



Six-arm star polymer based on discotic liquid crystal as high performance all-solid-state polymer electrolyte for lithium-ion batteries

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HIGHLIGHTS

- A discotic liquid crystal-based six-arm star polymer electrolyte was prepared.
- The film showed high ion conductivity due to orientation of the electrolyte.
- The electrolyte displayed excellent electrochemical performances.

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ABSTRACT

All-solid-state polymer electrolyte (SPE) matrices prepared by molecular design are still needed to be further perfected with excellent performance. In this paper, a controlled-structure discotic liquid crystal (DLC)-based six-arm star copolymer was designed and synthesized from a DLC initiator (2,3,6,7,10,11-hexakis(2-bromoisobutyryloxy)triphenylene) via the sequential atom transfer radical polymerization (ATRP) of styrene and poly(ethylene glycol) methyl ether methacrylate (PEGMA). Here, this class of discotic liquid crystal star polymer is applied as an SPE in LIBs for the first time. By solution casting, a suitable self-standing SPE film composed of the six-arm copolymer and lithium bis(trifluoromethanesulfonimide) (LiTFSI) can be easily formed, and the film shows long-range molecular orientation after annealing. It is confirmed that the electrolyte shows wide electrochemical window (5.1 V) and high lithium-ion transference number (0.37). Especially, the ionic conductivity (1.46×10^{-4} S cm⁻¹, 30 °C) of the obtained SPE is more than 8 times higher than that of the corresponding linear copolymer electrolytes. Furthermore, the results of battery performance demonstrate that the polymer electrolyte displays eminently reversible electrochemical reaction and outstanding cycling performance. The present work not only shows the advantages of DLC-based star SPE for LIBs but also paves the way for the design of SPE with excellent performances.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in applications from portable electronic devices to electric vehicles because they are lightweight materials with high energy densities and good long-term stabilities [1–6]. It is well known that commercial organic liquid electrolytes are still widely used in lithium batteries, because liquid electrolytes have high conductivity and promote excellent wetting of the electrode surfaces [7,8]. However, liquid electrolytes usually suffer from low ion selectivities, inadequate electrochemical and thermal stabilities, and especially safety risks (such as electrolyte leakage, fire

and explosion) [9]. All of these problems with liquid electrolytes hinder the large-scale commercialization of LIBs [10–13]. To overcome these issues, more focus must be put on electrolytes, because they are a key component in the ion transport between electrodes and affect the overall device performance [14,15]. Recently, all-solid-state polymer electrolytes (SPEs) have been proposed as one of the most promising candidates for cells (LIBs) because of their characteristic mechanical strength, and their potential to eliminate the need for electrode separators and flammable organic liquids [16–18]. However, it is difficult to simultaneously achieve both high mechanical strength and room temperature (RT) ionic conductivities in SPEs, and the development of

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polymer electrolyte membranes with both of these characteristics remains challenging.

Linear block copolymers are one of the most common motifs for SPE matrices. Linear block copolymers containing both rigid and flexible segments for use in SPE matrices have been extensively investigated. Although the typical linear copolymer SPE systems offer improvements in mechanical strength and RT conductivity [19–21], their RT ionic conductivities are still low and needed to be further improved. For instance, a recently reported polystyrene (PS)-*b*-poly(ethylene oxide) (PEO) copolymer SPE system only present optimal ionic conductivity in the range of 5×10^{-7} to 1×10^{-5} S cm⁻¹ at RT [16,20,22].

Compared to linear copolymer, the application of branched polymer as SPE matrix provides another effective method for improvement of the properties of the corresponding SPE [23]. Particularly, the ionic conductivity can be notably increased due to lower crystallinity of the branched matrix [24]. Star polymers (one of the simplest deviations from one-dimensional linear polymers, represent a broad class of branched polymers) have attracted immense interest from scientists because of their unique topological structures and physical properties, which are not found in their corresponding linear structures [25]. More specifically, the unique topological structures of star polymers allow for higher mobility in the outer sphere of arms, which likely can improve the ionic conductivity. Considering these characteristics, synthesis of new star polymers and application in solid polymer electrolytes may be promising to further improve the overall performance of SPEs.

To further improve the ionic conduction property of SPEs, ion conductive pathways must be constructed. Fortunately, liquid crystal materials with ordering properties can be used to construct ion conductive pathways for SPEs, offering a promising design strategy for such materials. Therefore, liquid crystal-decorated polymers have been received attention as polymer electrolyte matrices, as their orientation can obviously improve the RT ionic conductivity of the resulting SPEs [26–31]. However, almost all of these reports neglect the interfacial properties, problems with lithium dendrite formation, and cycle performance of liquid crystal-based polymer electrolytes in LIBs. Very recently, we synthesized a hyper-branched star liquid crystal polymer as an all-solid-state polymer electrolyte for LIBs, and this material showed good comprehensive electrochemical properties [32]. However, the electrochemical and cell performances were still not perfect. Obviously, the electrochemical and cell properties needed to be investigated further in order for mesogen-based polymers to realistically be applied as polymer electrolyte matrices for safe LIBs.

Herein, in order to combine the advantages of topological polymers and liquid crystals, a discotic liquid crystal-based six-arm star polymer (DLC-(PS-*b*-PPEGMA)₆) with a controlled degree of polymerization (DP) was synthesized via atom transfer radical polymerization (ATRP) and used as an SPE for LIBs for the first time. Especially, triphenylene (discotic liquid crystal) was selected as the core of the six-arm star polymer because of its remarkable self-assembly behaviors [33,34]. At temperature below the isotropic phase transition, the ordered nanocolumns can organize into superstructures with positional orders. This organization is attributed to the strong π - π interactions between aromatic cores, the nanophase separation between the rigid discotic cores and the flexible chain ends [35–37], and allows for the formation of ion-conductive channels.

To the best of our knowledge, there are very few reports on the development of polymer electrolytes based on discotic liquid crystal (DLC) and no reports use six-arm star polymers (with discotic liquid crystal used as the core for orientation) as high performance all-solid-state polymer electrolytes for LIBs. Compared to traditional linear copolymers-based electrolytes, the discotic liquid crystal-based six-arm star copolymer electrolyte shows much higher RT ionic conductivity (more than 8 times higher) because of their more flexible arms and long-range molecular orientation. In addition, the star polymer easily forms film, has a wide electrochemical window and has favorable lithium-ion transport number (t^+). Simultaneously, the prepared cells

based on the six-arm star SPE have highly reversible electrochemical reactions and outstanding cycling performances. The present work shows the advantages of DLC-based star SPEs for LIBs and provides a new method for designing polymer electrolytes with excellent performances.

2. Experimental

2.1. Materials

Veratrole (99%, Macklin, China), sulfuric acid (98–95%, Beijing Chemical Works), anhydrous ferric chloride (98%, Aladdin, China), glacial acetic acid ($\geq 95\%$, Beijing Chemical Works), 2-bromo-2-methylpropionyl bromide (98%, Aladdin, China), hydrogen bromide (48%, Aladdin, China), methanol (MeOH, Beijing Chemical Works) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 950$ g mol⁻¹, Aldrich) were used as received. N,N,N',N',N'-pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin, China) and styrene ($\geq 99\%$, Sinopharm Chemical Reagent Co., Ltd, China) were dried with CaH₂ and distilled under reduced pressure before use. Dichloromethane ($\geq 99.5\%$), tetrahydrofuran (THF) and toluene were purchased from Beijing Chemical Works and dried with CaH₂, and distilled before use. Triethylamine (TEA, 99%, Aladdin, China) was dried with 4 Å molecular sieves for 24 h before use. Copper(I) bromide (CuBr, 99%, Aladdin, China) was used after washing with acetic acid, methanol, and ether, respectively. Lithium bis(trifluoromethanesulfonimide) (LiTFSI, 99%, Aladdin, China) was dried under vacuum at 80 °C for 24 h before use.

2.2. Synthesis of polymers

The triphenylene central core was synthesized according to the literature [38]. 2,3,6,7,10,11-hexamethoxytriphenylene (I) was synthesized in the presence of FeCl₃ and CH₃COOH (ACOH) by a trimerization reaction. I was completely demethylated using HBr and ACOH while refluxing to give 2,3,6,7,10,11-hexahydroxytriphenylene (II). Subsequently, II was subjected to an esterification with 2-bromo-2-methylpropionyl bromide (to give the product III). Finally, the six-arm star polymers were obtained in two ATRP steps (III, the synthetic routes of the products are shown in Scheme 1)).

2.2.1. Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene (I (DLC-OCH₃))

H₂SO₄ (0.35 mL) was added to a suspension of FeCl₃ (25.5 g, 0.157 mol) in CH₂Cl₂ (150 mL). A solution of veratrole (6.91 g, 0.05 mol) in CH₂Cl₂ (50 mL) was added dropwise into the mixture. The reaction was stirred at 23 °C for 3 h after the addition of veratrole. Then, MeOH (200 mL) was slowly added into the mixture. The reaction mixture was stirred for another 30 min. Subsequently, the product was filtered, washed with 50 mL of MeOH (three times) and dried at 45 °C. ¹H NMR (400 MHz, CDCl₃, 27 °C, TMS): $\delta = 3.98$ (s, 18H, 6CH₃) and 7.89 (s, 6H, ArH).

2.2.2. Synthesis of 2,3,6,7,10,11-hexahydroxytriphenylene (II (DLC-OH))

2,3,6,7,10,11-hexamethoxytriphenylene (I) (1.25 g, 3.85 mmol) was added to a solution of HBr (48%, 45 mL) and ACOH (45 mL). The suspension was degassed by three freeze-pump-thaw cycles. Then, the mixture was refluxed at 125 °C for 24 h under N₂. A precipitate was formed after cooling the mixture to room temperature. The product was filtered and washed with 50 mL of cold water (three times). Colorless needles were obtained after recrystallizing the product from the suspension of activated carbon and AcOH/H₂O (1:1, 40 mL). ¹H NMR (400 MHz, DMSO, 27 °C, TMS): $\delta = 7.61$ (s, 6H, ArH) and 9.28 (s, 6H, 6OH).

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