the development of ion gels received growing attention in many of the fields in which ionic liquids are being used such as electrochemical sensors, fuel cells, solar cells, separation membranes or high capacitance gate dielectrics.[18] Additionally, the use of ion gels as drug delivery agents, electrochemical transistors for biosensors, and mediums for biocatalysis also represent important emerging applications where the bio-compatibility of prepared material is indispensable.[19] Although there are several techniques described in the literature for the preparation of ion gels, all of them are based on toxic ionic liquids such as the classic imidazolium ones.[20] Ion gels can be prepared, for instance, through block copolymer gelification of ionic liquids, the gelation of ionic liquids using polymers or through the sol−gel technique.[21] In this work, we prepared ion gels by photopolymerization of the cholinium lactate methacrylic monomer inside the cholinium lactate ionic liquid.

As shown in Figure 2, two different ion gels containing 60 wt % of cholinium lactate ionic liquid and 40 wt % of cholinium lactate methacrylic monomer without and with 4 wt % ethyleneglycol dimethacrylate cross-linker were synthesized by photopolymerization. As it can be seen in Figure 2, the prepared ion gels displayed jelly like viscous properties in addition to being homogeneous and highly optically transparent. In fact, the integrity of the ion gel was significantly improved by the incorporation of the cross-linker, while its optical transparency was slightly reduced. Elastic (G') and viscous (G'') moduli of the ion gels were examined as a function of frequency (see Figure S16) at room temperature. G' and G'' values were congruent across most frequencies and near parallel indicating that the sample slightly passed the gel point for the ion gel without the cross-linker. G' became almost independent of frequency over the entire measured range and greater than G'' for the ion gel with 4 wt % difunctional cross-
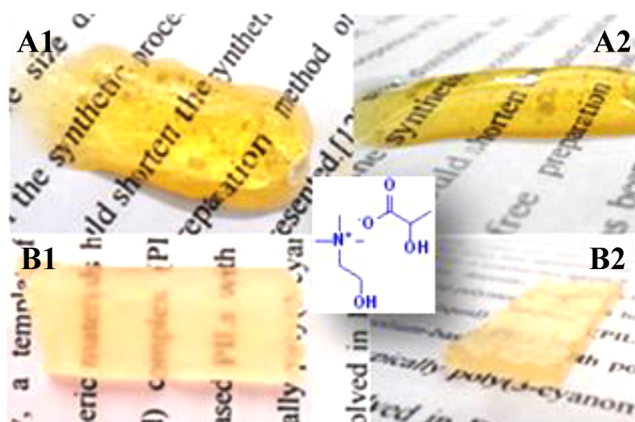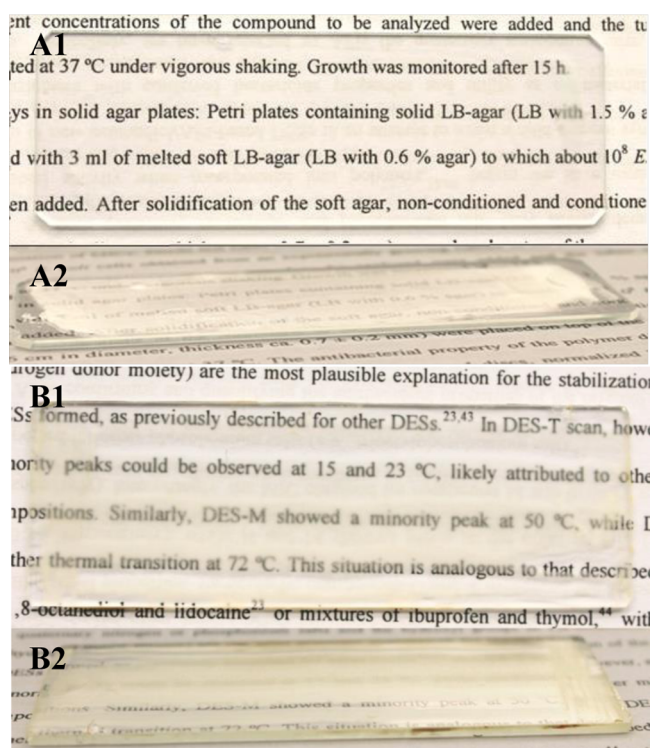

Figure 2. (A1, B1) Top view and (A2, B2) side view of ion gels prepared with mixtures containing 60 wt % of cholinium lactate ionic liquid and 40 wt % of 2-cholinium lactate methacrylate monomer (A) without and (B) with difunctional cross-linker. Molecular structure of the cholinium lactate ionic liquid is shown in the middle.

linker indicating that the sample behaves as cross-linked soft solid ion gel. To our knowledge, these are the first examples of ion gels made with low toxicity cholinium ionic liquids.

On the other hand, the same bioionic liquid monomer 2-cholinium lactate methacrylate was used to obtain poly(ionic liquid)−cellulose composites. Cellulose, the major component of plant cell walls, is undoubtedly, the most abundant biopolymer on earth and one of the most exploited natural resources.[22] During the past decade, a tremendous amount of research has been conducted regarding the dissolution of cellulose in ionic liquids. It is well-known that some ionic liquids are able to efficiently dissolve cellulose.[23] For instance, ionic liquids containing halide, carboxylate, and phosphate

anions have been shown to possess high capability to efficiently break the strong inter- and intramolecular H-bonds present in the macromolecular structure of cellulose. On the other hand, and despite the minor role of the cation, cyclic cations are known to better support the dissolution process.[24] Poly(ionic liquid)−cellulose composites have been prepared through the use of cellulose previously dissolved in mixtures of imidazolium-based ionic liquids in which one component is a polymerizable ionic liquid monomer.[25] For this application, only imidazolium-based ionic liquid monomers have been used. Therefore, in this work we focused in the preparation of poly(ionic liquid)-cellulose biocomposite coatings using 2-cholinium lactate methacrylate monomer as precursor to form the polymer matrix. The procedure applied for the biocomposite preparation was very simple and straightforward. Basically, different amounts of cellulose (5 and 10 wt %) were dissolved in 2-cholinium lactate methacrylic monomer by stirring at room temperature for 3 days. Then, the resulting solutions were applied onto glass surfaces and cured by UV light in the presence of the 2,2-dimethoxy-2-phenylacetophenone photoinitiator. The obtained coatings are shown in Figure 3.

Figure 3. (A1, B1) Top view and (A2, B2) side view of the cellulose−poly(2-cholinium lactate methacrylate) biocomposite coatings with (A) 5 wt % and (B) 10 wt % of cellulose.

Interestingly, the coating containing 5 wt % of cellulose displayed an excellent optical transparency. As it can also be seen in Figure 3, once the cellulose concentration was increased up to 10 wt %, a slight decrease in the optical transparency of the coating was observed, probably due to the limit of solubility of cellulose in the ionic liquid, which commonly is about 10%. Summary: Cholinium-based ionic liquid methacrylic monomers having halide, lactate, and acetate counteranions were prepared for the first time and successfully polymerized. Their properties were assessed and compared with the noncholinium type methacrylic analogs. Poly(ionic liquid)s having lactate as counteranion displayed relatively better thermal stability and had lower glass transition temperatures compared to those combining acetate counteranions. Moreover, cholinium lactate methacrylate monomer was used for the preparation of biocompatible ion gels containing cholinium lactate ionic liquid. To the best our knowledge, these materials are the first ion gels that are fully composed of biocompatible liquids. The same monomer was also utilized to prepare cellulose biocomposite coatings by a fast UV curing process. The hydroxyl functionality attached to the alkyl substituent of ammonium cation of the cholinium ionic liquids in combination to the lactate counteranion makes it liquid at room temperature which facilitates its applications as ion gels or cellulose composites.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed information about the materials used, procedures applied for the synthesis and characterization of the prepared monomers and poly(ionic liquid)s, and ^{1}H NMR spectra, TGA, and DSC signals. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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