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Ion transport properties of ionic liquid-based polyelectrolytes

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ABSTRACT

Three imidazolium-based ionic liquid monomers with polymerizable vinyl groups and the resulting polyelectrolytes have been synthesized and characterized. Particular attention was paid to the purity of the materials. Furthermore, a synthetic route via a 2-methylidene-imidazoline was used, which should be of general interest for the synthesis of polyelectrolytes with different spacer lengths between backbone and side chains. Besides comprehensive monomer and polymer analytics, electrical impedance spectroscopy was carried out to obtain information about the ion conducting properties of the three systems under investigation: P1 poly(3-ethyl-1-vinylimidazolium) bis(trifluoromethanesulfonyl)imide ($N(Tf)_2$), P2 poly(3-methyl-1-(4-vinylbenzyl)imidazolium) $N(Tf)_2$ and P3 poly(1-butyl-3-methyl-2-(4-vinylphenethyl)imidazolium)$N(Tf)_2$. The pure polymers, which are $N(Tf)_2$ anion conductors, exhibit room-temperature conductivities in the range from 10^{-11} S/cm to 10^{-8} S/cm. The anion conduction mechanism is strongly influenced by the length of the spacer group between the polymer backbone and the imidazolium cations in the side chain. In polymers P1 and P2 with short spacer groups, intra- and inter-cation hopping of the $N(Tf)_2$ anions can be distinguished below the glass transition temperature, while this is not possible in the case of polymer P3 with longer spacer groups. Furthermore, we have studied several mixtures of the best conducting polymer P2 with $LiN(Tf)_2$, zwitterions and monomeric ionic liquid. While the zwitterions were capable of compensating for the conductivity drop due to Li salt addition, the addition of monomeric IL as plasticizer leads to a considerable conductivity enhancement without a significant loss of mechanical stability.

1. Introduction

Room temperature ionic liquids (RTILs) exhibit remarkable physicochemical and electrochemical properties which are of interest for a broad range of applications. The low vapor pressure, the high chemical and electrochemical stability and the high ionic conductivity of RTILs make them promising candidates for a new generation of safe electrolytes in electrochemical cells for energy storage and conversion [1]. Currently, intense research efforts are being made to prepare RTIL-based solid, gel or polymeric electrolytes without the loss of the promising RTIL properties [2–4]. Such electrolytes have important advantages compared to liquid ones, in particular higher mechanical stability, simpler processibility and avoidance of cell leakage problems.

A straightforward method to prepare RTIL-based polymer electrolytes is the attachment of a polymerizable group to the organic cations, for instance a vinyl group. From a chemical point of view, the resulting PolyILs are closely related to the monomeric RTILs, resulting in a high miscibility of PolyILs and RTILs. Furthermore, the electrochemical window of the PolyILs should be at least as broad as that of the monomeric RTILs [5–8].

In case of the imidazolium-based RTILs, pioneering work was carried out by Ohno and co-workers. They started with 3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide $[EtViIm]N(Tf)_2$ in order to build a polycationic system [9], then switched over to polyanion-type ILs [5], copolymers [10] and poly(zwitterion)s [11]. Polycationic systems based on vinylimidazolium compounds were also investigated by Marcilla et al. [12,13] and by Vygodskii et al. [14]. Highly crosslinked derivatives have been studied by Garcia-Bernabé et al. [15] and Sans et al. [16]. Contradictory results were published on the ionic conductivity of the pure polymers, indicating that their electrical properties are highly sensitive to the amount of impurities and also to the applied polymerization technique, the latter determining the degree of polymerization and cross linking. Thus, despite the numerous imidazolium-based polyelectrolyte systems which have been synthesized, there is a lack of systematic investigations of structure–property relationships for pure and well-characterized materials. Exceptions are studies by Yoshizawa et al. and Washiro et al., who investigated radically polymerizable systems with poly(ethylene oxide) (PEO) and alkyl spacer of different lengths between polymer backbone and ionic unit [17,18].

In this study we synthesized two new and – for comparison – one well-known polymerizable imidazolium-based ionic liquids. We polymerized these RTILs and carried out comprehensive monomer and polymer analytics. By means of impedance spectroscopy, we studied anion conduction in the polymers and analyzed the influence of the cationic side chain on the anion transport mechanism. Furthermore, we prepared lithium electrolytes by adding lithium salt, zwitterions [11,19–23] and monomeric RTIL.

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2. Experimental

2.1. Materials and techniques

All reactions and manipulations were carried out under an atmosphere of purified argon using *Schlenk* techniques and an inert atmosphere glove box (MBraun MB 150 BG-I). All solvents were dried using standard procedures [24] and stored in absorption columns over Al_2O_3/molecular sieve 3 Å/R3-11G-catalyst (BASF AG). For anion exchange procedures, only high-purity Milli-Q water was used ($\sigma =$ 59 nS/cm at 25 °C). ^{1}H and ^{13}C NMR spectra were acquired on the following spectrometers: Bruker AC 300, Bruker ARX 300. Chemical shifts δ are reported in ppm relative to tetramethylsilane (TMS).

Thermogravimetric analyses were carried out using a Mettler Toledo TGA/SDTA 851^e under a constant stream of nitrogen in alumina crucibles. Dynamic scanning calorimetry measurements were carried out with a Mettler Toledo DSC 821^e under a constant stream of nitrogen in aluminum crucibles. Gel permeation chromatography (GPC) was carried out on a modified GPC unit from PSS with an UV and a refractive index detector at 30 °C. DMF was used as eluent.

2.2. Synthesis of IL monomers and polymers

In Fig. 1, the three different families of monomer-precursors are depicted. The general synthetic procedure was to first prepare an imidazolium halide followed by a salt metathesis reaction to introduce the desired $N(Tf)_2$ anion. Anion exchange prior to the polymerization reaction leads to a very low level of halide impurities. In case of 3a, a synthetic route via a 2-methylidene-imidazoline was used, which facilitates access to many similar side-chain polyelectrolytes with different spacer lengths. Because of the absence of a proton at C2, the electrochemical stability of these imidazolium derivatives is potentially enhanced. All synthesized monomers with $N(Tf)_2$ anions are room temperature ionic liquids, which could be of interest for other electrochemical applications, for instance as additives for organic lithium battery electrolytes in order to ensure the formation of stable solid electrolyte interfaces [25].

In a last step, the vinyl monomers were polymerized using radical starters like 2,2′-azobis(2-methylpropionitrile) (AIBN).

[ViEtIm]Br (1a) was synthesized in a modified way as compared to reference [9]. 2-bromoethane (2.0 mL, 25.0 mmol) was added slowly to 1-vinylimidazole (1.20 mL, 13.0 mmol) under stirring at 0 °C via a dropping funnel. The reaction mixture was stirred for 4 h at 0 °C, 15 h at 20 °C and 7 h at 35 °C. The product was obtained by filtration and subsequent washing with ethyl acetate as a crystalline colorless solid in 85% yield (2.25 g, 11.0 mmol). ^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta =$ 1.63 (t, $^3J_{HH} = 7.2$ Hz, 3 H, CH_3), 4.45 (q, $^3J_{HH} = 7.2$ Hz, 2H, CH_2), 5.40 (dd, $^2J_{HH} = 3.0$ Hz, $^3J_{HH} = 8.4$ Hz, 1H, $CH-CH_2$), 5.97 (dd, $^2J_{HH} =$ 3.0 Hz, $^3J_{HH} = 8.4$ Hz, 1H, $CH-CH_2$), 7.45 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} =$ 15.6 Hz, 1 H, $CH-CH_2$), 7.65 (br, 1H,(Im) *H*5), 7.82 (br, 1H,(Im) *H*4), 10.93 (br, 1H,(Im) *H*2) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$ 15.7 (CH_3), 45.7 (CH_2), 109.9 ($CH-CH_2$), 119.6 ((Im) *C*5), 122.8 ($CH-CH_2$), 128.3 ((Im) *C*4), 135.6 ((Im) C_2) ppm. IR (ATR) $\tilde{\upsilon}$/cm^{-1}: 591(s), 779(m), 851(m), 923(m), 975(m), 1166(s), 1257(m), 1331(m), 1455(m), 1544(m), 1654(m, C═C−*H*), 2983(m, C═C−*H*), 3053(s, C═C−*H*). ESI-MS (CH_3CN): pos.: *m*/*z* (%) = 123.0 (100) [cation]$^+$ ESI-HRMS (CH_3CN): $C_7H_{11}N_2$ [cation]$^+$ calculated: 123.0922, found: 123.0917 mp.: 101 °C.

[MeVbIm]Cl (2a) was synthesized in a modified way as compared to reference [26]. 4-vinylbenzylchloride (1.7 mL, 12.5 mmol) was added to a solution of 1-methylimidazole (1.0 mL, 12.5 mmol) in 8.0 mL of chloroform at room temperature. Subsequently, the reaction mixture was stirred over night at 50 °C. All volatiles were removed in vacuo, and the resulting yellow residue was dissolved in 10 mL of chloroform. This solution was washed with ethyl acetate and dried in vacuo, resulting in 2.66 g (11.3 mmol, 91%) product as highly viscous bright yellow liquid. ^{1}H NMR (300.1 MHz, D_2O): $\delta = 3.77$ (s, 3H, CH_3), 5.24 (s, 2H, CH_2), 5.27 (d, $^3J_{HH} = 10.8$ Hz, 1H, $CH-CH_2$), 5.80 (d, $^3J_{HH} =$ 17.1 Hz, 1H, $CH-CH_2$), 6.69 (dd, $^3J_{HH} = 10.8$ Hz, $^3J_{HH} = 17.7$ Hz, 1H, $CH-CH_2$), 7.26 (d, $^3J_{HH} = 8.1$ Hz, 2H, (Bn)), 7.33 (m, 2H, (Im) *H*5, *H*4), 7.42 (d, $^3J_{HH} = 8.1$ Hz, 2H, (Bn)), 8.72 (br, 1H, (Im) *H*2) ppm. ^{13}C NMR (75.5 MHz, D_2O): $\delta = 35.8$ (CH_3), 52.5 (CH_2), 115.4 ($CH-CH_2$), 122.1 ((Im) *C*5), 123.9 ((Im) *C*4), 123.8 ($CH-CH_2$), 126.9 (Bn*C*3, *C*5), 129.0 (Bn, *C*2, *C*6), 133.0 (Bn, *C*1), 135.8 ((Im) C_2), 138.23 (Bn, *C*4) ppm. ESI-MS (CH_3CN): pos.: *m*/*z* (%) = 199.12 (100) [cation]$^+$ ESI-HRMS (CH_3CN): $C_{13}H_{15}N_2$ [cation]$^+$ calculated: 199.1235, found: 199.1230 IR (ATR): $\tilde{\upsilon}$/cm^{-1}: 616(s), 744(m), 914(m), 993(m), 975(m), 1058(s), 1257(m), 1564(m, C═C−*H*), 3054(m, Ar−*H*).

[BMVpIm]Cl (3a) was synthesized according to the following procedure. To a stirred solution of 1-butyl-3-methyl-2-methylidene-imidazoline (1.0 g, 6.57 mmol) in 6 mL of tetrahydrofuran, 4-vinylbenzylchloride (1.08 mL, 6.57 mmol) was added dropwise at −78 °C. The reaction mixture was allowed to warm up to room temperature during a time period of 12 h. The resulting precipitate was washed with tetrahydrofuran and dried in vacuo to give [BMVpIm]Cl (1.16 g, 58%) as beige crystals. ^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta = 0.83$ (t,$^3J_{HH} = 7.2$ Hz, 3 H, CH_2-CH_3), 1.21 (m, 2H, CH_2-CH_3), 1.53 (m, 2H, $CH_2-CH_2-CH_2$), 2.95 (t, $^3J_{HH} = 6.6$ Hz, 2H, $Bn-CH_2-CH_2-Im$), 3.43 (t, $^3J_{HH} = 6.6$ Hz, 2H, $Bn-CH_2-CH_2-Im$), 3.73 (s, 3 H, $Im-CH_3$), 3.80 (t, $^3J_{HH} = 7.5$ Hz, 2H, $Im-CH_2-Pr$), 5.16 (d, $^3J_{HH} = 11.1$ Hz, 1 H, $CH-CH_{2cis}$), 5.62 (d, $^3J_{HH} = 11.1$ Hz, 1 H, $CH-CH_{2trans}$), 6.59 (dd, $^3J_{HH} = 10.8$ Hz, $^3J_{HH} = 17.4$ Hz, 1 H, $CH-CH_2$), 6.90 (d, $^3J_{HH} = 7.8$ Hz, 2H, Bn*H*5, *H*3), 7.23 (d, $^3J_{HH} = 7.8$ Hz, 2H, Bn*H*2, *H*6), 7.46 (br, 1 H, Im*H*5), 7.83 (br, 1 H, Im*H*4) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 13.3$ (CH_2-CH_3), 19.6 (CH_2-CH_3), 26.0 ($Bn-CH_2-CH_2-Im$), 31.7 ($CH_2-CH_2-CH_3$), 32.9 ($Im-CH_3$), 35.7 ($Bn-CH_2-CH_2-Im$), 48.1 ($Im-CH_2-Pr$), 114.3 ($CH-CH_2$), 121.0 (Im*C*5), 123.9 (Im*C*4), 126.8 (Bn*C*2, *C*6), 128.7 (Bn, *C*3, *C*5), 135.8 ($CH-CH_2$), 136.7(Bn, *C*4), 137.3 (Bn, *C*1), 145.3 (ImC_2) ppm. IR (ATR): $\tilde{\upsilon}$/cm^{-1}: 494(s), 822(s), 1118(m), 1178(m), 1462(s), 1526(s,C═C−*H*), 2896(m), 2957(m), 3024(s, Ar−*H*) ESI-MS (CH_3CN): pos.: *m*/*z* (%) = 269.20 (100) [cation]$^+$ ESI-HRMS (CH_3CN): $C_{18}H_{25}N_2$ [cation]$^+$ calculated: 269.2018, found: 269.2012, decomp.: 190 °C.

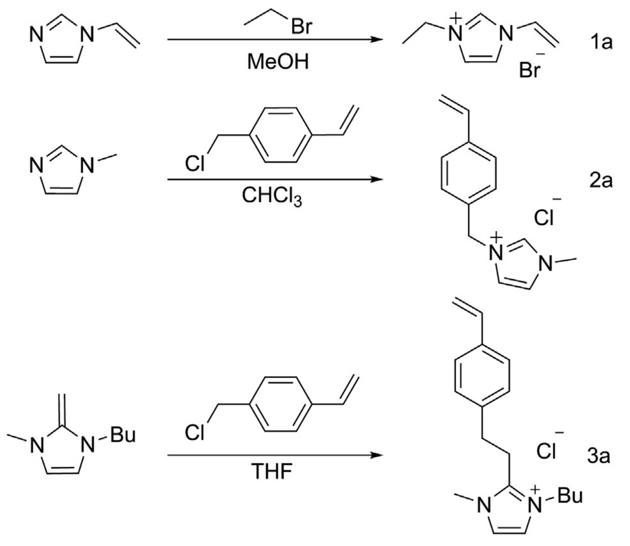

Fig. 1. Synthetic routes to monomer-precursors 1a, 2a, and 3a.

2.3. General procedure for anion exchange through salt metathesis (1b, 2b, 3b)

The corresponding halide salt 1a, 2a or 3a was dissolved in Milli-Q water. At room temperature, a solution of $LiN(Tf)_2$ (1.0 eq) in water was slowly added under stirring, resulting in a white emulsion.