



Synthesis and characterization of polyphosphazene electrolytes including cyclic ether side groups



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HIGHLIGHTS

- Investigation of polyphosphazene derivatives composing cyclic ether side groups.
- Synthesis of a new polyphosphazene derivate composing a cyclic ether side group.
- Synthesis of a similar polymer composing two ether functionality per ring.
- Ion conductivity comparison of both polymers as salt-in-polymer electrolytes.

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ABSTRACT

This paper presents the synthesis and detailed characterization of two polyphosphazene based polymers, including different cyclic ether side groups. The final polymers were obtained by a well-known method employing a living cationic polymerization and subsequent nucleophilic substitution. The synthesized polymers Poly [(1,3-dioxane-5-oxo) (1,3-dioxolane-4-methoxy)phosphazene] (DOPP) and Poly[bis(2-Tetrahydro-3-furanoxy)phosphazene] (THFPP) were mixed with varied amounts of lithium bis(trifluoromethane)sulfonamide (LiTFSI) and the interactions between the salt and the polymer chains were studied by Fourier transform infrared (FT-IR) and differential scanning calorimetry (DSC) measurements. Electrochemical characterization was performed by electrochemical impedance spectroscopy (EIS) and direct current polarization in the temperature range of 20–60 °C. These measurements were utilized to calculate the lithium transference number (t_+), the lithium conductivity (σ) and its activation energy in order to elucidate the lithium transport behavior. Relatively high lithium transference numbers of 0.6 (DOPP) and 0.7 (THFPP) at 60 °C are found and reveal maximum lithium conductivities of $2.8 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ and $9.0 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ for DOPP and THFPP at 60 °C, respectively.

1. Introduction

Polymers are macromolecular chains, composed of thousands of monomer units. Characteristics of each monomer unit contribute to the overall properties of the whole polymer. Thus, many synthetic approaches exist for adjusting and optimizing polymer materials. Polymers have been known to function as electrolytes since 1973, as a result of the previous decades of polymer inventions [1]. Between 1910 and 1950, many milestones were achieved in polymer history: for example PVC, acrylate polymers, polyethylene, polyvinylchloride and polyamide, to name a few. This period can be truly determined as the beginning of the “plastic age”. An important subgroup of polymers are polyphosphazenes (PP), for the first time synthesized in 1897

by *H.N.Stokes*. [2] The synthesis of the phosphorous-nitrogen backbone is quite difficult and about 70 years elapsed until major advances were reported by *H.R. Allcock*. [3] The facile side chain substitution of the dichloropolyphosphazene (DCPP), first synthesized in 1965, started a synthetic race and resulted in the publication of thousands of polymer derivatives [4]. The first PP-electrolyte was reported in 1984 and contained ether side groups in order to complex and allow transport of lithium ions [5]. The electrochemical performance of the so called MEEP (poly[bis((methoxyethoxy)ethoxy)phosphazene]) led to a large number of new synthesis routes to couple other lithium chelating groups to the PP-backbone (e.g. different size polyethers [6], sulfone, sulfoxide, sulfonate [7–9], and esters [10,11]). Nearly each size of the linear polyether side groups has been investigated and the best ionic

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conductivity was found for short groups of 3–4 oxygen-bridges. The present work attempts to fill a gap in the knowledge by investigating and comparing different sizes of short, cyclic ether side groups. Therefore, we synthesized one new polyphosphazene with 3-hydroxytetrahydrofuran as side group and compared this to a known 5-hydroxy-1,3-dioxane side chain polyphosphazene [12]. The pristine polymers and mixtures with different salt contents, including lithium bis(trifluoromethane)sulfonamide (LiTFSI), were investigated by several methods. Nuclear magnetic resonance and infrared spectroscopy were performed to provide information about the structure, ion complexation and salt interactions. Moreover, the stability was tested by differential scanning calorimetry. Finally, the ionic conductivity was investigated by electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials

All reactions were performed under dry argon atmosphere using an argon glovebox and Schlenk technique. N-pentane (Aldrich anhydrous 99%), diethylene glycol dimethyl ether (Aldrich anhydrous 99.5%), methyl alcohol (Aldrich 99.8%), racemic glycerol formal (Aldrich 47–67% 5-hydroxy-1,3-dioxane to 33–53% 4-hydroxymethyl-1,3-dioxolane), racemic 3 hydroxytetrahydrofuran (Aldrich 99%) and tetrahydrofuran (Aldrich 99.9%, inhibitor-free) were dried statically and dynamically over molecular sieves. Toluene (Aldrich 99.9%) was distilled and stored over molecular sieves. Sulfuryl chloride (Aldrich 97%) and phosphorous trichloride (Aldrich 99%) were freshly distilled prior to use. Phosphorous pentachloride (Aldrich 98%) was purified by vacuum sublimation and bis(trifluoromethane)sulfonamide lithium salt (Aldrich 99.95%) was vacuum dried for 24 h at 200 °C. After purification, all salts - including sodium hydride (Aldrich powder 95%) - were stored in the argon glovebox. A 0.05 mm lithium foil (Rockwood Lithium 99.9%) was used as an electrode and polished 0.5 mm nickel foil (99.5% Alfa Aesar) was used as a substrate. Both 3 Å and 4 Å molecular sieves (Aldrich) were used after purging and activation under vacuum for 48 h by 300 °C. The dialysis tubes (Aldrich, molecular weight cut off 12,000–14,000 g·mol⁻¹) were washed with methanol before use.

2.2. Synthesis and membrane preparation

There exist many synthetic protocols in the literature [13–15]. We performed the monomer synthesis using the one pot method from Wang et al. [16] followed by a trap-to-trap distillation of the monomer [17]. The polymerization was performed by a living cationic polymerization from Allcock et al. [18] The reaction mixture was composed of a monomer to initiator ratio of 350:1 and was stirred at room temperature for 48 h. After purification, the resulting polymer was immediately used in the next synthesis step or was stored in diglyme [19].

The coupling of the alcohol was also performed as previously described in the literature [13–15]. First, 0.9 g (37.5 mmol) of sodium hydride was suspended in 50 mL THF and cooled to 0 °C. One equivalent of the respective alcohol was then added dropwise to the vigorously stirred suspension. The solution was stirred under said reaction conditions until the evolution of gas ceased. Next, 2.06 g (17.81 mmol; 5% less than calculated) of DCPD was dissolved in 25 mL of THF and added dropwise to the reaction solution. The mixture was allowed to warm up to room temperature and stirred for an additional 24 h. After separation of the precipitated sodium chloride by centrifugation and solvent evaporation, the raw polymer/THF solution was purified by dialysis three times against methyl alcohol. After the final solvent evaporation, pure Poly [(1,3-dioxane-5-oxy) (1,3-dioxolane-4-methoxy) phosphazene] DOPP [12] and Poly[bis(2-Tetrahydro-3-furanoxy)phosphazene] THFPP were obtained (Fig. 1).

DOPP was obtained in a yield of 81.8% (alcohol coupling). ¹H NMR

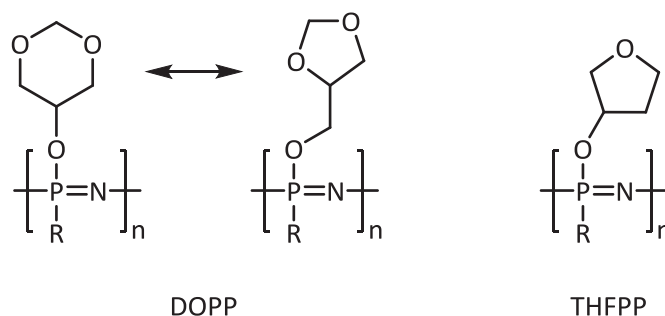


Fig. 1. Structural comparison of DOPP including both isomeric side groups (left) to THFPP (right).

(600 MHz, THF-d₈, 303 K): δ (ppm) = 4.87 (1H, s, CH₂, 6-ring); 4.70 (1H, s, CH₂, 6-ring); 4.32 (1H, s, CH, 6-ring); 4.01–3.97 (2H, m, CH₂, 6-ring); 3.77 (2H, s, CH₂, 6-ring); 4.67–4.63 (2H, m, CH₂, 5-ring); 4.18 (1H, s, CH, 5-ring); 4.01–3.97 (2H, m, CH₂, 5-ring); 3.84 (1H, m, CH₂, 5-ring); 3.64 (1H, m, CH₂, 5-ring). ¹³C NMR (600 MHz, THF-d₈, 303 K): 93.61 (s, CH₂, 6-ring); 70.04–69.91 (m, CH₂, 6-ring); 68.30 (s, CH, 6-ring); 95.53–95.48 (m, CH₂, 5-ring); 74.61–74.45 (m, CH, 5-ring); 67.24–66.80 (m, CH₂, 5-ring). ³¹P NMR (600 MHz, THF-d₈, 303 K): δ (ppm) = –7.74 to –9.82 (m).

THFPP was obtained in a yield of 80.4% (alcohol coupling). ¹H NMR (600 MHz, Chloroform-d₆, 303 K): δ (ppm) = 4.93 & 5.08 (1H, s, CH); 3.78 (4H, s, CH₂); 2.02–2.08 (2H, m, CH₂). ¹³C NMR (600 MHz, Chloroform-d₆, 303 K): δ (ppm) = 78.85–79.10 & 76.85–77.82 (m, CH); 73.50 & 73.76 (s, CH₂); 66.88 (s, CH₂); 33.75 & 33.97 (s, CH₂). ³¹P NMR (600 MHz, Chloroform-d₆, 303 K): δ (ppm) = –9.08 to –10.23 & –13.31 (m).

Both polymers were formed by use of racemic alcohols. This complicates the spectra, as it causes additional unexpected signals for each atomic position. The enantiomeric signal splitting can be seen for all structural elements at the junction point where both alcohols are coupled to the polyphosphazene backbone.

The polymers were dissolved in THF and mixed with the appropriate amount of LiTFSI. All concentrations in this publication are expressed in ratios between polymer composing oxygen to lithium ions of the salt (e.g. 20:1 means 20 polymer oxygen atoms to 1 LiTFSI molecule). THF solvent was partially evaporated under vacuum until a highly viscous salt-in-polymer solution remained. Polymer membranes were received by spin coating of the solutions on lithium covered nickel substrates (9 mm diameter). The spin coating parameters varied between 30 rps and 100 rps, depending on the viscosity of the polymer solutions. The resulting polymer layers of 30 μ m were dried under vacuum at room temperature for 3 h.

2.3. Spectroscopic and thermal analysis

NMR spectra were performed in CDCl₃ and THF-d₆ on a Bruker Avance II 600 MHz. For ³¹P NMR we used 85% H₃PO₄ as reference. ATR-IR was measured on a Thermo Scientific Nicolet iS5 with a diamond crystal attachment iD5 ATR. Glass transition and decomposition temperatures of the polymers were obtained by differential scanning calorimetry (DSC) on a Mettler Toledo DSC-700 in the temperature range between –100 °C and 300 °C and a heating rate of 10 K min⁻¹ under a nitrogen atmosphere.

2.4. Transference number of lithium ions

Lithium transference number t_+ was measured using the steady state method of Evans, Vincent and Bruce [20]. A symmetric cell setup with a Li/polymer/Li architecture was applied and experimentally controlled by a potentiostat BioLogic SP-300. To consider the interfacial reactions, AC impedance (EIS) measurements were performed before

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