Solid State Ionics 320 (2018) 45–54

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Polymer electrolytes through functionalization of poly (poly (ethylene glycol) methacrylate) with zwitterionic pendant groups: The role of ion clusters upon conductivity

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ARTICLE INFO

Keywords:
Polymer electrolyte
Poly(poly(ethyleneglycol) methyl ether methacrylate)
Sulfobetaine group
Ionic conductivity
$LiPF_6$

ABSTRACT

The present study proposes a complete (pMPS8) and partial (pMPS8-*co*-PEGDMA) functionalization of poly(poly (ethyleneglycol) methyl ether methacrylate) (pPEGMA) with zwitterionic pendant groups to improve the mobility of polymer chains and ion-ion associations during Li^+ conduction (weak electrolyte). Structural, thermal and electrochemical characterizations of the polymer electrolytes are conducted to analyze the dependence of conductivity on $LiPF_6$ concentration. The ionic conductivity of pMPS8 ($3.22 \times 10^{-5}\,S\,cm^{-1}$ at 25 °C) in the presence of $LiPF_6$ is due to the incorporation of the zwitterionic pendant groups into the pPEGMA. In pMPS8, a more significant interaction of Li^+ with the sulfobetaine group at low $LiPF_6$ concentrations, decreases its ion movement. While at higher salt concentrations, the saturation of sulfonate groups with Li^+ makes possible its interaction with ethoxy sites, thus, increasing ionic conductivity. pMPS8 is less sensitive (i.e. ionic conductivities remain constant) to the increases of salt concentration compared to the pMPS8-*co*-PEGDMA (larger number of ethoxy sites per pendant groups) due to its complete functionalization (short range mobility). The ionic conductivity for pMPS8-*co*-PEGDMA polymer starts to be significant at molar ratios higher than 1.0: 1.0, suggesting that above this stoichiometry the interactions between zwitterion pendant groups and lithium salt become suppressed, enabling its use at higher $LiPF_6$ concentrations. The analysis of TGA, DSC, XRD and EIS exhibit that ionic conductivity is coupled with the mobility of chains, hence the transport mechanism occurs through dynamic percolation theory where the translational dynamics of the ions depends on segmental dynamics and by renewal of hopping probabilities.

1. Introduction

An alternative to solve the drawbacks reported for liquid electrolytes in Li-ion batteries can be the use of solid polymer electrolytes (SPE), mixing a lithium salt with a solvent-free polymer matrix [1]. Under this condition, SPE should present characteristics as solvents and charge carriers. Of particular interest to solvation is the complete salt dissociation, which is influenced by chain structure coordination and the high concentration of sequential polar groups on its backbone (e.g. ether groups), thus, the distance between coordinating centers, flexible backbone, and low steric hindrance for bond rotation are important factors, affecting force solvation and consequently Li^+ ion transport [2–4]. High ionic conduction has been typically associated with amorphous phases, rather than crystal ones [5], with the lowest possible transition temperature (T_g) to achieve a good flexibility of polymer chains. During this process, Li^+ ions are transported in the remaining space left by the free volume of the polymer host, enabling conduction above T_g of the polymer. This behavior exhibits a diffusive liquid-like effect in the SPE.

Polyethylene oxide (PEO) contains oligo(oxyethylene) side chains able to dissolve salts without the addition of any liquid solvent [6]. Ethylene oxide (EO) -$(CH_2\text{-}CH_2O)_n$- provides suitable spacing for solvation and wrapping of cations, while methylene oxide -$(CH_3O)_n$- and propylene oxide -$(CH_2CH_2CH_2O)$- do not present these properties [7]. However, its cyclic oligomers chains induces a high degree of crystallinity since they are interlocked to form helical tunnel or cylinders [6,8]. At low salt concentrations, amorphous phases of PEO provide an adequate ionic conduction [5], but charge segregation occurs at high

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https://doi.org/10.1016/j.ssi.2018.02.031
Received 14 December 2017; Received in revised form 13 February 2018; Accepted 15 February 2018
0167-2738/

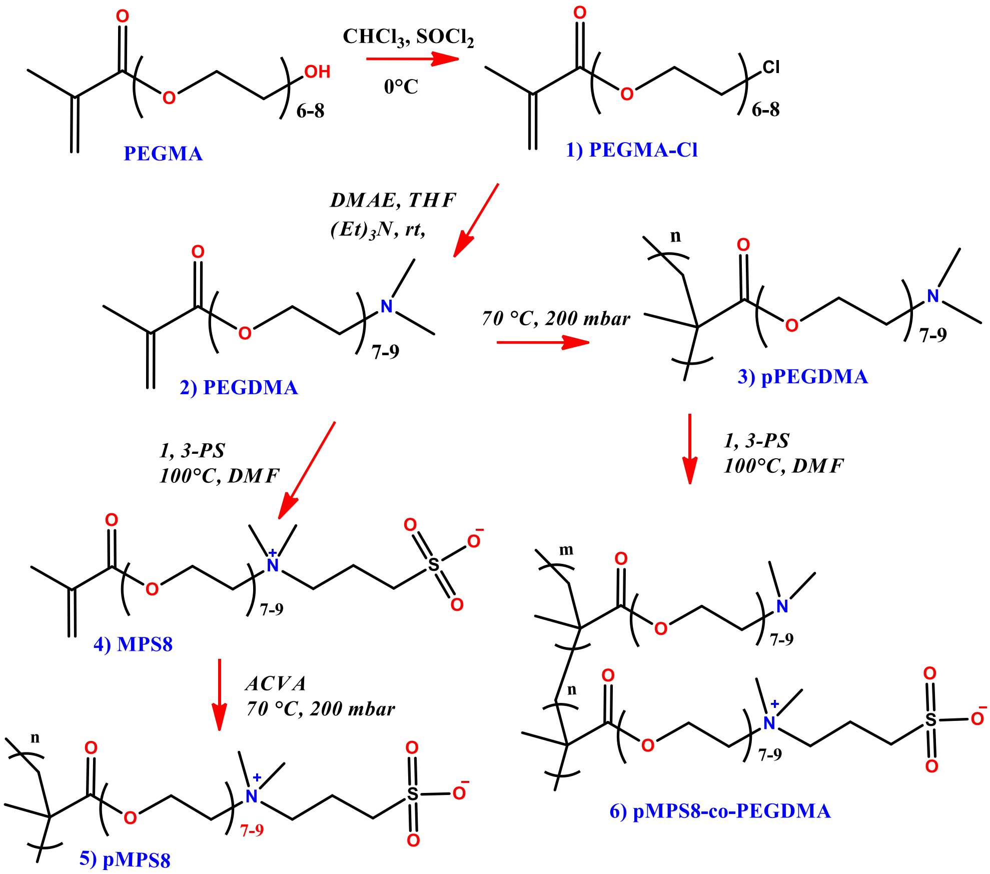

Fig. 1. Synthesis pathway to obtain a complete (pMPS8) and partial (pMPS8-*co*-PEGDMA) functionalization of zwitterionic polymers.

concentrations ($[Li^+]/[EO] = 0.2 \approx$ 1.0:0.03 M ratio), since Li^+ ions are trapped into these cylinders; and the "salting out" phenomenon appears at high temperature, where ion-ion interactions become significant because bond length decreases. The presence of these aggregates and cross-link formation restrict the number of free ions and mobility of polymer chains, thus, decreasing ionic conductivity [4,6,9,10]. Copolymers containing flexible blocks such as poly(poly (ethyleneglycol) methyl ether methacrylate (pPEGMA) can be used to minimize these structural limitations. The preparation of an amorphous methacrylate-type polymer is an alternative to abate T_g as the number of ethoxy groups in its side chains are increased [11]. The oxygen atoms of ethoxy and carbonyl groups develop weak coordination shells with Li^+, allowing ion-ion associations as a weak electrolyte that are unstable at high temperatures. The internal energy becomes great enough to overcome the barrier causing a significant chain motion and releases Li^+ ions [12]. Thus, amorphous segmental chains are increased in pPEGMA, where Li^+ transference favourably occurs at higher temperatures than T_g. The properties of amorphous pPEGMA can be enhanced by the introduction of functional groups, decreasing a strong interaction between polymer chains and lithium salt, which can unfavourably decrease the ionic conductivity. To this concern, the insertion of zwitterionic pendant groups in a methacrylate-type polymer enables to interact with different inorganic salts in a 1.0:1.0 M ratio (e.g. LiCl, LiTFSI and $LiClO_4$), without compromising the phase separation or altering its fundamental skeleton [11]. Additional studies of this zwitterionic polymer have revealed that its T_g decreases as a function of the number of ethoxy groups in lateral [11,13] chains, from 254 °C when there is one ethoxy group to 18 °C for four groups, which can enhance mobility of polymer chains.

On the other hand, favourable effects have been reported in ionic conductivity when $LiPF_6$ concentration is increased to values around 20 wt% for PEO [14], and a previous study conducted by our research group has demonstrated that the augment of $LiPF_6$ concentration in pPEGMA ($Li^+/O = 0.54 \approx$ 1.0:1.0 M ratio) enhances ionic conductivity [12]. Not surprisingly, these benefits are rendered from the strong dependence of free ion concentration, which on its turn relies on salt solubility and energy of anion-cation (i.e. EO groups - Li^+ interaction) dissociation in the electrolyte. However, as any other solvent, polymer structure is able to assimilate a limited concentration of salt, otherwise, ion pair or cluster formation results in restricted Li^+ transference. Thus, the present study aims to account for the influence of functionalization with zwitterionic pendant groups in poly(poly (ethylene glycol) methacrylate) (pMPS8) and copolymerized with dimethylamine-poly (ethyleneglycol)methacrylate (pMPS8-*co*-PEGDMA) upon thermal and electrochemical properties. The premise under the comparison of these two polymer electrolytes is to evaluate if a complete or partial functionalization provides better active sites for ionic conduction due to the probable saturation of certain sites along the polymer (i.e. near by the pendant group), and the role of ion cluster formation in order to promoting Li^+ conduction. Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), X-ray diffraction (XRD), Attenuated total reflection Fourier transform infrared (AR-FTIR) and Electrochemical Impedance Spectroscopy (EIS) are used for these purposes.

2. Materials and methods

Poly(ethyleneglycol)methacrylate (Molecular weight = 360 g mol^{-1}) (PEGMA), dimethylethanolamine (DMA), thionyl chloride ($SOCl_2$), triethylamine ($(Et)_3N$), 1,3-propanesultone (PS), 4,4′-Azobis(4-cyanovaler-icacid) (ACVA) and lithium hexafluorophosphate ($LiPF_6$), were obtained from Sigma-Aldrich and used as received.