



Research Paper

Comb-like solid polymer electrolyte based on polyethylene glycol-grafted sulfonated polyether ether ketone



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ABSTRACT

Solid polymer electrolytes based on a novel comb-like copolymer, polyethylene glycol-grafted sulfonated polyether ether ketone (SPEEK-g-PEG), was designed and synthesized through the reaction between partially hydroxyl-functionalized sulfonated polyether ether ketone (SPEEK) and epoxy-functionalized PEG. The resulting SPEEK-g-PEG was fully characterized by FTIR, ¹H NMR, TGA, and DSC. All data proved the successful grafting of PEG onto the SPEEK main chain. The resulting comb-like structure effectively inhibited the crystallization of PEG. After doping with a lithium salt, the obtained SPEEK-g-PEG polymer electrolyte membrane showed an improved ionic conductivity. The effects of chain length and PEG grafting ratio on the ionic conductivity of SPEEK-g-PEG were also investigated by electrochemical impedance spectroscopy (EIS). Moreover, the effect of this comb-like structure on increasing the ionic conductivity is higher than that of SPEEK/PEG blends, making these comb-like SPEEK-g-PEG copolymers attractive for an application in LIBs.

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1. Introduction

Lithium ion batteries (LIBs) have a higher energy density, higher open-circuit voltage, and longer lifetime compared with other rechargeable systems such as nickel-cadmium and nickel-metal hydride batteries. Therefore, LIBs are considered as one of the most promising power systems [1,2]. As one of the critical components, the electrolyte plays a vital role in preparing safe and high-performance LIBs. In most of the current commercial LIBs, liquid electrolytes based on lithium salts containing volatile organic solvents and separators have been widely used because of their high ionic conductivity and low electrode–electrolyte contact impedance. However, performance decay and safety problems of liquid electrolytes, including leakage, explosion, and flammability, present obstacles for the large-scale commercialization of LIBs [3–

5]. Therefore, seeking alternatives to liquid electrolytes has been the major focus in LIB research in recent decades.

Solid polymer electrolytes (SPEs) with excellent safety, good mechanical performance, and shape flexibility have drawn considerable attention as important alternatives to liquid electrolytes [6–8]. Since Wright et al. [9,10] firstly proved the ionic conduction ability in polyethylene oxide (PEO)-lithium ion complexes, the use of many polymers, such as PEO [11–13], polypropylene oxide (PPO) [14,15] and polyethyleneimine (PEI) [16], as SPEs has been widely studied. As the earliest and most extensively studied systems, PEO-based SPEs stand out for their strong Li⁺ solvating ability, good chemical stability, wide electrochemical window, excellent film-forming property, and toughness [13]. In PEO-based electrolytes, lithium ions are mainly conducted through the ether oxygen atoms, which can act as coordination sites and thus promote the association/dissociation of lithium salts. However, although PEO-based systems show relatively high ionic conductivities at high temperatures, the crystallization of PEO at low temperatures severely hinders the ion transport through the electrolyte system because the ion conduction mainly occurs in the amorphous phase of PEO [17–19]. Furthermore, the

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preference for crystallization, especially for linear PEO, may result from the long polymer chain packing of PEO during usage, thus decreasing the ionic conductivity. Hence, finding ways to reduce the crystallinity, thus to improve the ionic conductivity, while maintaining the appropriate mechanical properties, is still a key issue for the practical application of PEO-based SPEs.

Many strategies, including blending [20,21], modifying [22,23], and preparation of PEO derivatives [24,25], have been utilized to solve the above problems of PEO. Among these approaches, fabricating graft copolymers by introducing PEO side chains can effectively decrease the crystallinity of PEO. Zuckermann et al. [26] prepared three new comb-like peptoid polymers with ethylene oxide (EO)_n side chains of varying lengths. In these copolymers, polypeptoids with longer (EO)_n side chains exhibited rapid segmental motion, and the maximum conductivity could reach $2.6 \times 10^{-4} \text{ S cm}^{-1}$ at 100 °C. Recently, they reported the follow-up work on the structure–conductivity relationships of two types of ethyleneoxy-containing block copolypeptoids pNeh-*b*-pNte (poly [N-(2-ethyl)hexylglycine]-*b*-poly[N-2-(2-(2-methoxyethoxy)ethoxy)ethylglycine]) and pNdc-*b*-pNte (poly[N-decylglycine]-*b*-poly [N-2-(2-(2-methoxyethoxy)-ethoxy)ethylglycine]) [27]. These two copolymers have the same conducting block, pNte-containing EO side chains, but different non-conducting blocks, amorphous pNeh and crystalline pNdc, respectively. It was observed that the same conducting block exhibited different crystallization behaviors and thus resulted in different ionic conductivities within the two copolymers, providing new ways for tailoring the ionic transport properties based on these PEO copolymer electrolytes. In addition, star-shaped [28,29] and comb-like [30] copolymers with flexible PEG or PEO branches are also a favorable solution to decrease the crystallinity of PEO. Niitani et al. [28] synthesized star-shaped poly [styrene]-*b*-poly[poly(ethylene glycol) methyl ethyl methacrylate] copolymer, which possesses the characteristics of a SPE for an application in LIBs. This SPE system showed high ionic conductivity and improved LIB performance. Zaghib et al. [30] demonstrated another possible candidate for SPEs based on the comb-like copolymers poly(styrene-*co*-4-vinylanisole) (PS-VA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA). The ionic conductivities of these copolymers can be higher than $10^{-5} \text{ S cm}^{-1}$ at room temperature depending on their PEGMA/PS-VA ratios.

Recently, we also synthesized PEO-based star polymers with arms of different chain lengths through atom transfer radical polymerization [31]. These star polymers were blended with PVDF to fabricate microporous polymer electrolytes. This star structure can effectively destroy the crystallization of PEO and lead to fast molecule motion. The blended microporous membranes exhibited good pore distribution and connectivity, which resulted in a significantly improved ionic conductivity. Based on this, we designed and synthesized herein the novel comb-like copolymer SPEEK-*g*-PEG through an epoxide ring opening reaction between partially hydroxylated SPEEK and PEG-epoxide. The PEG side chains in this comb-like copolymer impeded the crystallization, while the highly rigid SPEEK main chain ensured high thermal stability and mechanical strength of the copolymer. We fully characterized structure and crystallization behavior of the SPEEK-*g*-PEG copolymer and evaluated the effects of temperature and PEG grafting ratio on the SPEEK-*g*-PEG SPEs.

2. Experimental

2.1. Materials

Polyetheretherketone (PEEK, 450PF, $M_w = 38,200$) was obtained from Victrex Inc. (England). Methoxy polyethylene glycol (PEG, $M_w = 350$ and 550, Aladdin Reagent Inc., China) was used as received. LiClO₄ (Sinopharm Chemical Reagent Co. Ltd., China) was

dried at 150 °C under vacuum for 24 h and stored in an argon-filled glove box before use. Concentrated sulfuric acid, sodium borohydride (NaBH₄), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), epichlorohydrin, triethanolamine, triphenylphosphine (TPP), and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used without further purification.

2.2. Synthesis of SPEEK-OH

First, Li⁺-functionalized SPEEK (SPEEK(Li)) was obtained by the direct lithiation of H⁺-type SPEEK (SPEEK(H); Scheme 1), which was prepared from PEEK using concentrated sulfuric acid as the solvent and sulfonating agent, as described in literature [30,31]. Typically, PEEK was dissolved in concentrated sulfuric acid at room temperature with a PEEK/H₂SO₄ ratio of 5/95 (w/v). After dissolution, the solution was heated to 55 °C and reacted for 2 h under mechanical stirring. Subsequently, the sulfonated PEEK solution was precipitated into deionized water to obtain SPEEK(H), which was then washed repeatedly with deionized water to remove the residual sulfuric acid until the pH value of the washing water was about 7. Finally, 0.5 g of SPEEK(H) was soaked in about 200 mL of an aqueous solution of lithium hydroxide (0.01 M) for three days to allow the full conversion of SPEEK(H) into its lithium salt to form SPEEK(Li).

Hydroxyl-functionalized SPEEK (SPEEK-OH) was synthesized by the reduction of the carbonyl groups of SPEEK(Li) according to the following procedure: 50 mL of DMSO and 0.1 g of NaBH₄ were added to a 100-mL round-bottomed flask. After the addition of 1.0 g of SPEEK(Li), the reaction was carried out at 120 °C for 12 h under continuous magnetic stirring. The mixture solution was then cooled down to room temperature, followed by precipitation in cold diethyl ether. The resulting SPEEK-OH was obtained by washing thoroughly with cold diethyl ether and then dried under vacuum.

2.3. Synthesis of PEG-epoxide

0.05 mol PEG was dissolved in 100 mL of dehydrated DMF containing 1% (w/v) of triethanolamine at 40 °C for 4 h under constant stirring. Then, 22.5 g epichlorohydrin was added to this solution, which was stirred overnight under reflux to convert the terminal hydroxyl group of PEG into an epoxide. The resulting mixture was precipitated in cold diethyl ether and then washed repeatedly with diethyl ether. The epoxide-derived PEG (PEG-epoxide) was obtained after drying under vacuum.

2.4. Synthesis of SPEEK-*g*-PEG

A 10-wt% solution of SPEEK-OH was mixed with PEG-epoxide in various concentrations and 2.5 wt% of TPP catalyst (based on PEG-epoxide weight) in DMSO and stirred until a transparent homogeneous solution was obtained. The reaction was carried out under constant stirring and reflux for 4 h. Then, the solution was precipitated in cold diethyl ether. The formed SPEEK-*g*-PEG was washed three times with cold diethyl ether and dried under vacuum. SPEEK modified with two differently long PEG chains ($M_w = 350$ and 550) were denoted as SPEEK-*g*-PEG350 and SPEEK-*g*-PEG550, respectively.

2.5. Preparation of SPEEK-*g*-PEG SPEs

SPEEK-*g*-PEG was dissolved in DMSO to form a 10-wt% homogeneous solution, and then LiClO₄ in the amount required for a molar ratio of [EO]/[Li⁺] = 8:1 was added into the SPEEK-*g*-PEG solution with stirring until a transparent homogeneous solution

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