



# Single-ion triblock copolymer electrolytes based on poly(ethylene oxide) and methacrylic sulfonamide blocks for lithium metal batteries



Luca Porcarelli <sup>a, b</sup>, M. Ali Aboudzadeh <sup>a</sup>, Laurent Rubatat <sup>c</sup>, Jijeesh R. Nair <sup>b</sup>,  
Alexander S. Shaplov <sup>d, e</sup>, Claudio Gerbaldi <sup>b, \*</sup>, David Mecerreyes <sup>a, \*\*</sup>

<sup>a</sup> POLYMAT, University of the Basque Country (UPV/EHU), Joxe Mari Korta Center, Avenida Tolosa 72, 20018 Donostia-San Sebastian, Spain

<sup>b</sup> Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

<sup>c</sup> CNRS/UNIV Pau & Pays Adour, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR5254, 64000, Pau, France

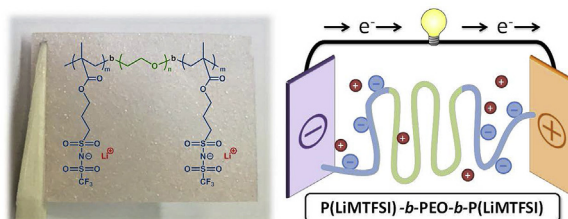
<sup>d</sup> A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, 119991 Moscow, Russia

<sup>e</sup> Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

## HIGHLIGHTS

- New triblock copolymer electrolytes synthesized by RAFT polymerization.
- High ionic conductivity and lithium single ion conduction in polymer electrolytes.
- High performance at elevated C-rate in all-solid lithium polymer cells.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 11 April 2017

Received in revised form

28 July 2017

Accepted 8 August 2017

### Keywords:

Polymer electrolytes

Block copolymers

Single ion conductors

Lithium batteries

## ABSTRACT

Single-ion conducting polymer electrolytes represent the ideal solution to reduce concentration polarization in lithium metal batteries (LMBs). This paper reports on the synthesis and characterization of single-ion ABA triblock copolymer electrolytes comprising PEO and poly(lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) blocks, poly(LiMTFSI). Block copolymers are prepared by reversible addition-fragmentation chain transfer polymerization, showing low glass transition temperature ( $-55$  to  $7$  °C) and degree of crystallinity (51–0%). Comparatively high values of ionic conductivity are obtained (up to  $\approx 10^{-4}$  S cm $^{-1}$  at  $70$  °C), combined with a lithium-ion transference number close to unity ( $t_{Li^+} \approx 0.91$ ) and a 4 V electrochemical stability window. In addition to these promising features, solid polymer electrolytes are successfully tested in lithium metal cells at  $70$  °C providing long lifetime up to 300 cycles, and stable charge/discharge cycling at C/2 ( $\approx 100$  mAh g $^{-1}$ ).

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Solid polymer electrolytes (SPEs), commonly composed of a lithium salt mixed with an ion-solvating polymer, are ideal candidates to replace flammable and toxic liquid electrolytes in lithium metal batteries [1,2]. Advantages of SPEs include increased thermal stability and non-flammability due to the absence of volatile

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [claudio.gerbaldi@polito.it](mailto:claudio.gerbaldi@polito.it) (C. Gerbaldi), [david.mecerreyes@ehu.es](mailto:david.mecerreyes@ehu.es) (D. Mecerreyes).

solvents. In addition, good mechanical properties allow the fabrication of flexible and thin batteries with increased energy density [3,4]. Among neutral ion-solvating polymers, poly(ethylene oxide) (PEO) shows the best ability to dissolve lithium salts but also slow lithium ion diffusion through its semi-crystalline phase [5]. Finally, SPEs having lithium-ion transference number ( $t_{Li^+}$ ) approaching unity can be prepared by tethering the anions of the lithium salt to the polymer backbone. The theoretical benefits of single-ion conductors include improved power delivery, reduction of polarization losses and suppression of lithium dendrites growth on lithium metal electrodes [6–9]. Sustained by this idea, many recent studies are focusing on combining the good solvating properties of PEO with single-ion conduction.

One simple strategy is to prepare composite membranes by mixing PEO with an anionic polyelectrolyte, such as lithium poly(styrenesulfonyl(trifluoromethylsulfonyl)imide) (PSTFSI). Adopting this approach, Armand and coauthors [10,11] reported moderate conductivities at 70 °C ( $\sigma = 9.5 \times 10^{-6} \text{ S cm}^{-1}$ ) resulting from inter-spherulitic segregation between PSTFSI and the semi-crystalline phase of PEO. Immiscibility issues can be attenuated by preparation of block copolymer of PSTFSI and PEO. Recently, Bouchet et al. [12] reported on triblock copolymers having a central PEO block and side PSTFSI ones, while Balsara and coworkers studied analogous dual block copolymers [13–15]. Again, the ionic conductivity was strongly depended on the polymer morphology. Near ambient temperature, an ordered lamellar structure was obtained, in which lithium ions were isolated into the glassy PSTFSI micro phase. At high temperature, a thermodynamic transition to a disordered structure resulted in a conductivity increase of several orders of magnitude (in the range of  $10^{-5} \text{ S cm}^{-1}$  at 70 °C). Interestingly, similar morphology–conductivity relationship were recently showed by Elabd and coworkers [16,17]. In conclusion, PSTFSI can be used to prepare SPEs with excellent mechanical and thermal stability, but the highest ionic conductivities are still limited to  $1.3 \times 10^{-5} \text{ S cm}^{-1}$  at 60 °C [12].

We recently reported on the synthesis of block copolymers based on a new methacrylic anionic monomer [18], namely lithium 1-(3-(methacryloyloxy)propylsulfonyl)-1-(trifluoromethylsulfonyl)imide (LiMTFSI), and poly(oligoethylene glycol methyl ether methacrylate). Our block copolymer showed high ionic conductivity values, in the range of  $10^{-5} \text{ S cm}^{-1}$  at 70 °C. However, these block copolymers have low glass transition temperatures and cannot form free standing membranes. In this paper, we present the synthesis and characterization of single-ion conducting triblock copolymer electrolytes based on linear PEO and side poly(LiMTFSI) blocks. By means of RAFT polymerization, it is possible to tailor the composition of block copolymers and the degree of crystallinity, which in its turn allows obtaining highly conductive and free-standing films with the lithium transference number close to unity. Finally, the electrochemical performance of lab-scale lithium cells are shown, demonstrating promising prospects of these materials for the next generation of safe lithium solid state batteries.

## 2. Experimental section

### 2.1. Materials

4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB, >97%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, ≥99%, Aldrich), hexane (Acros), tetrahydrofuran (THF, Acros), dichloromethane (DCM, Acros), acetonitrile (ACN, HPLC grade 99%, Acros), 2,2'-azobis(2-methylproprionamide) dihydrochloride (AIBA, initiator, 97%, Aldrich), and lithium hydride (LiH, Aldrich), carbon-coated lithium iron phosphate (LiFePO<sub>4</sub>, Advanced Lithium Electrochemistry Co.

Ltd.), carbon black C<sub>65</sub> (Timcal), lithium metal foil (Chemetal Foote Corporation) and carbon coated aluminum foil (Showa Denko) were used as received. Poly(ethylene oxide) (PEO,  $M_w = 8000$  and  $35000 \text{ g mol}^{-1}$ , Aldrich) was firstly dried by azeotropic distillation with toluene and further on was thoroughly dried at 80 °C under high vacuum for 12 h. The Spectra/Por 3 (Spectrumlabs) dialysis membranes with MWCO 3500 and 12–14000 Da were used for polymer dialysis.

### 2.2. Lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethanesulfonyl)imide (LiMTFSI)

LiMTFSI was synthesized via a three step synthetic procedure in full accordance with previous reports [18,19].

### 2.3. Synthesis of PEO based macro-chain transfer agents (PEO macro-CTAs)

10 g of freshly dried PEO (0.29 mmol,  $M_w 35000 \text{ g mol}^{-1}$ ) were dissolved in 100 mL of anhydrous DCM and cooled down to 0 °C under inert flow (N<sub>2</sub>). The CPADB (0.95 g, 3.42 mmol) and DCC (0.77 g, 3.76 mmol) were dispersed in 20 mL of anhydrous DCM and the obtained dispersion was slowly added to the PEO solution under inert atmosphere. The stirring was continued at 0 °C for 15 min, whereupon the solution of DMAP (0.13 g, 1 mmol) in the smallest amount of DCM ( $V < 2 \text{ mL}$ ) was added to the reaction flask. The reaction proceeded for 48 h at 0 °C and the precipitated by-products were removed by filtration. The obtained polymer solution was precipitated from cold diethyl ether. Solvents were decanted; the obtained polymer was re-dissolved in anhydrous DCM and precipitated twice from cold diethyl ether. The product in form of a slightly pink powder was thoroughly dried under high vacuum at 25 °C and stored at 5 °C before further use. Yield: 8.8 g (88%); Anal. Calcd. for C<sub>1616</sub>H<sub>3206</sub>N<sub>2</sub>S<sub>4</sub>O<sub>798</sub> (35577.07), %: C, 54.57%; H, 9.09%; N, 0.08%; Found, %: C, 54.52%; H, 9.07%; N, 0.08%; IR (ATR mode): 2880 (s,  $\nu_{C-H}$ ), 2740 (w,  $\nu_{C-H}$ ), 2694 (w,  $\nu_{C-H}$ ), 1735 (w,  $\nu_{C=O}$ ), 1466 (m), 1359 (m), 1342 (s), 1279 (m), 1241 (m), 1146 (s), 1102 (vs,  $\nu_{C-O-C}$ ), 1060 (vs,  $\nu_{C-O-C}$ ), 961 (vs), 841 (vs), 528 (w), 509 (w), 387 (w), 368 (w)  $\text{cm}^{-1}$ . The same procedure was applied on 10 g of PEG (1.25 mmol,  $M_w = 8000 \text{ g mol}^{-1}$ ) using the following amount of reactants: CPADB (4.1 g, 15 mmol), DCC (3.4 g, 16.5 mmol) and DMAP (0.5 g, 4.5 mmol). Yield: 8.3 g (83%); Anal. Calcd. for C<sub>390</sub>H<sub>754</sub>N<sub>2</sub>S<sub>4</sub>O<sub>185</sub> (8560.30), %: C, 54.72%; H, 8.88%; N, 0.33%; Found, %: C, 54.57%; H, 8.71%; N, 0.36%.

### 2.4. Synthesis of triblock copolymers, poly(LiMTFSI)-*b*-PEO-*b*-poly(LiMTFSI)

The example is provided for the preparation of poly(LiMTFSI)<sub>11k</sub>-*b*-PEO<sub>35k</sub>-*b*-poly(LiMTFSI)<sub>11k</sub> (**11k-35k-11k**): a solution of PEO<sub>35k</sub> macro-CTA (0.7 g,  $M_w \approx 35 \text{ kg mol}^{-1}$ , 20  $\mu\text{mol}$ ), LiMTFSI (0.47 g, 1.35 mmol) and AIBA (1.09 mg, 4  $\mu\text{mol}$ ) in 4.7 mL of milli-Q water was placed in a Schlenk tube equipped with a magnetic stir bar. The reaction mixture was subjected to three freeze-pump-thaw cycles, flashed with nitrogen, and placed into an oil bath pre-heated at 65 °C. The reaction reached the desired monomer conversion of ~80% after 11 h at 65 °C, whereupon the tube was opened and the reaction mixture was diluted with milli-Q water. The obtained solution was dialyzed against milli-Q water for 3 days ( $M_w$  cutoff of 3500 was used) and freeze-dried. Finally, triblock copolymer was thoroughly dried at 80 °C high vacuum for 24 h. All lithium triblock copolymers were prepared similarly by changing the ratio between the initial concentration of the PEO macro-CTA and the LiMTFSI monomer. The theoretical molar masses of triblock copolymers were calculated using the following equation:

Download English Version:

<https://daneshyari.com/en/article/5148693>

Download Persian Version:

<https://daneshyari.com/article/5148693>

[Daneshyari.com](https://daneshyari.com)