



Lithium-based oligomer ionic liquid for solvent-free conducting materials

C. Vancaeyzeele ^a, G.T.M. Nguyen ^a, A.L. Michal ^b, M. Viallon ^a, C.A. Michal ^{b, **}, F. Vidal ^{a, *}

^a Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI, I-MAT), University of Cergy-Pontoise, 95000 Cergy-Pontoise, France

^b Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

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ABSTRACT

The synthesis of a new lithium conducting oligomer ionic liquid (IL), noted Jeffamine diLi, was obtained from a two-step grafting of bis(trifluoromethanesulfonyl) imide on the commercial diamine-telechelic poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) (PPO-PEO-PPO). This oligomer IL, with a conductivity of $4.8 \times 10^{-3} \text{ S cm}^{-1}$ at 100°C , is liquid from -21°C and stable up to 300°C . An all-solid-electrochromic device using Jeffamine diLi as electrolyte was successfully fabricated. Then, two types of polymer network were selected to develop the lithium conducting materials. Jeffamine diLi was incorporated either in a poly(ethylene oxide) (PEO) or in a PPO-PEO-PPO network. The resulting semi-interpenetrating networks (semi-IPNs) are transparent, amorphous, self-standing and have ionic conductivity of $1.10^{-4} \text{ S cm}^{-1}$ at 80°C . The diffusion and relaxation NMR measurements paint a picture of the cations being much more strongly interacting with the anions of the IL in the PPO-PEO-PPO semi-IPN's than in the PEO semi-IPN's.

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1. Introduction

Among current research on energy storage, there is a focus on all-solid lithium-based batteries incorporating solid polymer electrolytes (SPE). This type of electrolyte should offer ease of manufacturing and enhanced safety by limiting internal short-circuits [1]. Several polymer electrolyte systems have been investigated in the past few decades. Classical polymer-salt complexes consisting of a lithium salt dissolved in a polymer matrix exhibit low ionic conductivity, about $10^{-7} - 10^{-8} \text{ S cm}^{-1}$ [2]. The selection of polymer matrix and low lattice energy lithium based salt, such as PEO/Li $[\text{N}(\text{SO}_2\text{C}_n\text{F}_{2n+1})(\text{SO}_2\text{C}_m\text{F}_{2m+1})]$, may allow reaching $10^{-5} \text{ S cm}^{-1}$ [3] in ionic conductivity. In addition, the ionic conductivity could be improved up to several mS cm^{-1} by adding small plasticizers, such as dimethylsulfoxide or propylene carbonate [4] or using a gel polyelectrolyte formulation [5].

Simultaneously, ionic liquid (IL) based electrolytes for electrochemical storage and conversion applications have gained

attention [6–8]. They offer many advantages over conventional liquid electrolytes based on organic solvents, in particular high chemical and thermal stability, broad electrochemical window [9,10], low vapor pressure, suitable viscosity [11], and no flammability [8,12]. The ionic conductivity of ionic liquids at room temperature is generally of the order of $10^{-3} - 10^{-2} \text{ S/cm}$ and thus sufficient for applications as electrolytes [13,14]. However in many electrochemical devices (actuator, capacitor ...) the overall ionic conductivity is not the only important parameter, but also the cation and anion transference numbers are relevant [15,16]. In the specific case of lithium battery applications, high transference numbers of Li^+ ions in the electrolyte are needed. In order to take advantage of ionic liquids in lithium batteries, an interesting strategy has been developed in dissolving lithium salt in an ionic liquid [17,18]. In this approach, the lithium salt contains the same anion as the ionic liquid. For instance, ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquid can be doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to give electrolytes with conductivities around mS/cm and viscosity of 200 mPa/s at 300K when composed of 25% LiTFSI [19].

However, the fact that cationic species are a mixture of lithium ions and the ionic liquid's cation reduces the neat lithium ion

* Corresponding author.

** Corresponding author.

E-mail addresses: michal@physics.ubc.ca (C.A. Michal), frederic.vidal@u-cergy.fr (F. Vidal).

transference number. To contend with this drawback Watanabe's group in 2004 reported the development of a lithium containing ionic liquid [20]. They synthesized lithium salts of borates having two electron-withdrawing groups (either 1,1,1,3,3,3-hexafluoro-2-propoxy or pentafluorophenoxy group) and two methoxy-oligo (ethylene oxide) groups. The obtained lithium salts were clear and colorless liquids with a viscosity of around 300–400 mPa s and an ionic conductivity around 10^{-5} S/cm at 300K. When dispersed in a PEO network the conductivity increased of one order of magnitude.

Following this strategy, we choose to synthesize a new lithium based oligomer IL that would be liquid at room temperature. The synthesis of this IL is carried out with a pathway similar to that of the single lithium ion conductor monomer, previously reported [21]. In a first part, bis(trifluoromethanesulfonyl) imide is grafted on diamine-telechelic polypropylene oxide-block-polyethylene oxide-block-polypropylene oxide oligomer. Then, the Lithium IL is obtained after deprotonation of this intermediate. The trifluoromethanesulfonamide derivative with diffuse negative charge was selected as lithium counter ion because it favors ion pair dissociation and thus better ion conductivity. [22] The resulting structure is characterized by NMR, FT-IR and elemental analysis. The ion conductivity is discussed in view of the thermal and rheological properties. Finally, the lithium IL was incorporated in an all-polymer-based organic electrochromic device to show that it could stand by itself as an electrolyte.

In the aim of developing an all-solid-system with lithium conducting polymer electrolyte with optimal conductivity, this lithium conducting IL is incorporated in either a polyethylene oxide network or in a polypropylene oxide-block-polyethylene oxide-block copolymer network. The lithium IL will be entrapped as a linear component in a partner network leading to a semi-Interpenetrating Polymer Network (semi-IPN). The thermal and mechanical analysis and ionic conductivity of the obtained semi-IPNs are detailed. Using pulsed-field gradient stimulated echo nuclear magnetic resonance (PFGSTE-NMR), we are able to measure the individual diffusion coefficients of mobile species in the material (^{19}F and ^7Li) [23]. Experimental results include NMR spin-spin (T_2) and spin-lattice (T_1) relaxation times in addition to diffusion coefficient measurements over a temperature range up to 100 °C. Practically, these diffusion measurements are extremely challenging, as the spin-spin relaxation times can be extremely short.

2. Experimental

2.1. Materials

Trifluoromethanesulfonic anhydride (98%, Acros), hydroquinone

(99%, Aldrich), 2-isocyanatoethyl methacrylate (98%, Aldrich), anhydrous chloroform (>99%, amylene stabilized, Aldrich), LiH (98%, Acros), LiClO_4 (99%, Aldrich), poly (ethylene glycol) dimethacrylate ($M_n = 750 \text{ g mol}^{-1}$, PEGDM 750, Aldrich) and diamine telechelic polypropylene oxide-block-polyethylene oxide-block-polypropylene oxide denoted as jeffamine ($M_n = 664.8 \text{ g mol}^{-1}$, $d = 1.035$, Jeffamine ED 600, Huntsman) were used without further purification. α, α' -azobisisobutyronitrile (AIBN) initiator (>98%, Aldrich) was recrystallized in methanol before use. Tetrahydrofuran (THF, Acros) was distilled over Na/benzophenone under argon atmosphere and dichloromethane (CH_2Cl_2 , Carlos Erba) was distilled over CaH_2 under argon atmosphere before use. 3,4-Ethylenedioxythiophene (EDOT, Bayer) was distilled under vacuum. ITO-coated glass slides were purchased from Solems S.A. and treated prior to use by sonication in acetonitrile.

2.2. Synthesis of Jeffamine diLi

3 g Jeffamine ED 600 (4.51 mmol) were dissolved in 20 mL anhydrous chloroform under argon. 1.4 g trifluoromethanesulfonic anhydride (4.96 mmol) was dissolved in 0.82 mL anhydrous chloroform and added drop wise to the former solution at 0 °C. The reaction was kept at 0 °C for 30 min and at room temperature for 16 h. The solvent was evaporated and the oily residue washed two times with diethyl ether and then dried under vacuum at 70 °C. The bis-trifluoromethanesulfonamide derivative **1** was recovered in pure form in 61% yield (Fig. 1).

^1H NMR (CDCl_3): δ 7.1 (s, NH), δ 3.8–3.2 (m, CH_2O , $\text{CHCH}_3\text{-CH}_2$ and CH_2N), δ 1.2 (m, $-\text{CHCH}_3\text{-CH}_2$). ^{19}F NMR (CDCl_3): δ -81.6 (s, CF_3).

1 g bis-trifluoromethanesulfonamide derivative **1** (1.07 mmol) was dissolved in 5 mL THF. 26 mg LiH (3.21 mmol) were added slowly to the solution at 0 °C. The reaction was kept at 0 °C for 30 min and at room temperature for 2 h. The solid (residual LiH) was then filtered off and the solvent was evaporated. The lithium IL was recovered in pure form in 91% yield. In the forthcoming, the lithium IL is denoted as Jeffamimne diLi.

^1H NMR (CDCl_3): δ 4.2–3.2 (m, CH_2O , $\text{CHCH}_3\text{-CH}_2$ and CH_2N), δ 1.2 (m, $-\text{CHCH}_3\text{-CH}_2$). ^{19}F NMR (CDCl_3): δ -81.6 (s, CF_3).

2.3. Synthesis of dimethacrylate jeffamine

The precursor of the PPO-PEO-PPO network was synthesized by reaction between Jeffamine ED 600 and isocyanatoethyl methacrylate in order to obtain a dimethacrylate derivative of Jeffamine (Figure S2). Briefly, 3 g Jeffamine ED 600 (4.51 mmol) were dissolved in 20 mL anhydrous chloroform under argon with 10 mg hydroquinone. 1.82 g 2-isocyanatoethyl methacrylate (11.7 mmol) were added drop wise to the former solution at -5 °C. The reaction was kept at -5 °C for 30 min and at room temperature for 48 h. The

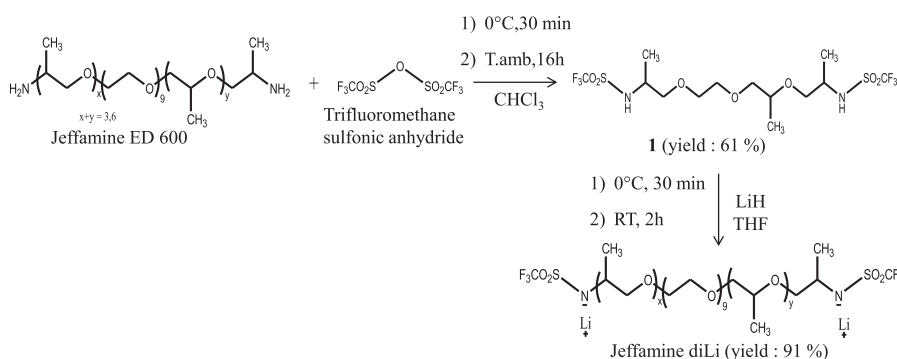


Fig. 1. Synthesis of lithium conducting ionic liquid: Jeffamine diLi.

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