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Conductivity and characterization of plasticized polymer electrolyte based on (polyacrylonitrile-*b*-polyethylene glycol) copolymer

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Abstract

A block copolymer polyacrylonitrile-*b*-polyethylene glycol was synthesized by the macroinitiator method. The copolymer mixed with a plasticizer—propylene carbonate (PC) and $LiClO_4$ to form plasticized polymer electrolytes. FT-IR spectra show that the lithium ion interacts with the groups that contain the un-bonded electrons. The results of FT-IR also indicate that the EO segment can improve the dissociation of lithium salt. The differential scanning calorimeter (DSC) used to study the thermal behaviors of different compositions. In this study, the conductivity increases with the content of PEG. Additionally, the plasticized polymer electrolyte based on the block copolymer has a good conductivity and can retain good mechanical strength.

Keywords: Macroinitiator; Block copolymer; Plasticized polymer electrolytes

1. Introduction

Interest in the development of rechargeable lithium batteries based on solid polymer films as electrolytes has increased in recent years [1]. Because the thin film used in the battery is anticipated achieving high-energy density of the battery. However, inadequate ionic conductivity of the solid polymer electrolyte (SPE) is hindering the development of these thin films.

Since Wright et al. [2,3] found that poly(ethylene oxide) (PEO) dissolved salts and had an ionic conductivity of 10^{-8} to 10^{-7} S cm^{-1} at ambient temperature. To improve the conductivity, modifications of the PEO system and evaluation various plasticizers to PEO system have been extensively studied [4]. However, the effectiveness of the plasticizers in PEO systems has not been achieved to a technically justified level of 10^{-3} S cm^{-1}, without an expense of mechanical rigidity of the plasticized polymer electrolytes. Thus, the PAN-based system has been investigated extensively, because of its favorable mechanical properties. Polymer electrolytes that are based on PAN contain plasticizers, such as propylene carbonate (PC) or a mixture of PC and ethylene carbonate (EC), and lithium salts. Unlike PEO, which is a solvent for lithium salts, PAN does not seem to dissolve significantly these salts [5]. Indeed, the function of PAN in a lithium battery is merely to hold the solution in its matrix and the ionic conduction takes place in the liquid medium. The conductivity of an electrolyte is generally determined by the nature, the concentration and the mobility of charge carrier. If the polymeric constituents in plasticized polymer electrolytes play an active role to affecting ionic dissociation and conductivity, the solvating ability of polymers themselves becomes an important factor. That is to say the ionic conductivity is also affected by the segmental motions of polymeric chains [6–8]. Rapid segmental motions of polymer chain normally increase the ionic mobility of both cations and anions by expanding local free volume, and by reducing local viscosity around charge transporting ions.

Some significant research has been performed to obtain polymer structures with a high conductivity and favorable mechanical properties. Common methods are copolymering [9,10], blending [11,12], grafting [13,14] and crosslinking [15,16]. Block copolymers, which contain two different segments, have high potential applications in polymer electrolytes because of their distinctive properties. Variations among blocks in structure and properties cause differences in apparent properties. For the polymer electrolyte application, the properties of

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block copolymer, such as its mechanical stability and ion conductivity, may be controlled by variations in molecular design and the preparation of the electrolyte.

A series of polyacrylonitrile-*b*-polyethylene glycol copolymers that contain PEG of different molecular weight were synthesized in this study. The copolymer, $LiClO_4$ and plasticizer-PC were mixed to form the plasticized polymer electrolyte. Additionally, the conductivity and mechanical properties of those block copolymers were also studied.

2. Experimental

2.1. Materials

Acrylonitrile (AN) (Aldrich) was distillated from CaH_2 under reduced pressure and stored under refrigerator at −20 °C. Polyethylene glycol (PEG 1000, 4000 and 10,000) was dehumidified by a vacuum system. Dichloromethane, propylene carbonate and *N*,*N*-dimethylformanide (DMF) were distilled twice and stored over molecular sieves (4 Å). 4,4′-Azobis(4-cyanopentanoic acid) (ACPA; Fluka) and thionyl chloride ($SOCl_2$) were used without further purification. Lithium perchlorate ($LiClO_4$; Fluka) was dried in vacuum oven prior to use.

2.2. Preparation of macroinitiator

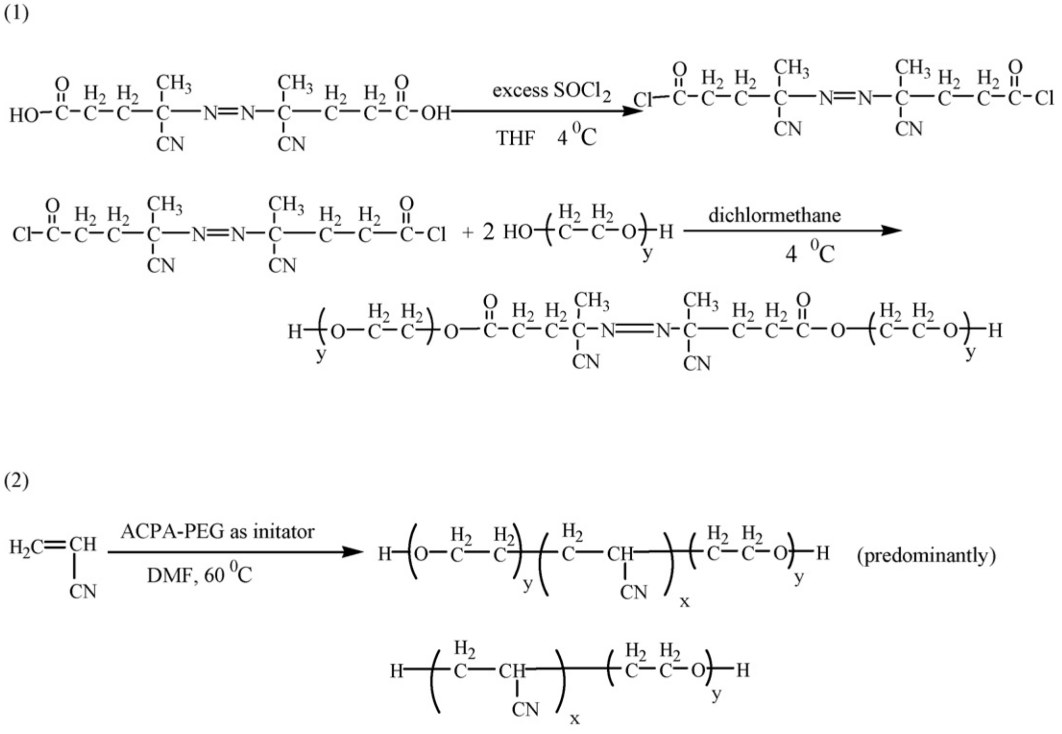
The ACPA was placed in the reactor equipped with nitrogen purge. $SOCl_2$ was then slowly added to the reactor, while the temperature was maintained at 4 ± 0.1 °C and stirred for 24 h. Then, the excess $SOCl_2$ was removed by distillation, and the moderate PEG and dichloromethane were added to the reactor. The reaction was controlled at 4 ± 0.1 °C for 24 h. Then, the yellow liquids were filtrated to remove the solid ACPA which does not react with PEG. Finally, the yellow liquids were purified by precipitating reaction mixture with ether, and the solid products were dried under vacuum for 6 h. The reaction process of macroinitiator and copolymer is presented in Scheme 1. The product code was ACPA-PEG1K, ACPA-PEG4K, and ACPA-PEG10K.

2.3. Preparation of block copolymer

Acrylonitrile (AN) and DMF were mixed and added to the reactor previously purged oxygen free by nitrogen gas. Macroinitiator (ACPA-PEG) was used as an initiator and the ratio of monomer/initiator was 2000/1. The reaction temperature was controlled at 60 ± 0.1 °C by a thermostat controlled water bath. After 24 h of polymerization, the flask was cooled to ambient temperature. The products were purified by precipitating reaction mixture into ethanol, and then filtrated. Two precipitation cycles were performed and finally dried under vacuum oven at 70 °C for 6 days. Moreover, we follow the methods [17] to evident that the predominant termination of this polymerization occurs by combination. Therefore, the (PEG-PAN-PEG) type of copolymer is the predominant product in this polymerization.

2.4. Preparation of plasticized polymer electrolyte

The hybrid films were obtained by dissolving the polymer, $LiClO_4$ and PC at 90 °C, then casting the solution onto a polytetrafluoroethylene (PTFE) substrate. Finally, the mixture was



Scheme 1. (1) The reaction process of macroinitiator. (2) The reaction process of copolymer.