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Supplementary Data

Synthesis and water uptake of 4,4-imidazolium ionenes

Tina Erdmenger, Igor Perevyazko, Jürgen Vitz, Georges Pavlov, and Ulrich S. Schubert

Experimental details

Materials

1,4-dibromobutane was distilled under reduced pressure prior to use and stored at room temperature. Imidazole, benzyl bromide, and sodium hydride were used as received. THF was dried and deoxygenated using a solvent purification system (PURE SOLV 400-4-MD, Innovative Technology). All other solvents, *e.g.* methanol, dimethylformamide, acetone, diethyl ether and ethylacetate were used as received. All substances used are commercially available.

The synthesis of the polymers was performed in a single-mode microwave reactor (Emrys Liberator, Biotage, Sweden) or in an oil bath. The reactions in the microwave (120 °C) and in the oil bath (60 to 80 °C) were performed in glass vessels (2 to 5 mL) sealed with a septum. The pressure of the system was controlled by a load cell connected to the vessel and the temperature of the reaction mixture was monitored using a calibrated infrared sensor, which is located at the side of the reaction vessel. All experiments were performed using a Teflon®-coated magnetic stirring bar. A maximum microwave power of 80 W was used. A maximum pressure of 20 bar was set as a safety threshold.

To remove water of the products either a vacuum oven at 45 °C or a freeze dryer Alpha 1-2 LD from Christ was used. The dried samples were stored under dry conditions in a desiccator.

^{1}H NMR spectra were recorded on a Varian Mercury spectrometer using a frequency of 400 MHz at 25 °C. Chemical shifts are given in ppm downfield from tetramethylsilane (TMS). IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer. Glass transition temperatures (midpoint of a small endothermic heat capacity change) were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from –100 to 150 °C with a heating rate of 20 K min^{-1} (a first heating cycle to 150 °C was not considered for the calculations). Thermogravimetric analyses were performed using a TG

209 F1 Iris by Netzsch under a nitrogen atmosphere in the range from 25 to 600 °C with a heating rate of 20 K/min. Elemental analyses were carried out on a EuroVector EuroEA3000 elemental analyzer for CHNS-O.

Water uptake

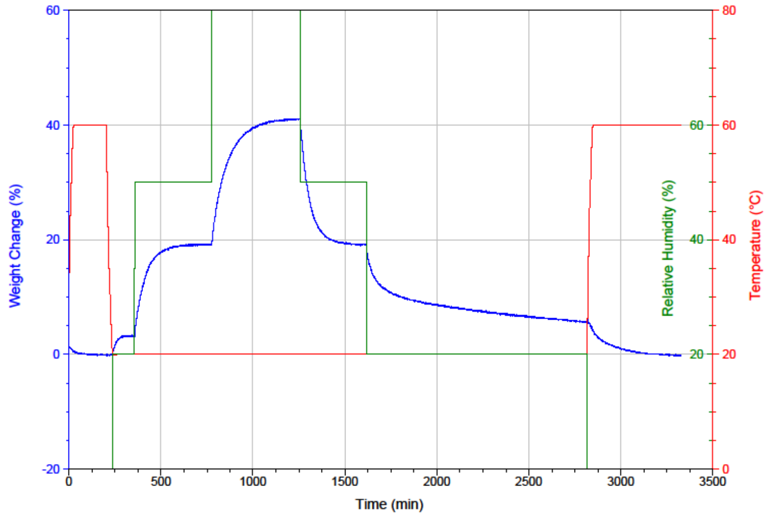

Figure 1: Representative water uptake measurement of 4,4-ionenes with bromide counter ion at 25 °C.

The water uptake measurements of the ionenes were performed on a Q5000 SA thermo gravimetric analyzer from TA Instruments containing a microbalance in which the sample and reference pans were enclosed in a humidity and temperature controlled chamber. The temperature in the Q5000 SA was controlled by Peltier elements. A dried N_2 gas flow (200 mL/min) was split into two parts, of which one part was humidified by passing it through a water-saturated chamber. The desired relative humidity (RH) for the measurements could subsequently be obtained by mixing proper proportions (regulated by mass flow controllers) of dry and wet stream. The standard isotherm measurement consisted of a number of subsequent steps. First, the sample was dried at 60 °C and 0% RH for a specific time until the weight change was stabilized to be less than 0.05% for a time period of 60 minutes. In the second step, the temperature was decreased to 25 °C and the relative humidity increased to 20%. The humidity was then increased step-wise (with steps of 20 or 30% RH) to a maximum of 90% RH. The weight change of the sample was stabilized after each step until it was smaller than 0.05% for a time period of 60 minutes. In addition, the reverse isotherm was also measured. In this case the humidity was decreased down to 0% (in steps of 20 or 30% RH) and the samples were allowed to stabilize after each step. In order to finalize the isotherm and to compare the results with the initial weight of the sample, an additional drying step was included (60 °C at 0% RH). In general, differences between absorption and desorption are less than 0.4% for 50% relative humidity.

Synthesis of 1,4-di(1*H*-imidazol-1-yl)butane

In a 500 mL round-bottomed flask sodium hydride (3.03 g, 126 mmol) was added to dry THF (220 mL) to yield a white suspension. 1*H*-imidazole (7.15 g, 105 mmol) in THF (30 mL) was added slowly at 0 °C. The mixture was stirred for 1 h at room temperature. 1,4-Dibromobutane (6.61 mL, 52.6 mmol) was added dropwise. The reaction mixture was heated to 60 °C for 2 days and subsequently diluted with diethyl ether (100 mL). The reaction mixture was filtered through a paper filter and the residue was washed with diethyl ether (20 mL). All solvents were evaporated to give yellow crystals. Further purification was achieved by dissolving the crude product in warm ethanol and precipitation in water. The white product was filtered and washed three times with water (~ 20 mL). The purified product (4.24 g, 42%) was freeze-dried in order to remove remaining water.

^{1}H NMR (400 MHz; CD_3OD, 25 °C): δ (ppm) = 1.75 (4 H, m, CH_2), 4.03 (4 H, m, CH_2), 6.95 (1 H, s), 7.09 (1 H, s), 7.63 (1 H, s); IR (neat): 3306 (OH), 2971 (CH alkyl), 2858 (CH alkyl), 2122 (N=C), 1638 (C=C, C=N), 1516 (C-C, C-N), 1446(CH alkyl deform.), 1383, 1283, 1030 (CH ring deform.) cm^{-1}; LDI-TOF-MS for $C_{10}H_{14}N_4 + H^+$(191.12): m/z 191 (100%), 192 (25%) g/mol; EA $C_{10}H_{14}N_4$ (190.12): Calcd. C 63.13, H 7.42, N 29.45, Found C 62.97, H 7.64, N 29.62.

Representative synthesis of poly(4,4-imidazolium bromide) – monomer imbalance

1,4-Di(1*H*-imidazol-1-yl)butane (105 mg, 0.55 mmol) was dissolved in either a mixture of MeOH (0.25 mL) and DMF (0.25 mL) or pure MeOH (0,5 mL). The reaction mixture was filled in a 0.5–2 mL Biotage pressure vial. 1,4-Dibromobutane (0.06 mL, 0.5 mmol) was added under stirring and the vessel was closed. The reaction mixture was stirred with a magnetic stirring bar for 1 h at 120 °C and subsequently poured into diethyl ether to precipitate the polymer (83% yield).

^{1}H NMR (400 MHz; CD_3OD, 25 °C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH_2), 4.40 (4 H, m, CH_2), 7.78 (2 H, s), 9.31 (1 H, s); IR (neat): 3395 (OH), 3148 (CH ring), 3097 (CH alkyl), 2946 (CH alkyl), 2871 (CH alkyl), 2058 (N=C), 1629 (C=C, C=N), 1564 (C-C, C-N), 1453 (CH alkyl deform.), 1333, 1159 (CH ring deform.), 1107, 1031, 835, 753 cm^{-1}; EA $(C_{14}H_{22}Br_2N_4)_n$ (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.57, H 5.71, N 13.97.

Representative synthesis of poly(4,4-imidazolium bromide) – chain stopper

1,4-Di(1*H*-imidazol-1-yl)butane (400 mg, 2.1 mmol) was dissolved in either a mixture of MeOH (1.05 mL) and DMF (1.05 mL) or pure MeOH (2.1 mL). The reaction mixture was filled in a 0.5 to 2 mL Biotage pressure vial. A mixture of 1,4-dibromobutane (0.25 mL, 2.1 mmol) and benzyl bromide (0.025 mL, 0.21 mmol) was added under stirring and the vessel was closed. The reaction mixture was heated for 1 h at 120 °C under microwave irradiation or for 24 h at 80 °C. The polymer solutions were subsequently precipitated in either diethyl ether, ethylacetate or a mixture with acetone.

^{1}H NMR (400 MHz; CD$_3$OD, 25 °C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH$_2$), 4.40 (4 H, m, CH$_2$), 7.78 (2 H, s), 9.31 (1 H, s); benzyl end group δ (ppm) = 5.50 (2 H, s, *N*-CH$_2$), 7.41–7.53 (5 H, m, H$_{\text{arom.}}$); IR (neat): 3391 (OH), 3148 (CH ring), 3103 (CH alkyl), 2952 (CH alkyl), 2864 (CH alkyl), 2068 (N=C), 1623 (C=C, C=N), 1564 (C-C, C-N), 1446 (CH alkyl deform.), 1339, 1159 (CH ring deform.), 1106, 1025 cm^{-1}; EA $(C_{14}H_{22}Br_2N_4)_n$ (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.10, H 5.62, N 13.49.