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Sequential effect and enhanced conductivity of star-shaped diblock liquid-crystalline copolymers for solid electrolytes

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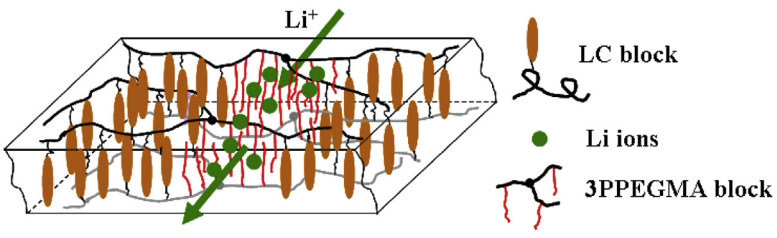
HIGHLIGHTS

- Novel star-shaped amphiphilic liquid crystalline copolymers are prepared.
- The copolymers consist of mesogenic segment and hydrophilic poly(-ethyleneoxide)s.
- Lamellar structures are achieved by cooperative assembly.
- The ionic channel is aligned greatly by orientation of the mesogens.
- Consequently ionic conductivity is improved.

GRAPHICAL ABSTRACT



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ABSTRACT

Star-shaped polymers are synthesized by atom transfer radical polymerization using poly-(methoxy-poly (ethylene glycol) methacrylate) (PPEGMA) as a hydrophilic segment and poly {10-[(4-cyano-4′-biphenyl) oxy] decatyl methacrylate} (PMALC) as a hydrophobic liquid crystalline segment. Lamellar morphology is also achieved by cooperative assembly of hydrophobic mesogen-containing polymethacrylates and the amorphous hydrophilic PPEGMA nanoscale aggregation, especially after liquid crystal thermal annealing. In addition, the sequential effect, that is, the position difference of the liquid crystalline segments in the copolymer electrolytes causes two quite different morphologies. The liquid crystalline segments arranged in the star polymer inner sphere makes it difficult for the mesogens to interact with each other efficiently, which leads to a discontinuous molecular packing. However highly ordered domains can be formed in the electrolytes with mesogens in the star copolymer exterior, which can provide a more favorable morphology for the ions transportation. As a result, incorporation of the liquid crystalline segments into the copolymer has improved ionic conductivity of electrolytes, especially for the 3PPEGMA-PMALC with the mesogen arranged in the outside of star copolymer sphere. Ionic conductivity of 3PPEGMA-PMALC annealed at liquid crystalline state is 1.0×10^{-4} S cm^{-1} at 25 °C, which is higher than that of 3PPEGMA electrolytes without mesogen groups.

1. Introduction

Solid polymer electrolyte (SPE) has been extensively studied for more than 20 years as an alternative for the traditional liquid electrolyte in lithium-ion cells because of their potential applications in many solid electrochemical devices such as high-energy density batteries, electrochromatic windows, chemical sensors, and light-emitting devices. [1,2] Most of the research work focused on poly (ethylene oxide) (PEO) and its derivatives as a polymer matrix, due to the ability of PEO to dissolve salts and high segmental flexibility for ion transport in the amorphous phase [3,4]. However, linear PEO-based polymer electrolytes show

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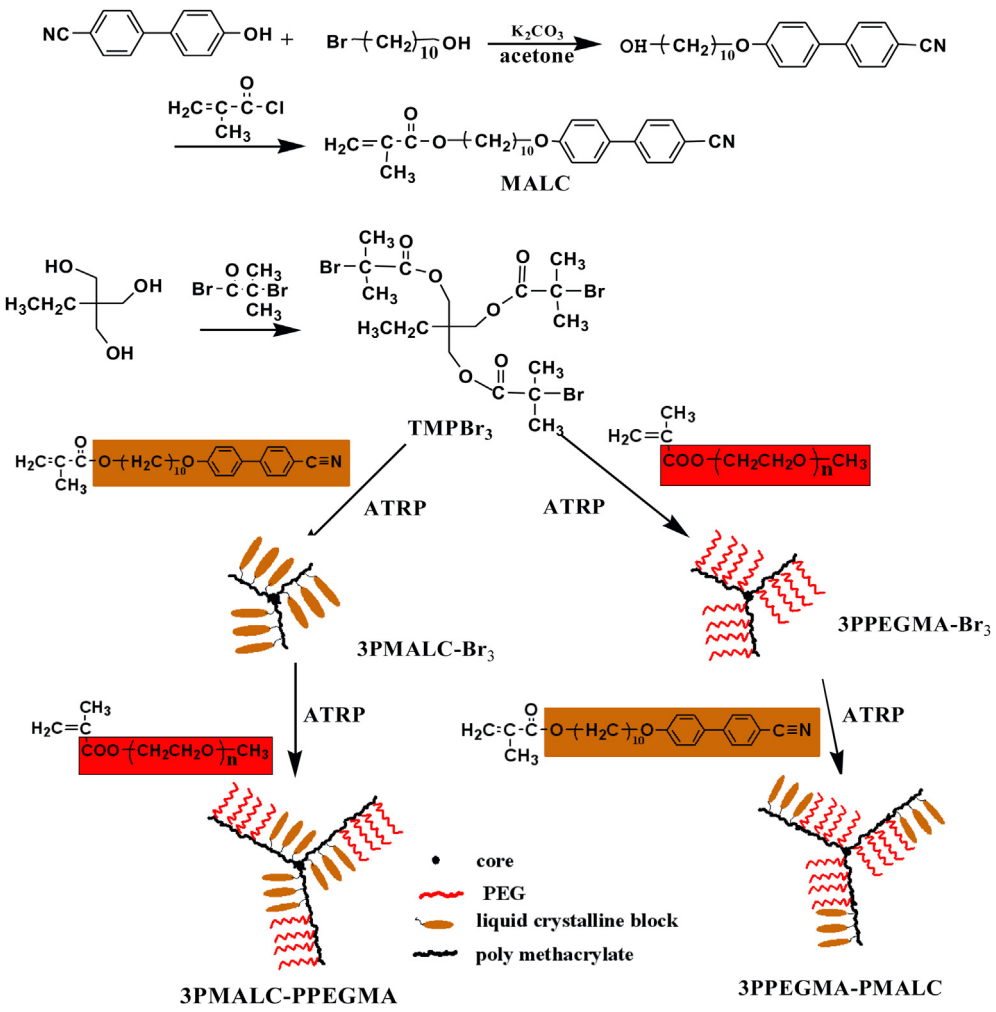

Scheme 1. Synthesis routes for monomers and copolymers.

comparatively low ionic conductivity ($\sim 10^{-7}$ S cm^{-1}) at ambient temperature. The inherent limitation of ion transport in a solid PEO-based electrolyte system makes it unlikely to reach the level of ionic conductivity for practical applications, because an ionic conductivity of 10^{-3} S cm^{-1} at room temperature is generally required for an energy storage device. Several research groups reported that the graft polymer electrolytes with more flexible oligomeric PEO side chains exhibited the higher ion conductivities (10^{-5}–10^{-6} S cm^{-1}) at ambient temperature [5,6]. Higa et al. [7] synthesized a graft copolymer electrolyte which contained a polyimide main chain and methoxy-poly (ethylene glycol) methacrylate side chains, showing a relatively high conductivity (6.5×10^{-6} S cm^{-1} at 25 °C) and excellent tensile strength (100 MPa). Zuo et al. [8] prepared a novel graft copolymer solid electrolyte, where methacrylate backbone is attached with (C_{16})-methoxyl terminated oligo(ethylene oxide) side chains, exhibited the ionic conductivity value of $\sim 1.3 \times 10^{-4}$ S cm^{-1} at 30 °C and 7.9×10^{-4} S cm^{-1} at 80 °C. Another favorable solution to this problem involves the use of molecular assembly of block copolymers, and much research effort focused on the production of novel block copolymers bearing liquid crystalline (LC) or hydrophobic blocks because of their fascinating ordered phenomena [9]. These block copolymers have the advantage of combining the properties of liquid crystals and block copolymers; which provides not only novel functionality but also the possibility of microphase separation formation due to the regular ordering of the liquid crystals. A variety of electrolytes with enhanced performance based on LC block copolymers have been reported [10–15].

Star-shaped polymers are a class of branched polymers having a globular architecture, which are expected to exhibit unique physical properties and morphologies not observed in the corresponding linear polymers. [16,17] In particular, the crystallinity and degree of chain entanglement of star-shaped polymers are smaller than those of the linear polymers [18]. Niitani et al. described the application of star-shaped polystyrene-*b*-poly((polyethylene glycol) methyl ether methacrylate) for SPE, finding that the star-shaped block polymer electrolytes exhibited the enhanced lithium battery performances [19]. Kim et al. also studied the star-shaped polymer electrolytes with POSS and PEG side groups for SPEs, yielding an ionic conductivities of 1.75×10^{-5} S cm^{-1} at 30 °C, which is two orders of magnitude higher than that of the star-shaped polymer electrolyte with MMA moiety [20].

In this study, we designed star-shaped polymers containing poly-(methoxy-poly (ethylene glycol) methacrylate) (PPEGMA) as a hydrophilic segment and poly {10-[(4-cyano-4′-biphenyl) oxy] decatyl methacrylate} (PMALC) as a hydrophobic liquid crystalline segment by atom transfer radical polymerization (ATRP) [21–23]. The novel star copolymer electrolytes, where a PMALC segment is responsible for orientation and a PPEGMA segment is used as lithium-ion conduction pathway, are expected to present the