Facile Incorporation of Natural Carboxylic Acids into Polymers via Polymerization of Protic Ionic Liquids

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INTRODUCTION The development of materials using products from natural and renewable resources is receiving an increased attention. The high price and future lack of fossil fuels are creating doubts about the sustainability for the actual polymer industry. For these reasons, there is a growing interest in the use of natural products for the development of polymers, which match or even improve the performance of the actual oil-based polymeric materials.[1–3] Carboxylic acids are widespread in nature and some of them such as lactic, itaconic, or fatty acids are already important raw materials for the synthesis of a number of industrial relevant polymers such as biodegradable polyesters, specialty polyamides and polyurethanes. However, there is a need for new synthetic routes for the incorporation of other natural carboxylic acids into advanced polymeric materials.

The introduction of new ionic moieties, cations and anions, coming from ionic liquids chemistry is extending the properties and classical applications of polyelectrolytes[4] to other fields such as energy,[5] supramolecular polymers,[6] gas membranes,[7] or stimuli responsive materials.[8] These new polyelectrolytes are being named polymeric ionic liquids or poly(ionic liquids) in analogy to their monomeric constituents. Poly(ionic liquids) are classically obtained by polymerization of nonprotic ionic liquid monomers. However, there is a second class of ionic liquids, named protic ionic liquids (PILs),[9–12] which have been only investigated in polymer science for the development of new polyelectrolytes and proton conducting fuel cell membranes. PILs are easily synthesized by the neutralization and subsequent proton transfer between a Brønsted acid and a base. The aim of this communication is to report the facile incorporation of natural carboxylic acids into polymers via PIL monomer chemistry and their subsequent polymerization.

EXPERIMENTAL

Materials and Methods

Acetic acid (>99.5%), butyric acid (>99.5%), hexanoic acid (>99.5%), benzoic acid (>99.5%), octanoic acid (>98%), oleic acid (puriss), 2-(dimethylamino)ethyl methacrylate (98%), 2,2′-azobis(2-methylpropionamidine) (AIBA) (97%), and 2,2′-azobis(2-methylpropionitrile (AIBN) (98%) were purchased in Aldrich and used without purification.

The ^{1}H and ^{13}C NMR measurements were carried out on a Bruker AC-500 instrument. The samples were dissolved in deuterated CDCl3, and the solutions were measured with tetramethylsilane as an internal reference. Fourier transform infrared (FTIR) measurements were conducted on a Nicolet Magna-IR 560 spectrometer. Gel permeation chromatography–size exclusion chromatography (GPC–SEC) with light-scattering detection was used to determine the molecular weight of the polymers using a water/acetonitrile (80:20) eluent with 0.25 mol/L NaCl and 0.03 mol/L NaH_2PO_4 at 25 °C and a rate of 0.8 mL/min. Water SEC was performed in a water SEC equipped with three columns (Ultrahydrogel 200, 250, and 150) and a MiniDawn Treos (Wyatt) light-scattering detector and an Optilab T-rex (Wyatt) refractive index detector. Differential scanning calorimetry (DSC) was measured in a TA Instruments Q1000 equipment. The scanning cycles consisted of a first cooling to −80 °C, then heating to 100 °C at 20 °C/min. Thermogravimetric test were measured in a TGA 2950/Q500 at 10 °/min under nitrogen from room temperature to 500 °C.

General Procedure for the Synthesis of Protic Ionic Liquid Monomers

In a typical reaction, for HDMAEMA-butyrate: 2-(dimethylamino)ethyl methacrylate (5056 g, 32 mmol) and butyric acid (2833 g, 32 mmol) were simultaneously added dropwise to a three-necked round bottom flask under vigorous stirring in

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nitrogen atmosphere. The proton transfer reaction was carried out for 30 min and the obtained 2-(dimethylammonium)ethyl methacrylate-butyrate (HDMAEMA-butyrate) PIL was characterized. ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 6.14 (s, 1H, =CH), 5.59(s, 1H, CH), 4.34(t, 2H, —COOCH$_2$, 2.82 (s, 2H, CH$_2$—N), 2.41 (s, 6H, CH$_3$N), 2.27 (t, 2H, CH$_2$—COO), 1.96 (s, 3H, CH$_3$—C=), 1.65 (m, 2H, —CH$_2$—), 0.97 (t, 3H, CH$_2$—CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 177.16, 166.37, 135.48, 125.29, 60.58, 56.30, 43.63, 36.83, 18.19, 17.66, and 13.30.

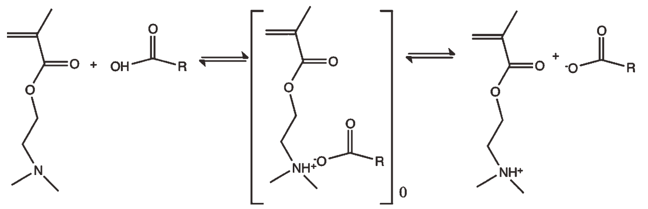
Same procedure was used for the other monomers. HDMAEMA-acetate: ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 6.12 (s, 1H, =CH), 5.58(s, 1H, CH), 4.34(t, 2H, —COOCH$_2$, 2.86 (s, 2H, CH$_2$—N), 2.44 (s, 6H, CH$_3$N), 1.99 (s, 3H, CH$_3$—C=), and 1.94 (s, 3H, —CH$_3$—COO).^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 174.82, 166.07, 135.48, 125.22, 60.21, 55.63, 21.03, and 17.39. HDMAEMA-hexanoate: ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 6.15 (s, 1H, =CH), 5.60 (s, ^{1}H, CH), 4.34 (t, 2H, —COOCH$_2$, 2.81 (s, 2H, CH$_2$—N), 2.41 (s, 6H, CH$_3$N), 2.27 (t, 2H, CH$_2$—COO), 1.96 (s, 3H, CH$_3$—C=), 1.65 (m, 2H, CO—CH$_2$—CH$_2$—), 1.34 (t, 4H, —CH$_2$—CH$_3$), and 0.90 (t, —CH3). ^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 177.16, 166.37, 135.48, 125.29, 60.58, 56.30, 43.63, 36.83, 18.19, 17.66, and 13.30.

HDMAEMA-octanoate: ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 6.15 (s, 1H, =CH), 5.60(s, 1H, CH), 4.34 (t, 2H, —COOCH$_2$, 2.81 (s, 2H, CH$_2$—N), 2.41 (s, 6H, CH$_3$N), 2.27 (t, 2H, CH$_2$—COO), 1.96 (s, 3H, CH$_3$—C=), 1.65 (m, 2H, CO—CH$_2$—CH$_2$—), 1.34 (t, 4H, —CH$_2$— CH$_3$), and 0.90 (t, —CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 177.05, 166.11, 135.36, 125.04, 60.43, 56.82, 43.45, 34.49, 30.74, 24.37, 21.75, 18.01, and 13.23. HDMAEMA-oleate: ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 6.15 (s, 1H, =CH), 5.60(s, ^{1}H, CH), 5.40 (s, 2H— CH=), 4.34 (t, 2H, —COOCH$_2$, 2.81 (s, 2H, CH$_2$—N), 2.41 (s, 6H, CH$_3$N), 2.30 (t, 2H, CH$_2$—COO), 2.08 (m, 4H, CH$_2$—CH=), 1.96 (s, 3H, CH$_3$—C=), 1.65 (m, 2H, CO—CH$_2$—CH$_2$—), 1.29 (t, 16H, —CH$_2$—), and 0.90 (t, 3 —CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 176.79, 165.93, 135.40, 129.64,124.92, 127.32, 60.42, 56.23, 43.47,34.48, 30.74, 29.13, 28.72, 28.57, 26.55, 24.96, 22.04, 17.51and 13.41.

HDMAEMA-benzoate: ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 8.07 (s, 2H, arom), 7.50 (s, 1H, arom), 7.41 (s, 2H, arom), 6.15 (s, 1H, =CH), 5.56 (s, 1H, CH), 4.44 (t, 2H, —COOCH$_2$, 3.02 (s, 2H, CH$_2$—N), 2.58 (s, 6H, CH$_3$N), and 1.94 (s, 3H, —CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$, δ ppm) 170.81, 166.05, 135.05, 133.28, 131.01, 130.79, 127.44, 122.51, 59.80, 55.90, 42.96, and 17.44.

General Procedure for Free Radical Polymerization of Protic Ionic Liquid Monomers

Methacrylic PIL monomers (HDMAEMA-acetate, HDMAEMA-butyrate, HDMAEMA-hexanoate, HDMAEMA-octanoate, HDMAEMA-benzoate, and HDMAEMA-oleate) were polymerized using conventional free radical polymerization. Typically, to a 50-mL glass reactor, monomer (HDMAEMA-hexanoate, 2 g), AIBA (0.01 g), and distilled water (40 g) were charged. The reactor was purged with N$_2$ for 30 min and then immersed in an oil bath at 70 °C for 3 h. After polymerization, the water was eliminated by evaporation in the rotavap and the polymer conversion was analyzed by ^{1}H NMR (>95% in all the cases). ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 4.11 (s, 2H, —COOCH$_2$, 2.69 (s, 2H, CH$_2$—N), 2.4–2.3 (m, 8H, CH$_3$N), 2.25–1.7(m, 2H, —CH$_2$—COO), 1.65 (m, 2H, CO—CH$_2$—CH$_2$—), 1.35–125 (m, 4H, —CH$_2$—CH$_2$—), and 1.25–0.75 (m, 6H, —CH3). GPC–SEC in water equipped with light-scattering detector gave a $M_w = 1.287 \times 10^5$ g/mol; $M_w/M_n = 1.53$.



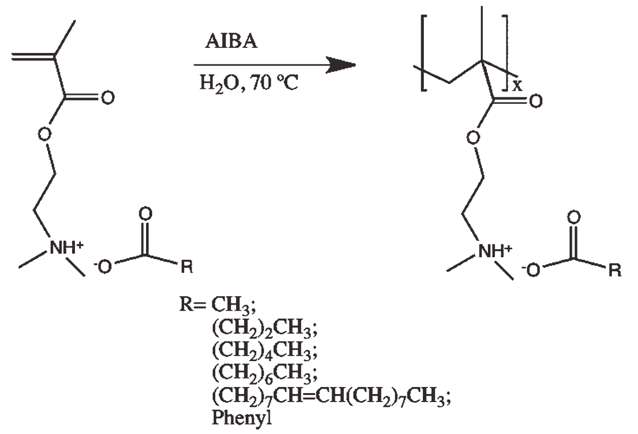
SCHEME 1 Proposed reaction for the synthesis of monomeric PILs.

General Procedure for Emulsion Polymerization of HDMAEMA-Oleate

In a typical experiment, a poly(HDAMAEMA-oleate) latex was synthesized by charging 3 g of HDMAEMA-oleate monomer, 0.006 g of surfactant Disponil A (nonionic), 0.003 g of AIBN initiator to a 100-mL glass reactor filled with 60 mL of water. The reactor was purged with N$_2$ for 30 min and then immersed in an oil bath at 70 °C for 4 h. Reaction was carried out under N$_2$ at a stirring rate of 150 rpm. After the reaction, the monomer conversion was measured by ^{1}H NMR (88%).

RESULTS AND DISCUSSION

At first, a series of PIL monomers were synthesized by reacting a methacrylic Brønsted base such as the tertiary amine, *N*-(2-(dimethylamino)ethyl) methacrylate (DMAEMA) with different carboxylic acids such as acetic acid, butyric acid, hexanoic or caproic acid, octanoic or caprylic acid, benzoic acid, and oleic acid (Scheme 1). The reactants were mixed at room temperature by simultaneous addition in an equimolar amount as neat liquids to eliminate the effects of the exothermic neutralization reactions. By this method, a series of protic ionic monomers were readily synthesized without need of purification steps. As the PILs are formed by neutralization reaction, a possible equilibrium may exist and usually the proton transfer is incomplete, resulting in the formation of neutral ion-pairs. The difference in pKa^{aq} values between the acid and the base and their chemical nature is still a matter of discussion in the ionic liquid community although a value of $\Delta pKa^{aq} > 6$ seem to be enough for full ionization. In our case, all the monomer characterizations were in good accordance to PILs formation due to the shift in the ^{1}H NMR signals associated to the methylene group near to the nitrogen atom and the methylene group near to the carboxylate together with the appearance of a new band in the carboxylate region of the FTIR (1550–1600 cm^{-1}) (Supporting information, Fig. S1).



SCHEME 2 Free radical polymerization of monomeric PILs based on DMAEMA and natural carboxylates.

Next step, polymerization of monomeric PILs was carried out using free radical polymerization conditions (Scheme 2). Although long alkyl carboxylic acids are not soluble in water, due to their ionic character all the monomers including the ones with the long alkyl carboxylates such as hexanoate (C6), octanoate (C8), or oleate (C18) solubilized in water at 5 wt % concentration. Thus, polymerizations were carried out in water at 70 °C using a water-soluble radical initiator, 2,2′-azobis(2-methylpropionamidine)dihydrochloride (AIBA). After 3 h reaction time, polymerizations proceeded in high yield (>95%) as verified by ^{1}H NMR. Water-soluble polymers were obtained in the case of poly(*N*-dimethylammonium-2-ethyl methacrylate) poly(HDMAEMA) having acetate, butyrate, hexanoate, and benzoate counter anions. In the case of poly(HDMAEMA) with octanoate and oleate counter-anions, the obtained polymers were not soluble in water.

The obtained polymers were characterized by nuclear magnetic resonance (NMR), FTIR spectroscopy, GPC–SEC, and DSC. Figure 1 shows, as an example, the ^{1}H NMR spectrum of poly(HDMAEMA-hexanoate). A signal associated to the transferred proton at 4.53 ppm and a shift in the signals associated to the methylene group near to the nitrogen atom and the methylene group close to the carboxylate indicates the protic ionic nature of the polymer. Further evidence was observed in the carboxylate region of the FTIR. Here, two bands were observed: the first one at 1722 cm^{-1} due to the ester of the polymethacrylic backbone and a second band at 1590 cm^{-1}due to the carboxylate pendant counter-anion. The polymers were also characterized by GPC–SEC using light scattering detector. The average weight molecular weights (M_w) ranged for all polymers between 1 × 10^5 and 6 × 10^5 g/mol and polydispersity values from 1.4 to 1.6 as expected for free radical polymerization in water.

Figure 2 shows the DSC curves of four of the protic ionic polymers. As expected, all the polymers are amorphous and show a decreasing glass transition depending on the carboxylate flexible chain. Whereas, poly(HDMAEMA-benzoate) has a glass transition (T_g) of 15 °C, the acetate polymer has a T_g

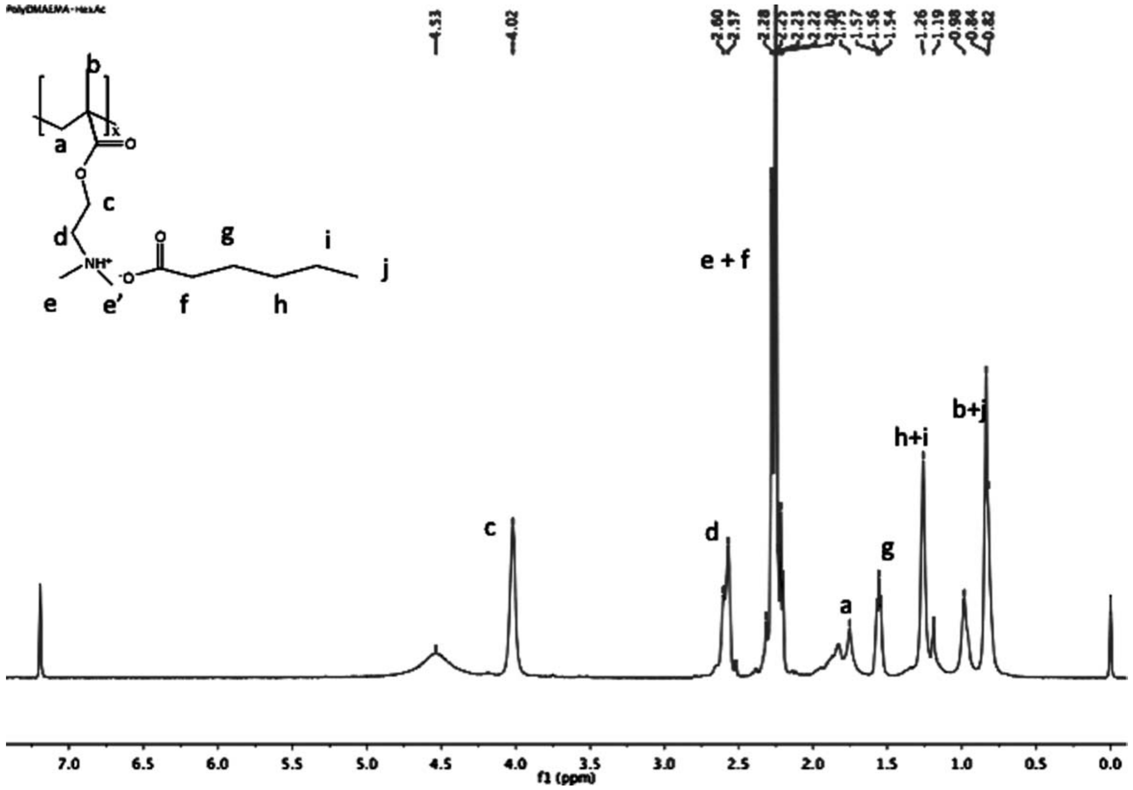


FIGURE 1 ^{1}H NMR of poly(*N*-dimethylammonium-2-ethyl methacrylate hexanoate) in $CDCl_3$.

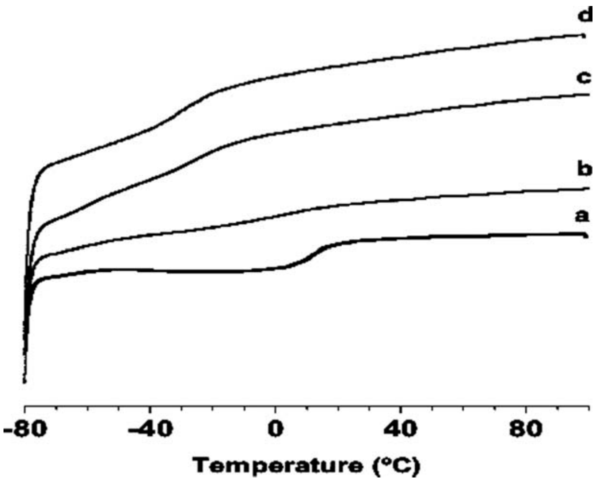


FIGURE 2 DSC thermograms (20 °C/min) of the protic ionic polymers (a) poly(HDMAEMA-benzoate), (b) poly(HDMAEMA-acetate), (c) poly(HDMAEMA-butyrate), and (d) poly(HDMAEMA-hexanoate).

of 4 °C, the butyrate a T_g of −24 °C, and the hexanoate a T_g of −34 °C. Further decreases of T_g are seen for the octanoate and oleate polymers which showed very broad transitions between −70 °C and −30 °C which made difficult to determine the exact value.

It is worth to remember that PILs are considered as intermediate compounds between fully ionic liquids, such as the widely available dialkylimidazolium salts, and molecular liquids such as hydrocarbons, alcohols, and water. For this reason, PILs are amphipathic molecules which in some cases can be miscible with polar solvents such as water and also nonpolar ones such as hexane. This property is translated into our polymers. For instance, all the protic ionic polymers are soluble in water with the exception of the poly(-HDMAEMA-octanoate) and -oleate having long alkyl carboxylates which are soluble in nonpolar solvents such as toluene, ethyl ether, and hexanes. Besides, all the polymers are soluble in solvents of intermediate polarity such as methanol and chloroform. Another consequence of the intermediate ionicity of the PILs is their lower thermal stability with respect to the nonprotic ionic liquids. This fact is translated to the thermal stability of our polymers. Here, an increase in the chain length of the carboxylic acid resulted in a decrease in the thermal decomposition temperature of the polymers. Hence, the thermal decomposition temperature at 50% weight loss (T50%) is 330 °C for the poly(HDMAEMA-acetate), 312 °C for the butyrate, 225 °C for the octanoate, and 216 °C for the oleate polymer, respectively (Supporting information, Fig. S2).

As a potential application of this monomer chemistry, the possibility of incorporating fatty acids in latexes was investigated. It is well known that the conventional emulsion polymerization of hydrophobic monomers derived from fatty acids such as oleyl or lauryl methacrylate does not proceed because of their slow migration kinetics through the aqueous phase to the polymer particles. Because of this, alternative strategies such as miniemulsion polymerization have been proposed for polymerizing fatty acid containing monomers.[13] Interestingly, our PIL monomer HDMAEMA-oleate is more hydrophilic than their fatty acids methacrylic ester equivalent. As a result, conventional emulsion polymerization could be successfully applied to the homopolymerization HDMAEMA-oleate monomer. Thus, emulsion polymerization was carried out at 70 °C under mechanical stirring and nitrogen atmosphere using Disponil A (nonionic) as emulsifier. After 3 h reaction time, a polymer latex was obtained showing a particle size of 230 nm which was already stable for more than five months. Further works are being carried out to exploit the versatility of this monomers to incorporate natural carboxylates into functional copolymer latexes obtained by emulsion polymerization.

CONCLUSIONS

In conclusion, a series of natural carboxylic acids were incorporated into polymers via simple PIL monomer chemistry and their subsequent free radical polymerization. The polymers show protic ionic characteristics including an amphipathic nature, glass transition, and thermal stability dependency in the type of carboxylate counter-anion. As a potential application, this chemistry can be used to incorporate fatty acids and other natural carboxylic acids into polymer latexes.

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