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New fully polymeric proton solvents with high proton mobility

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Abstract

The preparation and characterisation of fully polymeric-bound heterocycles as proton solvents is presented. Two different types of polymers are prepared: Polystyrene with imidazole terminated flexible side chains and benzimidazole covalently bonded to an inorganic SiO₂ network by a flexible spacer. High proton conductivities of up to 7×10^{-4} S cm⁻¹ at 200 °C have been obtained for these polymers in the absence of water. The presence of protonic charge carriers (protonated and deprotonated heterocycles) is a result of self-dissociation and the proton conductance is suggested to occur via intermolecular proton transfer and structural reorganisation within a dynamical hydrogen bond network formed by the aggregation of the terminating heterocycles. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the high proton conductivity of conventional hydrated polymers generally used as separator materials in hydrogen fuel cells is closely related to high levels of hydration, the maximum operation temperature is approximately given by the boiling point of water. This put several constraints on the use of hydrogen rich reformates (usually containing traces of CO) or methanol as fuels requiring somewhat higher operation temperatures [1]. It has been shown, however, that substitution of water by heterocycles, such as imidazole, pyrazole or benzimidazole leads to proton conductivities in the temperature range between 150 and 250 °C which are comparable to the conductivities of hydrated polymers [2]. Such heterocycles form similar hydrogen bond networks compared with water, and the transport properties in the liquid state are similar to those of water for a given temperature relative to the melting point [2,3]. While such adducts are of high interest for applications in closed electrochemical cells, such as

supercapacitators and electrochemical devices, the volatility of the heterocycles prevents them from being used in open electrochemical systems, such as fuel cells. In contrast to using water as a proton solvent, which is usually supplied to the membrane by humidifying the anode gases and is produced by the electrochemical reaction itself at the cathode, the use of heterocycles as the proton solvent requires their immobilisation in the polymer membrane in such a way that high mobility of the protonic charge carriers is still guaranteed [4]. While the proton mobility in hydrated polymers is subject to large contributions from the diffusion of hydrated protons [5,6], the proton mobility in an environment of immobilised heterocycles must completely rely on structure diffusion (Grotthuss-type mechanism) comprising proton transfer between heterocycles and hydrogen bond breaking and forming processes.

As a first step towards a full immobilisation of imidazole as a proton solvent, short oligo-ethyleneoxide chains of different length terminated by imidazole groups have been prepared as model compounds and characterised with respect to their thermal and transport properties (proton mobility, proton self diffusion coefficients and conduction mechanism) [7]. As a next step, in this paper we present the preparation and dc conductiv-

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Scheme 1. Increasing immobilisation of proton solvents (here: imidazole).

ities of fully polymeric proton solvents with high proton mobility (Scheme 1). These are characterised by flexible spacers covalently bound to an organic (polystyrene) or inorganic (siloxane) network and terminated by either imidazole or benzimidazole.

2. Experimental

Melting points (m.p.) were measured on a Büchi melting point B-540 apparatus and were left uncorrected. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AMX 300 spectrometer operating at 300 (¹H-) and 75.4 (¹³C-) MHz in the presence of tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) under nitrogen atmosphere was performed on a Mettler-Toledo DSC-30, and thermo gravimetric analysis (TGA) was also carried out under nitrogen on a Mettler-Toledo TG-50 at a heating rate of 10 K min⁻¹. Temperature-dependent dc-conductivities were determined by a HP-ac-impedance analyser (4192A LF), whereas the polymers have been measured as mouldings between two platin electrodes.

2.1. 5-(1H-Benzimidazol-2-yl)-pentan-1-ol (3)

A mixture of 1,2-phenylenediamine (1) (9.70 g, 0.09 mol), ε -caprolactone (2) (11.4 g, 0.1 mol) and *p*-toluenesulphonic acid hydrate (0.3 g, 1.6 mmol) was melted under an atmosphere of argon and then stirred at 200 °C for 2 h. The reaction mixture was cooled and fractional distillation at 200–230 °C/0.01 mbar gave a yellow oil, which was further purified by crystallisation (2 ×) from acetonitrile (1 × charcoal) to obtain 5-(1*H*-benzimidazol-2-yl)-pentan-1-ol (3) (10.5 g, 57%) as white crystals. M.p. 143–144 °C. ¹H-NMR (CD₃OD) δ 1.54–1.69 (2H, m), 1.70–1.83 (2H, m), 2.00 (2H, quin), 3.06 (2H, t), 3.73 (2H, t), 7.35 (2H, dd), 7.67 (2H, dd). ¹³C-NMR (CD₃OD) δ 27.0, 29.5, 30.2, 33.7, 63.1, 115.7, 123.5, 140.0, 157.2.

2.2. 3-(Triethoxysilyl)propyl carbamic acid-5-(1Hbenzimidazol-2-yl)-pentyl ester (4)

Under an argon atmosphere, a solution of 5-(1Hbenzimidazol-2-yl)-pentan-1-ol (3) (4.29 g, 0.021 mol), (3)-(isocyanatopropyl)triethoxysilane (5.44 g, 0.022 mol), and dibutyltin dilaurate (1.26 g, 2 mmol) in 1,2dimethoxyethane (70 ml) was stirred at 45 °C for 12 h. The solvent was evaporated and the resulting solid was dried at 0.02 mbar. The crude product was purified by recrystallisation from 1,2-dimethoxyethane-hexane under argon atmosphere yielding 4 (3.3 g, 79%) as a white solid. M.p. 100–101 °C. ¹H-NMR (DMSO-d⁶) δ 0.51 (2H, pt), 1.14 (9H, t), 1.33-1.47 (4H, m), 1.58 (2H, quin), 1.77 (2H, quin), 2.80 (2H, t), 2.92 (2H, pq), 3.73 (6H, q), 3.92 (2H, t), 7.03-7.12 (3H, m), 7.39 (1H, d), 7.50 (1H, d), 12.12 (1H, s). ¹³C-NMR (d⁶-DMSO) δ 7.1, 18.1, 22.9, 25.1, 21.2, 28.4, 42.9, 57.6, 63.4, 110.6, 118.0, 120.6, 121.2, 134.2, 143.3, 154.9, 156.3.

2.3. Sol-gel process (a typical experimental procedure is as follows)

Precursor 4 (1.04 g, 2.3 mmol) and tetraethoxysilane (TEOS) (0.48 g, 2.3 mmol) were dissolved in ethanol (5 ml). Then deionised water (0.4 ml) and hydrochloric acid (1 M, 0.02 ml) were added and the mixture was stirred for 20 h at ambient temperature. The solvent was evaporated and the resulting white solid **5a** was dried for 12 h at 80 $^{\circ}$ C/0.01 mbar.

2.4. 6-(4-Vinylbenzyloxy)-hexan-1-ol (7a)

Sodium hydride (4.4 g, 0.11 mol) was added to a cold solution (0 °C) of 1,6-hexanediol (30.0 g, 0.25 mol) in dimethylformamide (300 ml) under argon. The mixture was stirred for 2 h at room temperature, and 4vinylbenzyl chloride (6) (15.3 g, 0.1 mol) was added dropwise at 0 °C. After stirring at room temperature for 20 h, the solvent was evaporated at reduced pressure, ethyl acetate and water were added and the mixture was extracted with ethyl acetate (3×150 ml). The combined organic layers were dried over sodium sulfate before the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate: petrol ether 40/60 = 1:1), followed by crystallisation from petrol ether to yield 6-(4-vinylbenzyloxy)-hexan-1-ol (**7a**) (18.3 g, 78%) as a white solid. M.p. 29–30 °C. ¹H-NMR (CDCl₃) δ 1.22–1.68 (8H, m), 3.41 (2H, t), 3.50 (2H, t), 4.42 (2H, s), 5.18 (1H, d), 5.69 (1H, d), 6.65 (1H, dd), 7.24 (2H, d), 7.33 (2H, d). ¹³C-NMR (CDCl₃) δ 25.2, 25.6, 29.2, 32.2, 61.8, 69.9, 72.0, 113.2, 125.7, 127.4, 136.1, 136.4, 137.7.

2.5. 12-(4-Vinylbenzyloxy)-dodecan-1-ol (7b)

The reaction was carried out as described above for **7a**, starting from 1,12-dodecanediol (52 g, 0.27 mol) and 4-vinylbenzyl chloride (**6**) (15.3 g, 0.1 mol) to yield, after crystallisation from petrol ether, 12-(4-vinylbenzyloxy)-dodecan-1-ol (**7b**) (14.7 g, 46%) as white crystals. M. p. 54 °C. ¹H-NMR (CDCl₃) δ 1.26 (16H, s, br), 1.48–1.69 (4H, m), 3.44 (2H, t), 3.59 (2H, t), 4.48 (2H, s), 5.22 (1H, d), 5.73 (1H, d), 6.70 (1H, dd), 7.28 (2H, d), 7.38 (2H, d). ¹³C-NMR (CDCl₃) δ 25.7, 26.1, 29.3, 29.4, 29.5, 29.7, 32.7, 62.8, 70.4, 72.5, 113.5, 126.1, 127.7, 136.5, 136.8, 138.2.

2.6. 6-(4-Vinylbenzyloxy)-hexanal (8a)

A solution of dimethyl sulfoxide (16.4 g, 0.21 mol) in dichloromethane (40 ml) was added dropwise to a solution of oxalyl chloride (15.6 g, 0.12 mol) in dichloromethane (150 ml) at a temperature between – 60 and -70 °C under argon. After 30 min., a solution of 7a (20 g, 0.085 mol) in dichloromethane (130 ml) was added dropwise. The resulting mixture was maintained at -60 °C for 1 h, before triethylamine (43.5 g, 0.43 mol) was added. The reaction mixture was warmed to room temperature, water was added and the mixture was extracted three times (100 ml) by dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was evaporated at reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate: petrol ether 40/60 =1:10) to obtain 6-(4-vinylbenzyloxy)-hexanal (8a) (14.4 g, 77%) as a pale yellow oil. ¹H-NMR (CDCl₃) δ 1.30– 1.46 (2H, m), 1.54-1.71 (4H, m), 2.37 (2H, t), 3.43 (2H, t), 4.47 (2H, s), 5.21 (1H, d), 5.72 (1H, d), 6.68 (1H, dd), 7.26 (2H, d), 7.36 (2H, d), 9.70 (1H, s). ¹³C-NMR (CDCl₃) δ 21.6, 25.6, 29.2, 43.5, 69.7, 72.3, 113.4, 126.0, 127.5, 136.3, 136.6, 138.0, 202.2.

2.7. 12-(4-Vinylbenzyloxy)-dodecanal (8b)

The reaction was carried out as described above for **8a**, starting from 12-(4-vinylbenzyloxy)-dodecan-1-ol (**7b**) (13.3 g, 0.042 mol). Recrystallisation from petrol ether yielded 12-(4-vinylbenzyloxy)-dodecanal (**8b**) (11.2 g, 84%) as white crystals. M. p. $37 \degree C$. ¹H-NMR

(CDCl₃) δ 1.27 (14H, s, br), 1.53–1.74 (4H, m), 2.38 (2H, t), 3.44 (2H, t), 4.47 (2H, s), 5.21 (1H, d), 5.73 (1H, d), 6.70 (1H, dd), 7.28 (2H, d), 7.37 (2H, d), 9.37 (1H, s). ¹³C-NMR (CDCl₃) δ 21.9, 26.1, 29.0, 29.2, 29.3 (2C), 29.4 (2C), 29.7, 43.8, 70.3, 72.4, 113.5, 126.1, 127.7, 136.5, 136.7, 138.3, 202.6.

2.8. 2-[5-(4-Vinylbenzyloxy)-pentyl]-1H-imidazole (9a)

At 0 °C, an ammonia solution in methanol (ca. 7 N, 17 ml, 0.12 mol) was added to a solution of 6-(4vinylbenzyloxy)-hexanal (8a) (9.0 g, 0.039) and glyoxal hydrate (2.9 g, 0.04 mol) in methanol (80 ml). After the reaction mixture was stirred for 6 h at 0 °C, the mixture was kept in a refrigerator (4 °C) for 2 days. Then water was added and the product was extracted by ethyl acetate (3×150 ml). The combined organic layers were dried over sodium sulfate and the solvent was evaporated at reduced pressure. The residue was purified by aluminium oxide 90 column chromatography (ethyl acetate: petrol ether 40/60 = 1:2), followed by crystallisation $(2 \times)$ from tert-butyl methyl ether to yield 2-[5-(4-vinylbenzyloxy)-pentyl]-1*H*-imidazole (9a) (7.2 g, 69%) as a white solid. M.p. 65 °C. ¹H-NMR (CDCl₃) δ 1.42 (2H, quin), 1.60 (2H, quin), 1.73 (2H, quin), 2.73 (2H, t), 3.42 (2H, t), 4.43 (2H, s), 5.22 (1H, d), 5.72 (1H, d), 6.69 (1H, dd), 6.90 (2H, s), 7.25 (2H, d), 7.36 (2H, d), 11.16 (1H, br). ¹³C-NMR (CDCl₃) δ 25.7, 28.2, 29.2, 70.1, 72.5, 113.7, 121.1, 126.1, 127.8, 136.4, 136.8, 138.0, 148.6.

2.9. 2-[11-(4-Vinylbenzyloxy)-undecyl]-1H-imidazole (9b)

The reaction was carried out as described above for **9a** starting from 12-(4-vinylbenzyloxy)-dodecanal (**8b**) (8.2 g, 0.026 mol), glyoxal hydrate (1.57 g, 0.027 mol) and ammonia solution in methanol (12 ml, 0.081 mol). The resulting precipitate was separated by filtration and purified as described above for **9a** to yield 2-[11-(4-vinylbenzyloxy)-undecyl]-1*H*-imidazole (**9b**) (5.5 g, 60%) as a white solid. M.p. 83 °C. ¹H-NMR (CDCl₃) δ 1.23 (14H, s, br), 1.54–1.82 (4H, m), 2.71 (2H, t), 3.45 (2H, t), 4.48 (2H, s), 5.22 (1H, d), 5.73 (1H, d), 6.69 (1H, dd), 6.93 (2H, s), 7.28 (2H, d), 7.37 (2H, d), 10.81 (1H, br). ¹³C-NMR (CDCl₃) δ 26.6, 28.5, 28.6, 29.2, 29.3, 29.4, 29.5, 29.7, 70.4, 72.5, 113.6, 121.1, 126.1, 127.8, 136.5, 136.8, 138.2, 148.9.

2.10. Polymerisation

Compounds **9a** and **9b** were polymerised in Schlenk tubes in the presence of AIBN (1 mol.%). The tubes were degassed and kept at 100 °C for 3 h. Due to the insolubility of the rubber-like products (**10a** and **10b**) in



IPTS = 3-(Isocyanatopropyl)-triethoxysilane

Scheme 2. Preparation of the hybrid organic-inorganic network.

common organic solvents, they were used as received for thermal analysis and impedance spectroscopy.

3. Results and discussions

In the following, the preparation routes and characterisation of two polymer architectures based on inorganic and organic backbones are described and discussed.

3.1. Siloxane-based architectures

The first route relies on a sol-gel process making use of organic-inorganic precursors [8]. As an inorganic component, Si-alkoxide has been chosen because of the availability of varieties containing hydrolysable groups and Si-C bonds in the same molecule 3-(isocyanatopropyl)-triethoxysilane (IPTS). Since the proton solvent has to be covalently bonded, in this particular preparation route, a benzimidazole derivative containing a hydrolysable oxide forming element is used. The general synthesis of the precursor is illustrated in Scheme 2. 1,2-Phenylenediamine 1 was reacted with ε - ε -caprolactone (2) in the presence of a catalytic amount of *p*-toluenesulphonic acid at 200 °C to yield 5-(1*H*-benzimidazol-2yl)-pentan-1-ol (3). In the next step, the hydrolysable triethoxysilane group is introduced by coupling of IPTS and 3. The benzimidazole terminated sol-gel monomer 4 was homopolymerised and copolymerised with TEOS by hydrolysis and polycondensation in the presence of a small excess of acidified water.



Fig. 1. TGA curves of the sol-gel materials.



Fig. 2. Temperature dependence of the dc conductivity of 3 and 5 as determined by ac impedance spectroscopy.

TGA measurements of the apparently dry materials show < 3% of weight loss up to 200 °C (Fig. 1). Further increase of the temperature leads to a progressive decomposition of the materials. Thermal stability is improved when the sol-gel process is carried out in the presence of the crosslinking reagent TEOS (**5a** and **5b**, about 1% of weight loss up to 200 °C), i.e. with an increasing degree of polycondensation. The degree of crosslinking in **5a** and **5b** seems to have no influence on the decomposition temperature. The proton conductivities of the sol-gel materials **5** are shown in Fig. 2 together with the conductivity of monomeric 5-(1*H*-benzoimidazol-2-yl)-pentan-1-ol (**3**). The homopolymerisation **5c** (n(TEOS) = 0) and the copolymerisation **5b** (with a low fraction of crosslinker; n(TEOS) = 0.2) of the triethoxysilane endcapped precursor **4** only leads to a small reduction of the conductivity in comparison to **3**. The conductivities of the systems reach a value of $\sigma = 7 \times 10^{-5}$ S cm⁻¹ at 150 °C. An equimolar conversion (**5a**) of precursor and



Scheme 3. Synthesis of the polystyrene derivatives.



Fig. 3. TGA curves of the polystyrene derivatives.

crosslinker results in a dramatic decrease of conductivity, supposedly due to a suppression of the dynamics of the benzimidazole terminated alkane spacers. This observation indicates that slight crosslinking leaves the proton conductivity almost unaffected.

3.2. Polystyrene-based architecture

In another route, imidazole is linked to a polystyrene backbone by means of flexible alkyl spacers of different lenghts. The synthesis of the monomer is illustrated in Scheme 3. In the first step, aliphatic diols (1,6-hexanediol, 1,12-dodecanediol) were benzylated by 4-vinylbenzyl chloride (6) in dimethylformamide at room temperature using NaH as a base to give the monobenzyl ether 7. Oxidation of the terminal hydroxy group with dimethyl sulfoxide and oxalyl chloride (Swern oxidation) led to the aldehyde **8**. Imidazole ring formation was achieved by reaction with glyoxal hydrate in methanolic ammonia solution. Due to the poor solubility of **10**, the radical homopolymerisation of **9** did not take place in common organic solvents. Therefore, the synthesis of the polystyrene derivatives was carried out as a mass polymerisation in the presence of AIBN.

The TGA curves of both polymers 10 suggests intrinsic thermal stability up to approximately 200 °C (Fig. 3). DSC clearly shows a glass transition temperature T_g of 10a at 51 °C and a decrease of T_g (19 °C) is observed with increasing length of the imidazole terminated side chain in the case of 10b.

The conductivities of both polymers are shown in Fig. 4 with a VFT-type temperature dependence reaching 7×10^{-4} S cm⁻¹ for **10b** and 3×10^{-4} S cm⁻¹ for **10a** at 200 °C. At low temperatures, the conductivity is highest in **10b**, which is the material with lower T_g while the conductivity at high temperatures is highest in **10a**, which is the material with the higher T_g . This behaviour may reflect the ambivalent role of hydrogen bonding as already observed for the proton mobility in imidazole compared with pyrazole [4] and discussed for hydrogen bonded systems in general [9].

3.3. A few common aspects

The proton conductivities of the sol-gel materials **5** and of the polystyrene derivatives **10** depend on the existence of charge carriers, which can only stem from the self-dissociation of the imidazole units. Assuming that the degree of self-dissociation in the polymeric



Fig. 4. Temperature dependence of the dc conductivity of 10 as determined by dc impedance spectroscopy.

systems is of the same order as in pure imidazole (ca. 10^{-3} [4]), the mobility of protonic defects in these waterfree polymers is very high ($\sim 10^{-5}$ cm² s⁻¹). The immobilised proton donor and acceptor functions exclude any vehicle-type transport and only permit proton mobility via structure diffusion (Grotthuss mechanism) involving proton transfer between the heterocycles with a corresponding reorganisation of the hydrogen bond network as described in more detail for pure imidazole [10]. The conductivity of poly(4vinylimidazole), where the imidazole is directly bonded to the backbone, is comparatively low $(2 \times 10^{-10} \text{ S})$ cm⁻¹ at 150 °C) [11]. Soft spacers, however, seem to allow for an aggregation of the terminating heterocycles and for the formation of dynamical hydrogen bonded structures, supporting high proton mobility.

4. Summary and conclusions

Several examples of polymer-bound heterocycles as proton solvents are presented. The proton conducting polymers have been synthesised by sol-gel processing of organically substituted alkoxysilanes and by radical polymerisation of styrene derivatives. The heterocycles (imidazole, benzimidazole) are immobilised in such a way that the formation of extended aggregates of heterocycles and their local dynamics allow for rapid long range transport of protons via structure diffusion. The polymeric systems, which are nominally free of low molecular weight solvents, show remarkable conductivities of the order of 10^{-3} S cm⁻¹ at 200 °C corresponding to a high mobility of protonic charge carriers (ca. 10^{-5} cm² s⁻¹ at 200 °C) which most likely originate from the self-dissociation of the heterocyclic functional groups. To the best of our knowledge, this is the first time that high proton mobility has been proven for an immobilised polymeric proton solvent (proof of concept).

With respect to the transfer of the presented concept to the development of new separator materials for fuel cells operating at intermediate temperatures $(150-200 \ ^{\circ}C)$ in a low humidity environment, the possibility to increase the concentration of intrinsic excess (and defect) protons by introducing acidic functions into the polymer architecture leaves some space for a further increase of the conductivity as already demonstrated for oligomeric systems [7]. While the choice of the presented chemistry was mainly based on accessible synthetical strategies, the development of membranes for fuel cell applications must be constrained by stability considerations from the very beginning.

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