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Crosslinked poly(acrylonitrile–glycidyl methacrylate) as a novel gel polymer electrolyte

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ABSTRACT

Novel gel polymer electrolytes (GPEs) based on poly(acrylonitrile–glycidyl methacrylate) (P(AN–GMA)) crosslinked with α,ω-diamino poly(propylene oxide) (Jeffamine) of various weight ratios and molecular weights have been prepared, and the crosslinked polymers were characterized by FT-IR and thermal analysis. It is revealed that the crosslinked polymers were amorphous in pristine state and became crystallized when doped with lithium electrolyte. Their swelling properties and mechanical behaviors were investigated and found to be heavily affected by the weight ratio and molecular weight of Jeffamine. The effect of weight ratios and molecular weights of Jeffamine on the ionic conductivity of the GPEs based on the crosslinked polymers were determined by AC impedance spectroscopy. GPEs consisting of Jeffamine of higher molecular weights and increased weight ratios showed higher ionic conductivity. The GPE based on P(AN–GMA) crosslinked with Jeffamine D2000 at a weight ratio of 1.5 exhibited the highest ionic conductivity of 8.23×10^{-4} S cm^{-1} at 25 °C, and preserved a moderate mechanical strength. The crosslinked polymers can be potential candidates for the construction of rechargeable lithium batteries.

1. Introduction

Polymer electrolytes for rechargeable lithium batteries received increasing attention because of their special characteristics such as high specific energy and specific power, safe operation, flexibility in packaging, low cost of fabrication, etc. [1]. Generally, there are three types of polymer electrolytes: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and composite polymer electrolytes (CPEs) [1–3]. In recent years, great efforts have been devoted to the development of GPEs for practical use, which enjoy the advantages of relatively high conductivity at room temperature (10^{-4} to 10^{-3} S cm^{-1}) and better safety [4–7].

A number of polymers including polyvinylidene fluoride (PVdF) [6,8], polyacrylonitrile (PAN) [9,10], polyvinyl chloride [11], poly(methyl methacrylate) [12] and polyurethane [13], have been considered as the host polymers for the preparation of polymer electrolytes. Among them, PAN-based electrolytes showed interesting characteristics such as high ionic conductivity, high thermal stability, desirable morphology for electrolyte uptake and compatibility with the lithium electrodes [14]. Moreover, it has been revealed that –CN group in PAN could interact with Li$^+$ ions and PAN might provide rigidity to the polymer electrolytes with high lithium ion conduction [15].

An obstacle to the practical applications of GPEs for rechargeable lithium battery is the high requirements that they have to posses a high ionic conductivity and retain sufficient mechanical stability [16]. Usually, the presence of large amounts of electrolyte solution promotes the ionic conductivity at the cost of mechanical stability, and thus a high ionic conductivity is accompanied with poor mechanical strength.

Modifying the polymer membrane by crosslinking has proved to be one of the most important means of improving the mechanical properties of GPEs [17]. Kuo et al. reported gelled polymer electrolytes based on poly(ethylene glycol) diglycidyl ether/diglycidyl ether of bisphenol A cured with α,ω-diamino poly(propylene oxide) [18]. They also prepared a hybrid polymer electrolyte system containing polysiloxane and polyether segments by crosslinking of epoxide using the same curing agents, which showed high ionic conductivity at room temperature and improved mechanical property [19].

In this paper, we prepared a series of polymer electrolytes based on crosslinked poly(acrylonitrile–glycidyl methacrylate) (P(AN–GMA)) with α,ω-diamino poly(propylene oxide) (PPO) polyamine as the curing agents, hoping to obtain high ionic conductivity and preserve the mechanical integrity of polymer membranes. The effect of the molecular weights and weight ratios of the curing agents on the structure, swelling properties, mechanical strength and ionic conductivity of the crosslinked copolymers and corresponding GPEs were all investigated. Under optimal conditions, the GPE based on the crosslinked copolymers possessed

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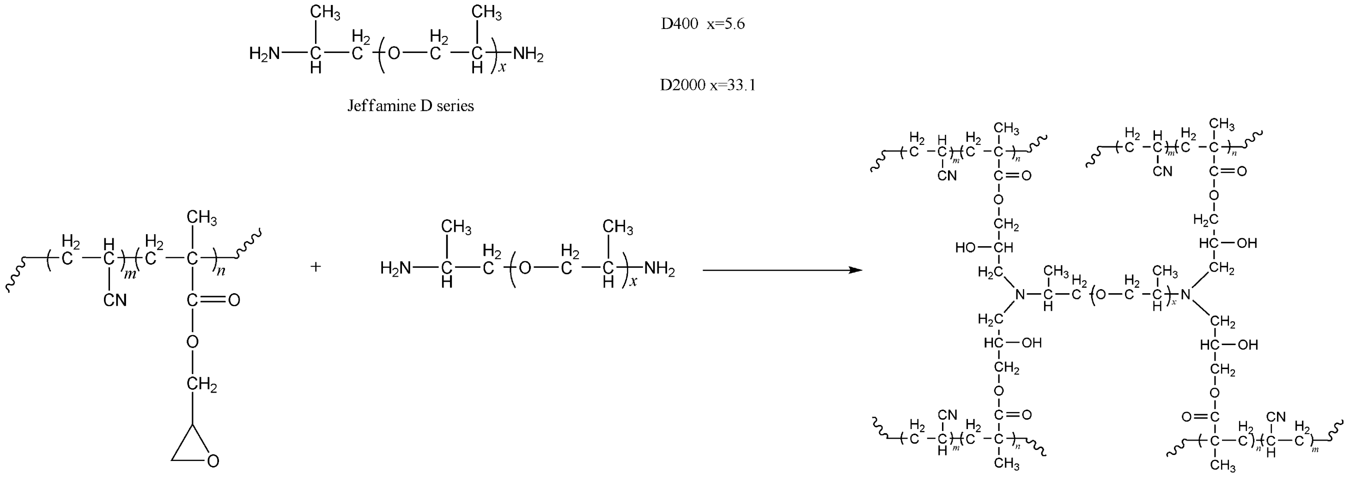

Scheme 1. The synthesis of P(AN–GMA) and the crosslinked copolymer.

an ionic conductivity close to 10^{-3} S cm^{-1} at 25 °C and a moderate mechanical property, which suggest their potential applications in rechargeable lithium batteries.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA) (Aldrich) was used as received, and acrylonitrile (AN) was distilled under reduced pressure. Both were stored in a refrigerator at −20 °C. PPO polyamines (Huntsman Corporation) were dehydrated at 80 °C under vacuum for 24 h prior to use. Their equivalent weights of active hydrogen were 115 g/equiv. and 514 g/equiv. for Jeffamine D400 and Jeffamine D2000, respectively. Lithium electrolyte (DMC:DEC:EC = 1:1:1 (w/w/w) $LiPF_6$ 1.0 M) (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.) was stored in a desiccator before use. Other reagents were of analytical grade and used as received.

2.2. Polymer synthesis

Copolymerization of GMA and AN (weight ratio = 1/1) was conducted at 70 °C for 6 h in a single-necked flask in N_2 atmosphere with azodiisobutyronitrile (AIBN) as an initiator and N,N-dimethylformamide (DMF) as a solvent. Upon cooling, the mixture was precipitated in methanol, filtered and washed with methanol, then dried in vacuo at 40 °C for 24 h to obtain the copolymer P(AN–GMA).

2.3. Preparation of gelled polymer electrolytes

P(AN–GMA) and Jeffamine D400 or Jeffamine D2000 were dissolved in DMF in different weight ratios, then heated at 80 °C for 8 h with vigorous stirring for pre-crosslinking. The resulting mixture was poured onto a PTFE plate, followed by evaporation of the solvent at room temperature and subsequent curing at 100 °C for 24 h. The obtained specimens were denoted as AGD400 (21) (P(AN–GMA): Jeffamine D400 = 2/1 in weight ratio), AGD400 (11) (weight ratio = 1/1), AGD400 (23) (weight ratio = 2/3), AGD2000 (21) (P(AN–GMA): Jeffamine D2000 = 2/1 in weight ratio), AGD2000 (11) (weight ratio = 1/1) and AGD2000 (23) (weight ratio = 2/3). They were dried in vacuo at 40 °C before use. Finally the gel polymer electrolytes were obtained by immersing the resulting membranes into the liquid electrolyte for 2 h.

2.4. Measurements

FT-IR spectra were obtained on a BRUKER VECTOR-22 spectrometer. ^{1}H NMR measurements were performed on a Bruker Advance DMX 500 spectrometer using deuterochloroform ($CDCl_3$) as the solvent. Thermal analysis was carried out in a TA DSC Q100 differential scanning calorimeter under N_2 atmosphere with a heating rate 10 °C min^{-1} from −80 to 150 °C.

The percentage of swelling (Sw) was obtained by using the following equation: $Sw = (W - W_0)/W_0 \times 100\%$,where W_0 and W are the weights of dried film and swelled film, respectively).

The degree of crosslinking was measured in terms of the percent gel content by using the equation $CD = W_2/W_1 \times 100\%$ (where W_1 is the initial weight of sample and W_2 is the weight of sample after extraction with tetrahydrofuran (THF) for 24 h) [20,21].

The mechanical properties of the crosslinked copolymer films were evaluated from stress–strain tests using an Instron model 5500 testing device. Tensile tests were carried out under a 1000 N load cell at a strain rate of 5 mm/min.

The ionic conductivity (σ) of the gel polymer electrolytes was determined by AC impedance spectroscopy (EG&G Model 273A potentiostat). The membrane was sandwiched between two parallel stainless steel discs (d = 1 cm). During the measurement, it was mounted in a sealed coin cell to prevent contamination of the sample. The frequency ranged from 100 kHz to 10 Hz at a perturbation voltage of 10 mV. The ionic conductivity was calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and the electrode area (A) according to the equation $\sigma = l/AR_b$.

3. Results and discussion

3.1. Characterization

The copolymer P(AN–GMA) was prepared by a simple radical polymerization. The synthesis of P(AN–GMA) and the crosslinked polymer was illustrated in Scheme 1. The ^{1}H NMR spectrum of the copolymer is shown in Fig. 1. The chemical shifts at 3.27 ppm (d), 2.87 ppm and 2.67 ppm (e) are attributed to the epoxide group. While the signal at 2.16 ppm (f) corresponds to the proton of methine carbon (CH) connected with cyanate carbon (CN) in P(AN–GMA). The neighboring signal at 1.98 ppm (g) is attributed to methylene protons in GMA segment. The composition of the copolymer can be determined by simply comparing the integrals of CH (3.27 ppm) of GMA and CH (2.16 ppm) of AN in the spectrum, and the mole ratio of AN units to GMA unit was calculated to be 2:1.

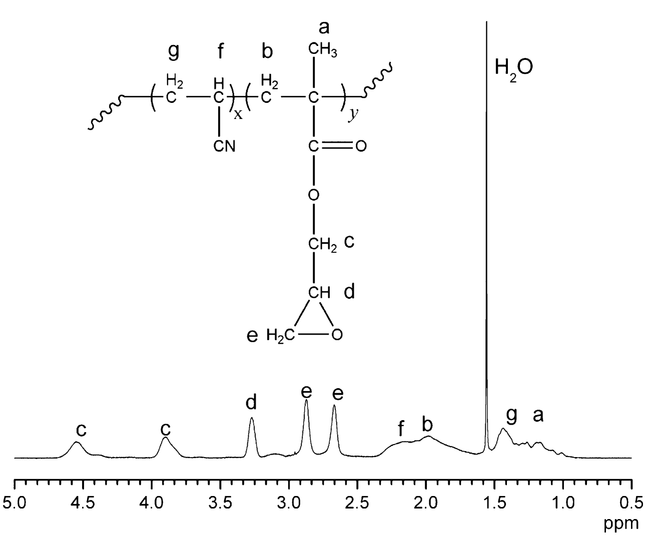

Fig. 1. ^{1}H NMR spectrum of P(AN–GMA).