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ORIGINAL PAPER

Synthesis and characterization of polymeric ionic liquid poly(imidazolium chloride-1,3-diylbutane-1,4-diyl)

Ananda S. Amarasekara · Preethi Shanbhag

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Abstract Polymeric ionic liquid poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) with imidazolium cation groups built into the main chain was prepared using two different routes in 92–95% yield, and characterized by FT-IR, ^{1}H, ^{13}C NMR, TGA, and elemental analysis. The first method involved the heating of neat 1-(4-chlorobutyl)-1*H*-imidazole, whereas the second method involved the heating of an equimolar mixture of 1,1′-(1,4-butanediyl)-bis-imidazole and 1,4-dichlorobutane.

Keywords Ionic liquid polymer · Imidazolium cation · Addition polymerization

Introduction

Ionic liquids are well known for their unique combination of attractive properties such as negligible vapor pressure, thermal stability, nonflammability, high ionic conductivity, and wide electrochemical stability window. Currently, there is a marked interest in using ionic liquids in a number of vital research areas such as lithium–ion batteries, dye sensitized solar cells, fuel cells, electric double-layer capacitors, electrochemical devices, and actuators, in addition to the initial interest as environmentally friendly solvent systems for chemical transformations [1–6]. Ionic liquid characteristics packaged into polymeric materials would have certain advantages in this new generation of applications which require properties like ease of processability and moldability. As a fusion of ionic liquid and macromolecular properties, a new class of functional polymers known as polymeric ionic liquid (PIL) is gradually receiving attention in the last 3–4 years and several researchers have synthesized polymeric compounds with ionic liquid pendant groups attached to the main polymer structure [7–15]. These polymeric ionic liquids are generally

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A. S. Amarasekara (✉) · P. Shanbhag
Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA
e-mail: asamarasekara@pvamu.edu

synthesized by means of free radical initiator or photochemical polymerization of acrylate or alkene substituent group attached to an imidazolium or quaternary ammonium ionic liquid core structure. This class of smart polymers has already found applications in electric field actuators [7], GC stationary phases [8], anion detectors [9], lithium-polymer batteries [10], gene-delivery vectors [11], gas separation membranes [12], conducting polymer coatings [13], electrospinable polymers [14] and dye sensitized solar cells [15]. Our interests in the applications of ionic liquids in biomass processing [16–18] have led us to explore possible synthetic methods for the preparation of PILs with ionic liquid structure in the main polymer chain, rather than as a pendant group. In this communication, we report the first preparation of this class of PIL with ionic core structure units built into the main polymer chain.

Experimental

Materials and physical measurements

Imidazole, 1,4-dichlorobutane, 1-bromo-4-chlorobutane, and NaH were purchased from Aldrich Chemical Co. ^{1}H-NMR Spectra were recorded in $CDCl_3$ or in D_2O on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR were recorded in the same spectrometer operating at 100 MHz; chemical shifts were measured relative to $CDCl_3$ and converted to δ(TMS) using $\delta(CDCl_3) = 77.00$. FT-IR spectra were recorded on a JASCO-470 PLUS IR spectrometer using KBr pellets. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out in air on a TA instruments TGA 2050 system. Number average molecular weight M_n and polydispersity index (PDI) of the polymer samples were measured on a Waters gel permeation chromatography (GPC) system with Waters Styragel columns, UV detector, and using tetrahydrofuran (THF) as the solvent. Elemental analysis was performed at QTI laboratories, New Jersey.

Synthesis of 1-(4-chlorobutyl) imidazole (**2**)

To a suspension of NaH (1.20 g, 50% w/w, 25 mmol) in 25 mL of dry THF was added imidazole (1.70 g, 25 mmol) and stirred at room temperature for 1.5 h. under a nitrogen atmosphere, then 1-bromo,4-chlorobutane (4.29 g, 2.87 mL, 25 mmol) was added and stirred at room temperature for 20 h. The resulting reaction mixture was poured into 100 mL of water, extracted with methylene chloride (4 × 20 mL), combined organic layer was dried (anhydrous Na_2SO_4) and concentrated in the rotavapor using a room temperature water bath to give 1-(4-chlorobutyl) imidazole as a colorless viscous oil, 3.53 g, 89% yield. Found: C, 52.88; H, 7.21; N, 17.51%. Calc. for $C_7H_{11}N_2Cl$: C, 53.00; H, 6.99; N, 17.66%. ^{1}H NMR ($CDCl_3$) δ 1.42 (m, 2H), 1.61 (m, 2H), 3.22 (m, 2H), 3.67 (t, J = 7.0 Hz, 2H), 6.65 (s, 1H), 6.73 (s, 1H), 7.19 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 28.1, 29.1, 44.1, 45.9, 118.7, 128.9, 136.8.

Synthesis of 1,1′-(1,4-butanediyl)-bis-imidazole (**3**)

A mixture of imidazole (2.72 g, 40 mmol) and sodium hydroxide (1.60 g, 40 mmol) in 10 mL of dimethylsulfoxide was stirred at 60 °C for 1 h. Then cooled to room temperature and 1,4-dichlorobutane (2.54 g, 20 mmol) was added and stirred at room temperature for 14 h. The resulting mixture was poured into 200 mL of ice-cold water and the precipitated product was filtered, washed with cold water (3 × 20 mL), and dried to give 1,1′-(1,4-butanediyl)-bis-imidazole as a white powder, 3.58 g, 94% yield. m.p. 88–9 °C.

Found: C, 62.90; H, 7.58; N, 29.23%. Calc. for $C_{10}H_{14}N_4$: C, 63.13; H, 7.42; N, 29.45%. ^{1}H NMR ($CDCl_3$) δ 1.72 (m, 4H), 3.90 (m, 4H), 6.83 (s, 2H), 7.02 (s, 2H), 7.40 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 28.1, 46.3, 118.6, 129.8, 136.9.

Synthesis of poly(imidazolium chloride-1,3-diylbutane-1,4-diyl)(**1**)

Method 1

1-(4-Chlorobutyl)-1*H*-imidazole (**2**) (0.500 g, 3.15 mmol) was heated in a round bottom flask, under a nitrogen atmosphere, at 110 °C, for 4.0 h. using an oil bath. The product was allowed to cool to room temperature and washed with methylene chloride (3 × 3 mL) and the resulting transparent, gummy solid, was dried under vacuum at room temperature to give 0.475 g of poly(imidazolium chloride-1, 3-diylbutane-1,4-diyl), 95% yield. Found: C, 45.33; H, 7.71; N, 15.12%. Calc. for $C_7H_{11}N_2Cl$. 1.5 H_2O: C, 45.29; H, 7.60; N, 15.09%.

FT-IR and NMR (^{1}H, ^{13}C) spectra are shown in Figs. 2 and 3, respectively. TGA: decomposition onset temperature 300 °C. Degree of polymerization (DP) was calculated as 42 by end group analysis method using the following formula:

$$\mathrm{DP} - 1 = (\text{area of the } -\mathrm{CH_2} - \mathrm{N} \text{ peak at } \delta\, 4.12)/(\text{area of the } -\mathrm{CH_2} - \mathrm{Cl} \text{ end group peak at } \delta\, 3.61).$$

$$\text{GPC molecular weight determination}: M_\mathrm{n} = 7,150\,(\mathrm{DP} = 45), \text{ and polydispersity index (PDI)} = 1.45$$

Method 2

A mixture of 1,1′-(1,4-butanediyl)-bis-imidazole (**3**) (0.380 g, 2.00 mmol) and 1, 4-dichlorobutane (0.354 g, 2.00 mmol) was heated in a round bottom flask, under a nitrogen atmosphere, at 110 °C, for 6.0 h. using an oil bath. The product was allowed to cool to room temperature and washed with methylene chloride (3 × 3 mL) and the resulting transparent, gummy solid was dried under vacuum at room temperature to give 0.675 g of poly(imidazolium chloride-1,3-diylbutane-1,4-diyl), 92% yield. IR 723, 840, 1110, 1162, 1377, 1463, 1565, 1638, 2856, 2928, 3146, 3401 cm^{-1}. ^{1}H NMR (D_2O) δ 1.78(4H, bs), 4.12(4H, bs), 7.38(2H, bs), 8.71(1H, bs). ^{13}C NMR (D_2O) δ 26.1, 48.7, 122.3, and 135.3. TGA: decomposition onset temperature 305 °C, and derivative thermogravimetric curve showed only one peak at 365 °C. Degree of polymerization (DP) was calculated as 25 by end group analysis method. GPC molecular weight determination: $M_n = 4{,}600$ (DP = 29), and polydispersity index (PDI) = 1.38.

Results and discussion

Synthesis of alkylimidazolium type ionic liquids by alkylation of the second nitrogen in *N*-substituted imidazoles is a well known reaction [1, 2], and this can be accomplished by conventional heating or microwave heating [19] with or without a solvent. We have explored two different routes for the preparation of poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) (**1**) as shown in Fig. 1. The first approach involved the polymerization 1-(4-chlorobutyl)-1*H*-imidazole (**2**) under solvent free conditions. This monomer was prepared by mono alkylation of imidazole with 1-bromo-4-chlorobutane, using NaH as the base [20]. Heating the monomer **2** under a nitrogen atmosphere at 110 °C for 4 h produced the polymer, which was purified by washing with dichloromethane to remove unreacted monomer, and gave poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) (**1**) as a transparent, highly hygroscopic and water soluble gummy solid in 95% yield. The new PIL was characterized by FT-IR, ^{1}H, ^{13}C NMR, TGA, and elemental analysis.

The FT-IR spectrum of the poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) (**1**) is shown in the Fig. 2. Strong infrared absorptions characteristic of the 1,3 dialkyl imidazolium cation [21] are observed at 1565, 1463, and 1162 cm^{-1}. The broad peak at 3,401 cm^{-1} is due to the absorbed water in the sample, showing the highly hygroscopic nature of the PIL. Thermogravimetric analysis (TGA) of **1** showed decomposition onset temperature at 300 °C and the derivative thermogravimetric curve showed only one peak at 363 °C. This PIL appears to be thermally more stable than the corresponding ionic liquid monomer 1-*n*-butylmethylimidazolium chloride, in which reported [22] decomposition onset temperature is 254 °C.

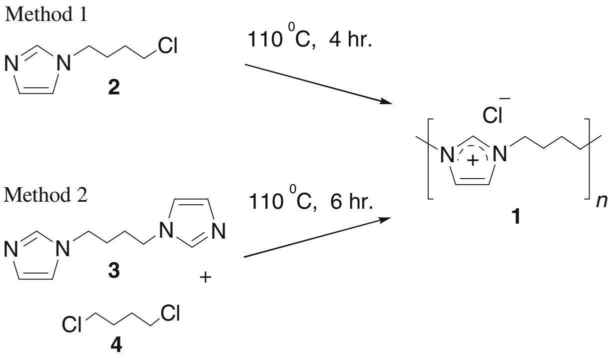

Fig. 1 Preparation of polymeric ionic liquid poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) (**1**) using two different methods

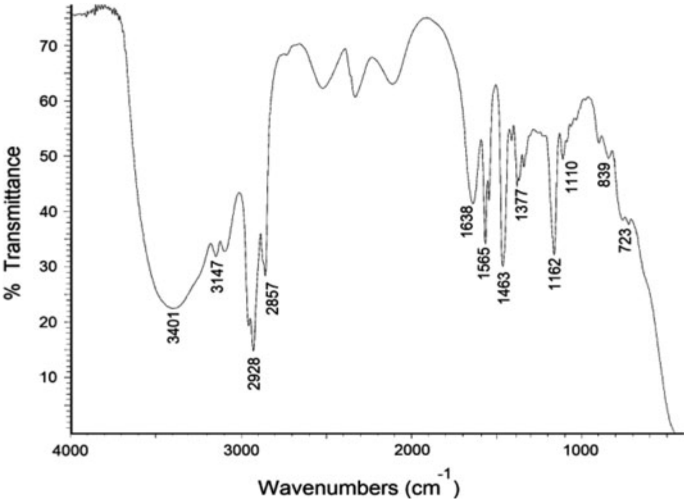

Fig. 2 FT-IR spectrum (KBr) of **1** prepared using Method 1

Proton NMR spectrum of the PIL **1**, recorded in D_2O showed four peaks at 1.79, 4.12, 7.38, and 8.72 ppm as shown in Fig. 3a. The C_2–H of the imidazolium ring appears at 8.72 ppm and the two protons at C_4 and C_5 were observed as a single peak at 7.38 ppm showing the symmetry of the imidazolium cation. ^{13}C NMR (Fig. 3b) was recorded in D_2O using a 5 s relaxation delay, and this spectrum showed four peaks at 26.1, 48.7, 122.3, and 135.1 ppm. Two low field peaks are due to the imidazolium ring, and 135.1 ppm was assigned to C_2, additionally C_4 and C_5 appeared as a single resonance at 122.3 ppm further confirming the symmetrical cation structure. Furthermore, these chemical shifts are comparable to the reported

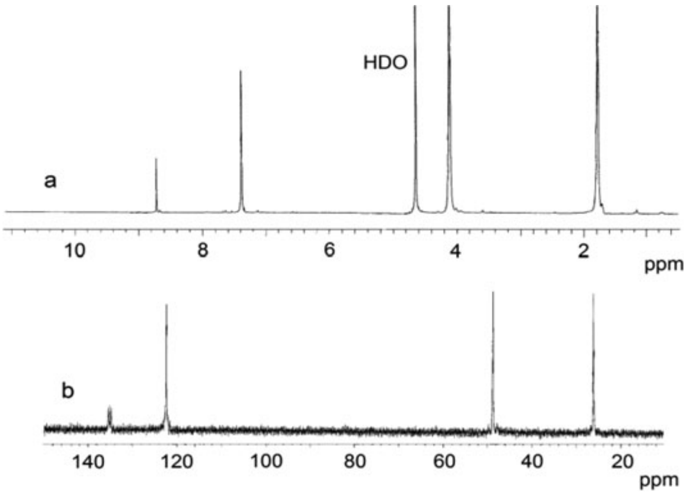

Fig. 3 ^{1}H (**a**) and ^{13}C (**b**) NMR spectrums of **1** prepared using Method 1, recorded in D_2O

NMR data of 1-*n*-butylmethylimidazolium chloride [22]. Degree of polymerization of the PIL sample from the first method was calculated as 42 by end group analysis method, using the ^{1}H NMR integration data.

Second method (Fig. 1) involved the addition polymerization of 1,1′-(1,4-butanediyl)-bis-imidazole (**3**) with 1,4-dichlorobutane. This monomer was prepared in 94% yield by condensation of two moles of imidazole with one mole of 1,4-dichlorbutane by using a modification of the known procedure [23]. In the polymerization reaction, an equimolar mixture of 1,1′-(1,4-butanediyl)-bis-imidazole (**3**) and 1,4-dichlorobutane (**4**) was heated at 110 °C for 6 h, without a solvent and the product was purified by repeated washing with dichloromethane. This product was also characterized by the same techniques used in the first preparation, and showed spectroscopic and thermogravimetric data identical to the PIL sample prepared using the first method, except the product from the second method showed relatively lower degree of polymerization.

Degree of polymerization values obtained from GPC molecular weight determinations are in reasonable agreement with the DP values calculated using end group analysis method. Polymeric ionic liquids reported earlier with ionic liquid moieties as pendant groups were prepared by free radical polymerization of acrylate monomers, and number average molecular weights in the range 18,000–300,000 were found [10, 11, 14] for these polymers. This new approach for polymeric ionic liquids gives relatively lower molecular weight polymers compared to the free radical polymerization approach.

Conclusion

We have shown that polymeric ionic liquid poly(imidazolium chloride-1,3-diylbutane-1,4-diyl) (**1**) with ionic imidazolium chloride units built into the main polymer chain can be prepared by two simple and alternative routes in excellent yields, and as far as we are aware this is the first report of this class of PILs.

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