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New approach to design solid block copolymer electrolytes for 40 °C lithium metal battery operation

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ABSTRACT

Block copolymer electrolytes (BCEs) are promising solid electrolytes in lithium metal batteries thanks to the versatility of the block chemistry. In this work, several triblock BCEs, based on a modified poly (ethylene oxide) (PEO) central block and two polystyrene (PS) lateral blocks, have been synthetized by controlled radical polymerization. By including few chemical defects homogeneously distributed along the PEO chains, we managed to break its stereo-regularity, which allows lowering significantly its melting temperature, and therefore obtaining good ionic conductivity at 40 °C. The mechanical properties were controlled by the length of the peripheral polystyrene blocks, which were varied from 2.9 to 11.3 kg/mol. We performed systematic analysis of morphologies, thermodynamic properties, mechanical properties, and ionic transport properties of these new BCEs that we compared to a triblock copolymer electrolyte based on a PEO central block. Finally, we characterized the performances of the BCE with the best compromise between mechanical strength and conductivity as electrolyte in a lithium metal battery using $LiFePO_4$ as positive electrode active material. This device has been cycled at different rates from 40 °C to 80 °C with promising performances especially at 40 °C.

1. Introduction

Due to safety issues solid polymer electrolytes are more and more envisioned for large scale applications such as electric vehicles (EV), and intermittent energy storage [1]. PEO has been known to be the polymer with the highest conductivity because of a low T_g and a good donor number thanks to the ether functions [2,3]. But PEO is a semi-crystalline polymer with a melting temperature around 60 °C. The problem is that conductivity is not sufficient below this temperature and mechanical properties are lost above, which do not preserve from dendritic growth [4,5] and leads to the death of the device. In order to have both good ionic conductivity and mechanical strength that are antagonist properties [6–8], one elegant solution is to design nano-structured block copolymers [9]. In these materials, a block, generally based on PEO, provides the lithium conductivity, and another block, based on high glass transition temperature polymer, like polystyrene, provides the mechanical strength. One of these copolymers is a triblock copolymer PS-PEO-PS (SEOS) [10], which presents really good mechanical strength above its melting temperature (Young's modulus of 0.3 MPa at 60 °C). However, the PEO block crystalizes below 55 °C, inducing a strong drop of ionic conductivity and limiting its use at temperatures above 55 °C. Therefore, further improvements are necessary to decrease the temperature of application of Lithium Metal Polymer (LMP) technologies to facilitate its widespread use.

One solution is to modify linear PEO by breaking its stereoregularity [11–14] or to prepare comb-like PEO based polymers [15–20] in order to decrease both the crystallinity and the melting temperature.

In the present work, series of BAB triblock copolymers are synthesized from an A block based on a linear modified PEO in which double bonds are introduced in the PEO chain, in order to decrease melting temperature and degree of crystallinity. Moreover, to raise mechanical strength, we decided to design triblock copolymer with polystyrene blocs.

In the present work, our approach was to synthesize a linear modified PEO A block in which chemical defects, herein double bonds, are homogeneously introduced in the PEO chains, in order

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to decrease the melting temperature and degree of crystallinity of the PEO based domain. We synthetized two modified PEO A blocks, varying the distance between the chemical defects in the PEO chain. To raise the mechanical strength, lateral polystyrene blocks have been used to produce a series of triblock copolymers varying the polystyrene content.

We carried out a systematic analysis of the physicochemical and electrochemical properties of these block copolymer electrolytes (BCEs). Especially, the effects of the modification of PEO as well as the composition of the BCE have been analyzed. The best compromise between ionic conductivity and mechanical properties allows the selection of the optimal composition. Finally, the best BCE has been used to assemble lithium metal batteries using $LiFePO_4$ as positive active material. The cycling life as well as the power performance at 40 °C, 60 °C and 80 °C have been characterized.

2. Experimental

2.1. Materials and block copolymers (BCP) synthesis

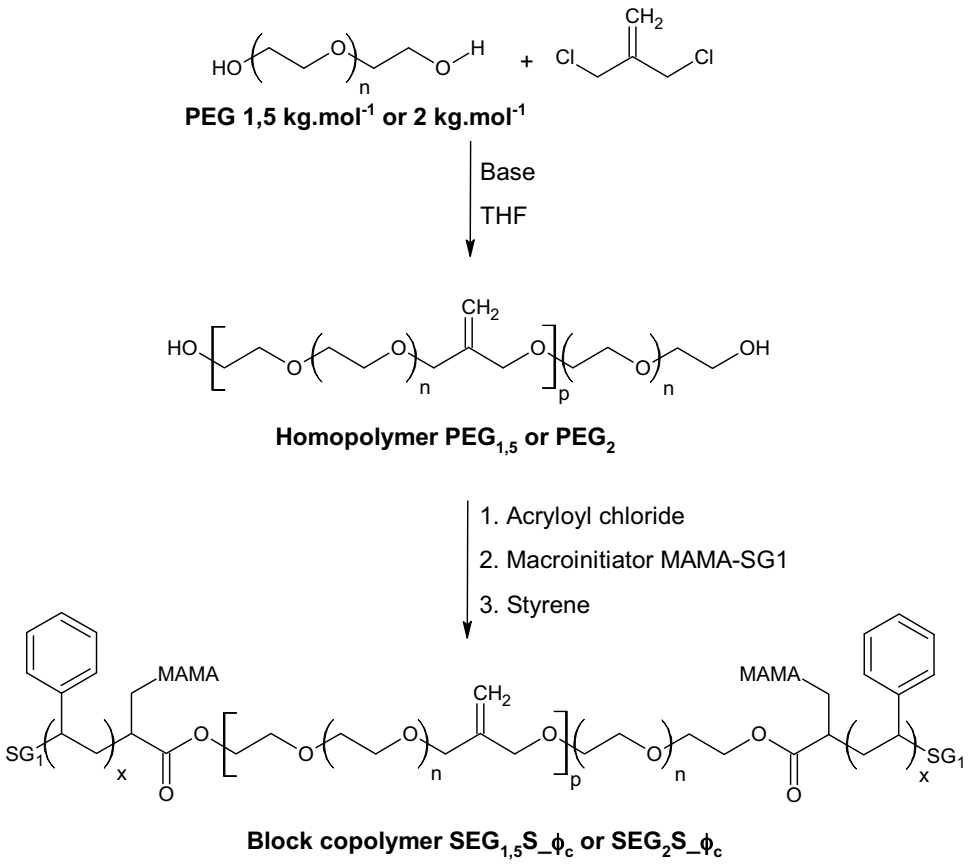
Styrene (99%), triethylamine (99%), acryloyle chloride (97%) and the bis-trifluoromethansulfonylimide lithium salt (LiTFSI) were purchased from Aldrich and used as received. MAMA-SG1 or BlocBuilder (>99%), an alkoxyamine based on the nitroxide SG1 {N-tert-butyl-N-[1- diethylphosphono(2,2-dimethylpropyl)]nitroxide} and the 1-carboxy- 1-methylethylalkyl moiety, was kindly provided by Arkema Co. The polyethylene glycol (PEG) with molecular weight of 1.5 kg mol^{-1} and 2 kg mol^{-1} were purchased from Alfa Aesar and used as received. All solvents and other reagents were synthesis grade and used without further purification.

The modified PEO blocks with molecular weight around 20 kg mol^{-1} were obtained by polycondensation [21] of either PEG of 1.5 or 2 kg mol^{-1} with 0.94 equivalent of 3-chloro-2-chloromethyl-1-propene (Scheme 1). The obtained polymer was purified by ultrafiltration through 3 kg mol^{-1} cutoff membrane. The ^{1}H NMR analysis shows signal of the expected product with a high purity. The number-average molecular weight (M_n) and dispersity of the obtained modified PEG were determined using size-exclusion chromatography. Measurements were performed in N,N-dimethylformamide + 0.05 M $NaNO_3$ salt at a flow rate of 1 mL/min. The chromatographic analysis has given a M_n of 19 kg mol^{-1} and 23 kg mol^{-1} for the 1.5 and the 2 kg mol^{-1} based PEG respectively. After purification, a polydispersity of 1.6 is obtained for both polymers.

The modified PEO terminated hydroxyl were then used to prepared BAB triblock copolymers using the nitroxide-mediated polymerization (NMP) method according to previously developed protocol [10]. Briefly, the synthesis of the BAB triblock copolymers involves three steps: i) the preparation of PEO-diacrylate by esterification of PEO terminated hydroxyl with an acryloyl chloride, ii) the intermolecular radical addition of MAMA-SG1 alkoxyamine onto PEO-diacrylate and iii) the polymerization of styrene using modified PEO-$(MAMASG1)_2$ as an initiator.

Finally, a series of BCP has been produced by varying the proportion of the A block. The list of the obtained materials with their molecular weight is given in the Table 1. The molar mass of PS was determined by ^{1}H NMR analysis knowing the molar mass of modified PEO block.

For simplicity, the BCE (Table 1), are labeled $SEG_xS\_\phi_c$, where x corresponds to the molecular weight of PEG condensate (1.5 kg mol^{-1} or 2 kg mol^{-1}) and ϕ_c to the volume proportion (%) of conducting phase (modified PEO laden with LiTFSI at EO/Li = 25).



Scheme 1. Scheme of the general synthesis of $SEG_xS\_\Phi_c$ copolymers.