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

Yu-Hao Liang^a, Cheng-Chien Wang^b, Chuh-Yung Chen^{a,*}

^a Department of Chemical Engineering, National Cheng-Kung University, Tainan 70148, Taiwan ^b Department of Chemical and Material Engineering, Southern Taiwan University, Tainan 710, Taiwan

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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.

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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

0378-7753/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2007.05.034 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

^{*} Corresponding author. Tel.: +886 6 2757575x62643; fax: +886 6 2344496. *E-mail address:* ccy7@ccmail.ncku.edu.tw (C.-Y. Chen).

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 CaH₂ 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(4cyanopentanoic acid) (ACPA; Fluka) and thionyl chloride (SOCl₂) were used without further purification. Lithium perchlorate (LiClO₄; 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. SOCl₂ 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 SOCl₂ 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 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

$$\begin{array}{c} O & H_{2} & H_{2} & H_{2} & H_{3} \\ HO - C - C - C - C - C - C - C - C \\ \hline & C \\ \hline \hline & C \\ \hline & C \\ \hline &$$

$$H_{2}C = CH \xrightarrow{ACPA-PEG \text{ as initator}}_{CN} H \xrightarrow{(0-C-C-C)_{y}} H \xrightarrow{(H_{2}-H_{2})_{y}} H \xrightarrow{(H_{2}-H_{2}-C)_{y}}_{C} H \xrightarrow{(P_{2}-H_{2}-C)_{y}}_{Y} H \text{ (predominantly)}$$

$$H \xrightarrow{(-C-C-C)_{y}}_{CN} H \xrightarrow{(P_{2}-C+C)_{y}}_{X} H \xrightarrow{(P_{2}-C-C)_{y}}_{Y} H$$

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

(2)

stored in a vacuum oven to remove the excess PC at 80 °C. The composition of the plasticized polymer electrolyte is polymer/plasticizer = 50/50 wt.% with LiClO₄ (0.25, 0.5, 1.0, 2.0 and 3.0 mmol (g-polymer⁻¹)), respectively.

2.5. Characterization of macroinitiators, copolymers and plasticized polymer electrolytes

High-resolution NMR measurements were performed on a Bruker AMX-400 spectrometer with ¹H and ¹³C resonance frequencies at 400.13 and 100.61 MHz, respectively. The macroinitiator was dissolved in deuterium oxide (D_2O) . The ¹H and ¹³C chemical shifts were referenced relative to tetramethylsilane (TMS) at 0.0 ppm. The molecular weight of the macroinitiator was determined via size exclusion chromatography with a Waters 410 differential refractometer calibrated with linear polystyrene (PS) standards. Tetrahydrofuran (HPLC-grade) was used as the eluent, and the flow rate was $0.7 \,\mathrm{mL}\,\mathrm{min}^{-1}$. Thermal analysis of the samples was carried out in a Dupont DSC 2910 differential scanning calorimeter with a heating at rate 10 °C min⁻¹ from -150 to 150 °C. FT-IR spectra were recorded at room temperature using a Bio-Rad FT-IR system coupled with a computer. The resolution and scan numbers of IR measurement were 2 cm^{-1} and 64 times, respectively. The spectra were collected in the range between 400 and 4000 cm^{-1} . The mechanical properties measurement of plasticized polymer was conducted via Tensile Test Instrument (Instron 1011) having a test rate at 5 mm min^{-1} .

2.6. Conductivity measurements

The ionic conductivity of the plasticized polymer electrolytes was obtained using an electrochemical cell consisting of the electrolytic film sandwiched between two stainless steel electrodes. The cell was placed inside a thermostat under Agron condition. Impedance analysis was recorded at 30 °C, using all Autolab PGSTAT 30 equipment (Eco Chemie B.V., Netherlands) with the software of Frequency Response Analysis (FRA) under an oscillation potential of 10 mV from 100 kHz to 10 Hz.



Fig. 1. IR spectra of (a) ACPA, (b) ACPA-PEG1K, (c) ACPA-PEG4K and (d) ACPA-PEG10K.

3. Results and discussion

3.1. Characteristics of macroinitiator

The macroinitiator was prepared by reacting 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) with PEG. Its structure was confirmed by FT-IR and ¹H NMR. In the FT-IR spectra of ACPA-PEG (Fig. 1), the absorption peaks at 1120 and $3450 \,\mathrm{cm}^{-1}$ corresponded to the -C-O-C- and -OH groups of PEG, respectively. An absorption peak appeared at 1740 cm^{-1} , corresponding to the -C=O stretching of the ester group. In addition, the intensity of the peak at 1740 cm^{-1} clearly decreases as the molecular weight of PEG increases, as shown in Fig. 1(b-d). Meanwhile, the C=O stretching of the acid group (1717 cm^{-1}) in ACPA disappears (Fig. 1(a)), indicating the formation of ester linkage between PEG and ACPA. Furthermore, the formation of ACPA-PEG was also confirmed from its' ¹H NMR spectrum. In the ¹H NMR spectrum (Fig. 2), resonance peaks other than that of PEG at 3.6-3.9 ppm, were observed at 1.5–2.8 ppm, corresponding to –CH₃ and –CH₂ protons of the azobis cyanopentanoyl moiety of the ACPA-PEG. The remarkable downfield shift of the peak from 3.7 to 4.2 ppm, which is attributed to the methylene protons next to the hydroxyl group, further confirms the esterification reaction between ACPA and



Fig. 2. The ¹H NMR spectrum of ACPA-PEG1K.

Symbol of macroinitiator $M_{\rm n}$ $M_{\rm w}$ PDI Symbol of polymer Elemental analysis Molar ratio of copolymer N:C:H EO:AN PEG1K 1.23×10^{3} 1.75×10^{3} 1.41 ACPA-PEG1K 2.66×10^{3} 3.31×10^{3} 1.25 PAN-PEG1K 25.87:66.02:5.62 2.42:97.58 5.03×10^{3} PEG 4K 4.24×10^{3} 1.19 7.34×10^{3} 8.28×10^{3} ACPA-PEG4K 1.23 PAN-PEG4K 24.56:65.65:6.09 8.29:91.71 PEG10K 1.13×10^{4} 1.35×10^{4} 1.20

PAN-PEG10K

The molecular weight (M_n, M_w) and polydispersion index (PDI) of PEG and ACPA-PEG from the GPC measurement, and the compositions of block copolymers from Elemental Analysis

PEG and the synthesis of ACPA-PEG. The molecular weight of ACPA-PEG was determined by GPC, and is presented in Table 1. It is nearly twice that of the homopolymer (PEG). This fact is further evidence that the macroinitiator, ACPA-PEG, was successfully prepared via the formation of ester linkages between PEG and ACPA.

 2.16×10^4

 2.91×10^{4}

1.35

3.2. Characteristics of copolymer

Table 1

ACPA-PEG10K

The formation of block copolymer was confirmed by the corresponding characteristic peaks of related homopolymer segments in the copolymer analysis. The characteristic peaks of related segments in the copolymer were identified by the FT-IR spectra, as shown in Fig. 3. FT-IR spectra of the block copolymers clearly show a -C=N group absorbance peak at 2245 cm⁻¹ and a -C-O-C- polyether peak at 1120 cm⁻¹. Table 1 tabulates the results of the elemental analysis of the copolymers. The FT-IR spectra and elemental analysis reveal that the copolymers with acrylonitrile and PEG were successfully synthesized.

The T_g of the block copolymer is studied using DSC instrument, as shown in Fig. 4. The T_g of copolymers decrease as the molecular weight of PEG increases and are lower than that of the homopolymer-PAN (ca. 90 °C). In Fig. 4(c), a melting peak appears in the DSC curve of PAN-PEG10K, attributed to the melting peak of the crystal of PEG10K segment. DSC measurements indicate that the block copolymer was synthesized and the PEG segment reduced the T_g of PAN segment.



Fig. 3. The IR spectra of (a) PAN, (b) PAN-PEG1K, (c) PAN-PEG4K and (d) PAN-PEG10K.



22.13:64.32:6.21

19.10:80.90

Fig. 4. The DSC thermograms of copolymer: (a) PAN-PEG1K, (b) PAN-PEG4K and (c) PAN-PEG10K.

3.3. Environment of lithium ion in plasticized polymer

Different complexes can be formed by the interaction of different coordination sites of the plasticized polymer electrolyte with lithium ions, as shown in Scheme 2. FT-IR was employed to investigate the interaction of lithium ions with the polar groups in the plasticized polymers. Fig. 5 shows the spectra that correspond to various concentrations of LiClO₄ in the ether oxygen stretching region ($1035-1185 \text{ cm}^{-1}$). The absorbance band of the ether oxygen changes as the salt concentration increases. This change is expected because of the well known coordination of lithium ions to the un-bonded electrons of the ether oxygen, which has been reported elsewhere [18–20]. Fig. 6 presents the absorbance FT-IR spectra of -C=O on the PC molecules



Scheme 2. Environment of lithium ion in plasticized polymer.



Fig. 5. The IR spectrum of -C-O-C- group of the plasticized polymer electrolyte with various concentration of lithium salt: (a) 0.25 mmol (g-polymer⁻¹), (b) 0.5 mmol (g-polymer⁻¹), (c) 1.0 mmol (g-polymer⁻¹), (d) 2.0 mmol (g-polymer⁻¹) and (e) 3.0 mmol (g-polymer⁻¹).

 $(1790 \,\mathrm{cm}^{-1})$. The frequency of band that corresponds to the stretching vibration of PC downward as the concentration of LiClO₄ is increased. This change is attributed to the interactions between Li⁺ and the -C=O group of PC [21]. Fig. 7 displays the characteristics of the spectra for the $-C \equiv N$ stretching region $(2220-2270 \text{ cm}^{-1})$ with various concentrations of LiClO₄. The IR spectra reveal a shoulder at around 2265 cm^{-1} , which results from an interaction between the Li^+ and $-C \equiv N$ groups [22]. This was attributed to the formation of an association between lithium ions and the pair of un-bonded electron on the nitrogen atom of the $-C \equiv N$ groups. Since the lithium ions preferentially interact with other groups, the weak shoulder at 2265 cm^{-1} is not obvious, especially when the lithium ion concentration is low. Briefly, this study established that lithium ions interact with PC, the -C-O-C- group and the -C=N group in this plasticized block polymer.



Fig. 6. The IR spectrum of C=O group of PC in the plasticized polymer electrolyte with various concentration of lithium salt: (a) $0.25 \text{ mmol (g-polymer}^{-1})$, (b) $0.5 \text{ mmol (g-polymer}^{-1})$, (c) $1.0 \text{ mmol (g-polymer}^{-1})$, (d) $2.0 \text{ mmol (g-polymer}^{-1})$ and (e) $3.0 \text{ mmol (g-polymer}^{-1})$.



Fig. 7. The IR spectrum of –CN group of the plasticized polymer electrolyte with various concentration of lithium salt: (a) $0.25 \text{ mmol (g-polymer}^{-1})$, (b) $0.5 \text{ mmol (g-polymer}^{-1})$, (c) $1.0 \text{ mmol (g-polymer}^{-1})$, (d) $2.0 \text{ mmol (g-polymer}^{-1})$ and (e) $3.0 \text{ mmol (g-polymer}^{-1})$.

The dissociation of lithium salt is an important parameter that determines the ionic conductivity of the electrolyte. FT-IR is also an effective tool for probing the degree of dissociation of the lithium salt in different polymer electrolytes. Fig. 8 presents the FT-IR spectra of electrolytes in the $580-680 \text{ cm}^{-1}$ range of the plasticized polymer electrolytes with 3 mmol LiClO₄ (gpolymer⁻¹). The absorption peak can be de-convoluted into two components centered that are at 624 and 640 cm^{-1} , respectively. According to the literature [21,23], the 624 cm⁻¹ band is attributable to the free ClO_4^- and the 640 cm⁻¹ mode is assigned to the ion-pair formation or the contact of ClO_4^- with lithium ion. The ratio of peak areas $(624 \text{ cm}^{-1}/640 \text{ cm}^{-1})$ can be used as an index of the degree of ionization of the lithium salt in the polymer electrolytes. In Fig. 8, the dissociation of LiClO₄ increased with the PEG content, indicating that the EO segment promoted the dissociation of lithium salt in electrolytes.



Fig. 8. FT-IR spectra of perchlorate anion v4 band in plasticized polymer electrolyte with LiClO₄ (3 mmol (g-polymer⁻¹)) (a) PAN, (b) PAN-PEG1K, (c) PAN-PEG4K and (d) PAN-PEG10K.



Fig. 9. The T_g of the plasticized polymer electrolyte doped with various LiClO₄ concentrations: (\triangle) PAN-PEG1K, (\bigcirc) PAN-PEG4K and (\blacksquare) PAN-PEG10K.

3.4. Thermal characteristics

DSC was employed to elucidate the effects of the composition of plasticized polymer electrolyte on its thermal properties. Owing to the PC plasticizer existence, the glass transition temperature of plasticized polymer is obviously present at lower temperature in the DSC thermogram. Fig. 9 plots the $T_{\rm g}$ value of polymer/plasticizer = 50/50 wt.% as a function of LiClO₄ concentration. T_g increases with the concentration of lithium salt. These phenomena are similar to those exhibited by polyether-based polymer electrolytes, which are attributed to the effective cross-linking of polyether segments by the cations [24–26]. The elevation of T_g in the plasticized polymer electrolytes is attributable to the lithium ion-PC interaction, which was verified by FT-IR analysis. Increasing the amount of lithium salt promotes the occurrence of interactions, reducing the motion of PC. Thus, the T_g of PC increases with the salt concentration.

In Fig. 9, the T_g of the plasticized polymer electrolyte exhibits another interesting phenomenon. As the low LiClO₄ concentration, the T_g of PC in the PAN-PEG1K system varies markedly. However, the change of T_g remains almost invariant as the LiClO₄ concentration increases from $1 \text{ mmol}(\text{g-polymer}^{-1})$. However, the T_g of PC in the PAN-PEG10K system increases with the concentration of LiClO₄ even at high lithium salt concentration. This result reveals that PEG increases the dissociation of lithium salt in this plasticized polymer electrolyte. Therefore, in the PAN-PEG1K system, the lithium ion major coordinated with PC at low LiClO₄ concentration. In addition, the amount of Li⁺ that was dissociated by PC is saturate when the LiClO₄ concentration is higher. Consequently, the $T_{\rm g}$ of PC does not increase rapidly with high LiClO₄ concentrations in the PAN-PEG1K system. In a system with higher EO content, the PEG interacts with lithium ions. Therefore, the T_g of PC increases slightly with LiClO₄ concentration at low values. Even at higher LiClO₄ concentrations, the amount of Li⁺ that is dissociated by PC does not easily saturate.



Fig. 10. The ionic conductivity of plasticized polymer electrolyte doped with various concentration of LiClO₄ (\blacksquare) PAN, (\bigcirc) PAN-PEG1K, (\blacktriangle) PAN-PEG4K and (\bigtriangledown) PAN-PEG10K for (I) polymer/plasticizer = 50/50 wt.%.

3.5. Ionic conductivity

The ionic conductivity of the plasticized polymer electrolytes was measured using two stainless steel electrodes to study the effect of copolymer composition on ionic conductivity. Fig. 10 plots the conductivity of polymer/PC = 50/50 wt.% as a function of lithium salt content at 30 °C. The conductivity increases with the salt concentration. However, in the system with low EO content, the ionic conductivity increases passes a maximum (the PAN system at LiClO₄ = 1 mmol (g-polymer⁻¹) and/or the PAN-PEG1K system at LiClO₄ = $2 \text{ mmol} (\text{g-polymer}^{-1})$), from which it decreases as salt concentration increases. This phenomenon is similar to that reported elsewhere [18,20]. At low concentrations of LiClO₄, the lithium salt is completely dissociated, and the number of mobile ions increases with lithium salt concentration. At higher concentrations of LiClO₄, the dissociated ions Li⁺ and ClO₄⁻ can form ion-pairs, reducing the ionic conductivity. However, this phenomenon is not favored in the PAN-PEG10K system. Fortunately, the EO unit promotes the dissociation of Li⁺ and ClO₄⁻ at higher LiClO₄ concentrations because the EO units strongly interact with Li⁺. Therefore, the existence of EO units in the copolymer promotes the complete dissociation of lithium salt at higher LiClO₄ concentrations, increasing the number of charge carriers. These interactions between the EO units and lithium ions are also evidenced by FT-IR spectra, as mentioned above. Moreover, the PAN-PEG10K system has the best conductivity in this study. The conductivity of PAN-PEG10K/plasticizer = 50/50 wt.% with $3 \text{ mmol}(\text{g-polymer}^{-1})$ LiClO₄ is $1.45 \times 10^{-3} \text{ S cm}^{-1}$. The value is one order of magnitude greater than that of the PAN system with same composition. Restated, the ionic conductivity of PAN-PEG10K/PC = 50/50 wt.% system is near that of PAN/PC = 20/80 wt.% system (1.90×10^{-3} S cm⁻¹).

3.6. Mechanical properties

The mechanical properties of plasticized polymers (polymer/PC = 50/50 wt.%), including Young's Modulus and 892

Table 2

The mechanical properties of plasticized block copolymers (polymer 50 wt.%/PC 50 wt.%) from stress–strain test

Symbol of polymer	Young's modulus (MPa)	Toughness (MPa)
PAN	68.5	320.9
PAN-PEG1K	59.8	247.1
PAN-PEG4K	41.0	144.0
PAN-PEG10K	31.8	108.0

The composition without LiClO₄.

toughness, were examined using an Instron instrument and presented in Table 2. Both the Young's Modulus and the toughness of the block copolymers decrease as the EO unit content increases. Notably, the PAN-PEG10K/plasticizer = 50/50 wt.% system has good conductivity – close to that of the PAN/plasticizer = 20/80 wt.% system – and has better mechanical properties than the PAN/plasticizer = 20/80 wt.% system (Young's Modulus = 0.18 MPa, toughness = 4.3 MPa). Therefore, in this work, the PAN-PEG10K/plasticizer = 50/50 wt.% system is used to enable the polymer electrolyte to reach a good conductivity and retain good mechanical strength.

4. Conclusion

A plasticized block copolymer electrolyte is synthesized from PAN-*b*-PEG complexes with PC. LiClO₄ is added as a lithium salt to study the conductivity of plasticized block copolymer electrolytes. FT-IR reveals that the lithium ions interact with PC, the -C-O-C- group and the -C=N group in the plasticized block copolymer. The DSC shows that the EO content of the block copolymer and the concentration of lithium salt affect T_g . The maximum conductivity in this study exceeds that of the typical PAN-based system with the same composition. The results reveal that the EO unit in the copolymer can increase the number of charge carriers, improving the conductivity of the plasticized polymer electrolyte.

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