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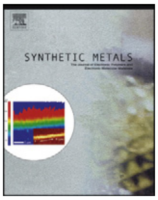

New type of anhydrous organic electrolyte based on carboxylic acid functional triazole as model system

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ABSTRACT

The model system of dicarboxylic acid functionalized 1H-1,2,3-triazole-terminated alkyl oligomers is presented as a new approach for obtaining high proton conductivity in proton solvating heterocycles covalently bound via spacers. The model materials have been characterized by FT-IR and NMR spectroscopy. Thermal stabilities were examined with thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) was used to measure melting and crystallization temperatures. The influence of spacer length on proton conductivity was investigated by AC impedance spectroscopy. Analysis of conductivity and permittivity measurements revealed the contribution of local dynamics and proton mobility on conduction mechanism which gives rise to proton conductivities of up to 10^{-5} S/cm at 120 °C in completely water-free pristine materials.

1. Introduction

Solid electrolytes play an important role in the development of new energy sources, like solid state batteries, fuel cells, photoelectrochemical solar cells, sensors and electrochromic displays [1,2]. Obtaining high ionic conductivity over a wide temperature range becomes crucial for the realization of these technological applications. Since last more than three decades various research groups [3–6] have been involved actively to synthesize polymer electrolytes with high conductivities, but up to now the desired conductivities, particularly at high temperatures, have not been attained. Hydrated perfluorosulfonic polymer shows superior performance in fuel cells operating at moderate temperature (<90 °C), however, the properties of such polymer membranes are insufficient at higher temperatures. This puts new demands on the development of alternative polymeric proton exchange membranes [7]. The substitution of water by suitable compounds may lead to high proton conductivities. The membranes, particularly comprising aromatic heterocyclic protogenic solvents such as imidazole, pyrazole or benzimidazole, have been reported to exhibit high conductivity in the anhydrous state [8]. The use of these heterocycles as proton solvents in membranes for fuel cells requires their immobilization in such a way that high mobility of the protonic charge carriers is still provided [9]. Schuster et al. prepared imidazole terminated short oligo(ethylene oxide) (EO) chains as a first attempt towards a full immobilization of imidazole as proton solvent [10]. This model system showed maximum conductivity of 5×10^{-3} S/cm at 120 °C for the triflic acid doped samples. A fully polymeric solvent with high proton mobility by tethering imidazole and benzimidazole units into polystyrene and siloxane network has also been synthesized [11]. The maximum conductivity of 7×10^{-4} S/cm was obtained at 200 °C. Moreover, imidazole functional cyclic oligomeric siloxane and polysiloxane has been synthesized by Scharfenberger et al. and highest conductivity of 10^{-3} and 5×10^{-4} S/cm has been obtained, respectively [12].

In recent studies, it has been shown that the heterocyclic 1H-1,2,4-triazole (Tri) is a promising material whose structure is similar to imidazole but contains three nitrogen atoms in the ring [13,14]. The proton conduction in acidic polymer/Tri system occurs via the structure diffusion mechanism comprising proton transfer between heterocycles and their reorganization [15]. The main problem of such host/guest systems is the leaching of the protogenic solvent during cell operation [16]. It was previously reported that the immobilization of Tri, which can be copolymerization of Tri with an acidic monomer or tethering onto polymer, can maintain this problem [17–19].

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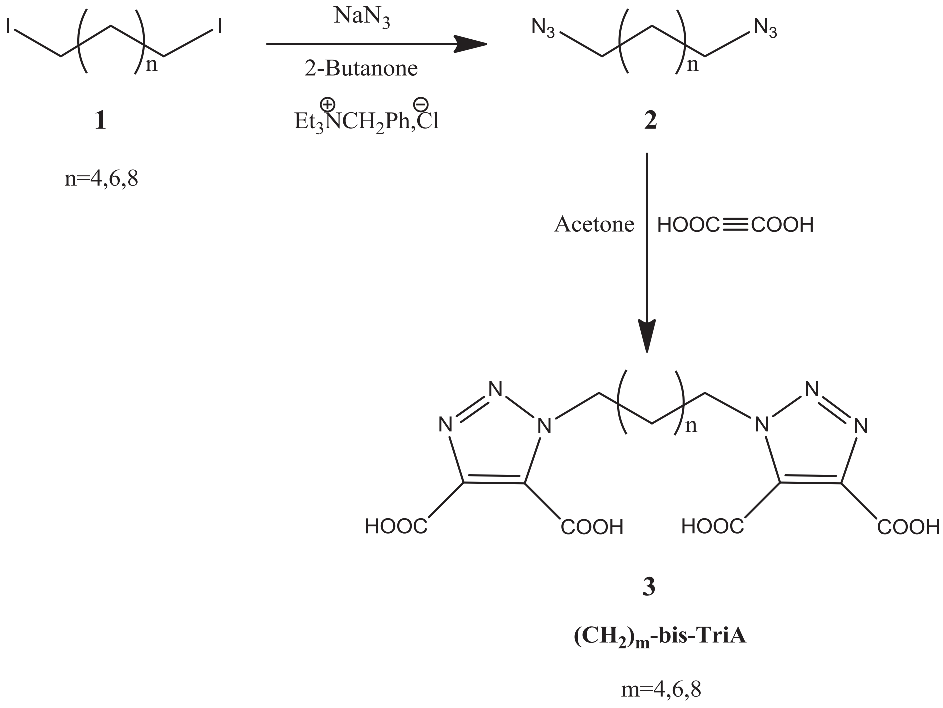

Scheme 1.

Combining the functions of the protogenic group and the proton solvent in a single molecule is another approach in the development of proton conducting membranes [10,20,21]. Such molecules must be amphoteric in the sense that they behave as both a proton donor (acid) and proton acceptor (base), and they must form dynamical hydrogen bond networks [22].

As another alternative attempt towards a full immobilization of triazole as proton solvent, we introduce in this paper the preparation and transport properties of model compound of $(CH_2)_m$-bis-TriA which is short alkyl (CH_2) chains terminated by functionalized triazole groups (Scheme 1). The (CH_2) segments are considered to be models for 'spacers', with which the triazole groups may be tethered to a polymer backbone in a final system. The samples were characterized by FT-IR, NMR, DSC and TGA. Proton conductivity of the samples was investigated by dielectric-impedance analyzer using complex dielectric permittivity.

2. Experimental

2.1. Materials

1,6-Diiodohexane (1,8-diiodooctane and 1,10-diiododocane) (97%), acetylenedicarboxylic acid (97%), sodium azide (98%) were obtained from Alfa Aesar, benzyl triethyl ammonium chloride (98%), 2-butanone (99%), acetone (99%) were from Merck. All solvents were reagent grade and used without further purification.

2.2. Synthesis of 1,6-diazidohexane

The synthesis of 1,6-diazidohexane (**2**) was carried out according to literature (Scheme 1) [23]. 1,6-Diiodohexane (**1**) (20 mmol), benzyl triethyl ammonium chloride (40 mmol) and 2-butanone (70 ml) was treated with a solution of NaN_3 (120 mmol) in 50 ml of water. The mixture was heated under reflux for 16 h. The mixture was extracted with ether (3 × 75 ml). The ether phase dried over magnesium sulfate and the solvent is evaporated under reduced pressure. The product was obtained with high yield, 95%.

$$\text{IR}: \quad \tilde{\nu} = 2100 \quad (N_3) \quad \text{cm}^{-1}$$

^{1}H NMR ($CDCl_3$): δ, ppm. = 1.30 (m,2H); 2.35 (m,2H); 3.6 (t,2H)

2.3. Synthesis of 1,6-bis(1H-[1-3]triazole-4,5-dicarboxylic acid)

1,6-bis(1H-[1-3]Triazole-4,5-dicarboxylic acid), C_6H_{12}-bis-TriA (**3**), was synthesized by cycloaddition reaction of azides with alkynes [24] (Scheme 1). A solution of 5 mmol of 1,6-diazidohexane (**2**) and 1 equivalent of acetylenedicarboxylic acid in acetone (15 ml) was heated under reflux for 6 h. The solvent was removed under vacuum and the final product was obtained as yellow powder. Yield: 95%.

$$\text{IR}: \quad \tilde{\nu} \quad (\text{cm}^{-1}) = 3450 \quad (\text{O–H}); \quad 1753 \quad (\text{C=O})$$

^{1}H NMR ($CDCl_3$): δ; ppm. = 1.35: c,c′ (m,2H); 1.85: b,b′ (m,2H); 3.45: a,a′ (t,2H)

^{13}C NMR (CD_3COCD_3): δ; ppm. = b,b′,c,c′: 25–29; a,a′: 50; e,e′: 130; d,d′: 141; f,f′: 159–161

2.4. Methods

FT-IR spectra were used to determine the progress of the reactions. FT-IR spectra were recorded on a Bruker Alpha-P in ATR.

NMR spectra were recorded on a Bruker AM 400 or an AC 200 instrument. Chemical shifts are reported in ppm relative to TMS as internal standard for the 1H spectra. Coupling constants (*J*) are in Hertz.

Thermal stabilities of the samples were investigated by a PerkinElmer STA 6000 Thermal Analyzer. The samples (~10 mg) were heated from room temperature to 750 °C under N_2 atmosphere at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) data were recorded using PerkinElmer JADE Scanning Calorimeters under dry nitrogen atmosphere at a scanning rate of 10 °C/min. The samples were weighted (10–15 mg) and loaded into aluminum pans, cooled down