Enhanced conductivity of plasticized polymer electrolytes containing chelating groups

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ABSTRACT

Poly(AN-co-GMA-IDA) has been prepared by copolymerizing acrylonitrile (AN) and 2-methylacrylic acid 3-(bis-carboxymethylamino-2-hydroxy-propyl ester) (GMA-IDA). The polymers were mixed with the plasticizer ethylene carbonate (EC) and lithium perchlorate (LiClO$_4$) to form gel polymer electrolytes (GPE). Fourier-transform infrared spectroscopy (FT-IR) has revealed that the GMA-IDA unit can improve the dissociation of the lithium salt. Furthermore, the GMA-IDA can hinder the crystallization of EC, thereby improving the conductivity of the GPE. This has been established by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis. The interaction between GMA-IDA and EC has been confirmed by FT-IR and ^{7}Li solid-state NMR. The maximum conductivity measured in this investigation was 9.75×10^{-4} S cm^{-1}.

1. Introduction

In recent years, continued research and development in the area of polymer electrolytes has yielded a number of polymers that may serve as hosts for electrolytes. Gel polymer electrolytes (GPE) have been attractive for the development of plastic Li ion batteries since they combine the advantages of liquid electrolytes (high ionic conductivity) and polymers (free from leaks, good mechanical strength). These systems display high ionic conductivity at room temperature and have sufficient mechanical strength [1–4].

Conductivity depends on the concentration of the charge carrier and its mobility in the electrolyte. The extent to which lithium salts are dissociated to form charge carriers is determined by the dielectric constant or donor number of the solvent or polymer, as well as by the nature of the salt itself. The mechanical strength of a GPE is determined by the nature and composition of both the polymer and the liquid electrolyte. Therefore, the electrochemical and mechanical properties not only depend on the nature of the liquid electrolyte and polymer, but also relate to the composition of the GPE.

The choice of liquid electrolyte is mainly determined by its macroscopic properties, such as dielectric constant, viscosity, and so on. Organic carbonates are the most suitable solvents for preparing liquid electrolytes. These carbonates can be divided, according

to their molecular structures, into cyclic and acyclic groups. Ethylene carbonate (EC) and propylene carbonate (PC) are the two well-known examples of cyclic carbonates, while the acyclic carbonates include dimethyl carbonate (DMC) and diethyl carbonate (DEC). In many respects, EC has superior properties to other organic solvents, including high dielectric constant (89.1), high donor number (16.4) [5,6], and a high boiling temperature (248 °C). Unfortunately, EC is a solid at room temperature, its melting point being 40 °C, which restricts the temperatures at which it may be applied. Therefore, EC is usually mixed with another organic solvent for use, but the properties of the mixed-liquid electrolytes are not as good as those of EC alone.

The polymer must display good mechanical properties and have a strong interaction with the liquid electrolyte. In our previous study [7], we found that introducing the monomer (3-(bis-carboxymethylamino-2-hydroxy-propyl ester)) (GMA-IDA) into a polyacrylonitrile (PAN) matrix by copolymerization not only increased the mechanical properties, but also enhanced the miscibility of the polymer and liquid electrolyte. The –COO⁻Li⁺ groups of GMA-IDA increased the number of charge carriers in a GPE with high PC content; however, the mechanical strength of the GPE was found to decrease with the increase in PC content. Therefore, in this study, ethylene carbonate (EC) has been used as a liquid electrolyte in place of PC with a view to more effectively exploiting the advantage of –COO⁻Li⁺ in increasing the conductivity of a GPE. Moreover, the polar groups of GMA-IDA can prevent the crystallization of EC, thereby expanding the range of temperatures at which it can be applied. Fourier-transform infrared spectroscopy (FT-IR)

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and solid-state ^{7}Li NMR spectrometry have been used to elucidate the interaction between the plasticizer EC and GMA-IDA. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis have been used to confirm the effect of GMA-IDA on the crystallization of EC.

2. Experimental

2.1. Materials and experimental procedure

Glycidyl methacrylate (GMA) (Aldrich) was distilled from CaH_2 under reduced pressure and stored under refrigeration at −20 °C. Iminodiacetic acid (IDA) (Avocado) and lithium hydroxide (LiOH) (RdH) were used as received. GMA-IDA was prepared as described in our previous reports [8,9]. Poly(AN-co-GMA-IDA) was synthesized by free radical polymerization. Copolymerization of GMA-IDA and acrylonitrile (AN) (Aldrich) was conducted at 60 °C under a nitrogen atmosphere using ammonium peroxodisulfate (APS) (Showa) as initiator and deionized water as medium in a 500 mL four-necked round-bottomed flask equipped with an anchor propeller stirrer. After 24 h, the flask was cooled to ambient temperature. The polymer was precipitated by pouring the reaction mixture into ethanol and then collected by filtration. Two precipitation cycles were performed and then the polymer was finally dried in a vacuum oven. Polymer samples with different molar ratios of GMA-IDA, i.e. AN/GMA-IDA = 1:0.02; 1:0.06; 1:0.10, are denoted by the abbreviations AG1, AG2, and AG3, respectively.

Lithium perchlorate ($LiClO_4$) (Fluka) was dried in a vacuum oven prior to use. Hybrid films were obtained by mixing the copolymer, ethylene carbonate (EC) (Fluka), and lithium perchlorate. When a clear solution was obtained, it was cast onto a poly(tetrafluoroethylene) (PTFE) substrate. The samples were controlled so as to have polymer/plasticizer compositions of ca. 50:50 and 40:60 wt.%.

2.2. Characterization of the plasticized polymers

FT-IR spectra were recorded at room temperature using a Bio-Rad FT-IR system coupled to a computer. The resolution was 2 cm^{-1} and the number of IR scans was 64. The spectra were collected in the range between 500 and 4000 cm^{-1}.

Thermal analysis of the gel-type polymer electrolytes was carried out in a Dupont DSC 2910 differential scanning calorimeter at a heating rate 10 °C min^{-1} from −60 to 150 °C.

X-ray diffraction (XRD) patterns were determined on a Rigaku RINT2000 X-ray diffractometer, using Cu-K$_\alpha$ radiation, at $2\theta = 0.05$ s^{-1} between 5° and 80°. The applied voltage was 40 kV, the generator current was 40 mA, and the measurements were carried out at 20 °C.

^{7}Li MAS NMR spectra with power decoupling were recorded on a Bruker AVANCE-400 NMR spectrometer equipped with a 7 mm double-resonance probe operating at 400.13 MHz for ^{1}H and 155.5 MHz for ^{7}Li. Typical NMR experimental conditions were as follows: $\Pi/2$ pulse length, 4 µs; recycle delay, 30–150 µs; ^{1}H decoupling power, 65 KHz; spinning speed, 3 KHz. Chemical shifts were externally referenced to a solution of LiCl (δ^7Li = 0.0 ppm).

2.3. Conductivity measurements

The ionic conductivity of the gel polymer electrolytes was measured using an electrochemical cell consisting of the electrolytic film sandwiched between two stainless steel electrodes. These cells were placed inside an argon-filled thermostated oven (30 °C) and maintained at a relative humidity of less than 1%. Impedance anal-
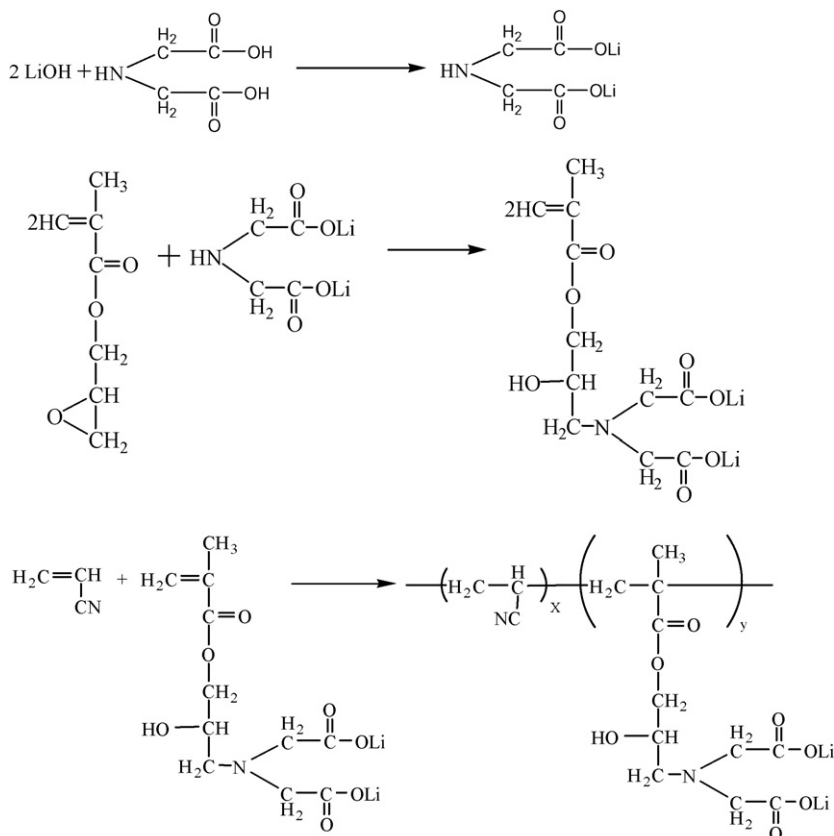
Scheme 1. Schematic representation of the procedures of GMA-IDA synthesis and the copolymerization of AN and GMA-IDA.
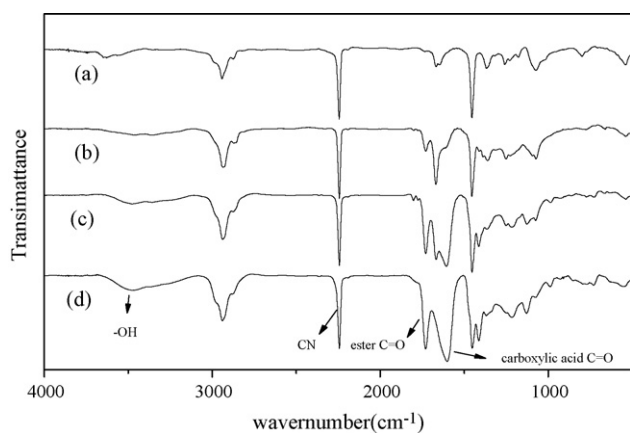
Fig. 1. FT-IR spectra of composite copolymers: (a) PAN, (b) AG1, (c) AG2 and (d) AG3.

Table 1
Chemical compositions of copolymer from elemental analysis.

Symbol of polymer	Elemental analysis (C:N:H)	Molar ratio of copolymer (AN:GMA-IDA)
AG1	65.56:24.59:5.79	1:1.69E−2
AG2	64.18:22.30:5.86	1:4.34E−2
AG3	58.82:18.36:5.93	1:11.01E−2

ysis was carried out using Autolab PGSTAT 30 equipment (Eco Chemie B.V., The Netherlands) employing frequency response analysis (FRA) software, with an oscillation potential of 10 mV from 100 KHz to 1 Hz. The ionic conductivity was calculated by

$$\sigma = \frac{1}{R_b} \times \frac{L}{A},$$

where R_b is the bulk resistance from AC impedance analysis, L is the thickness of the polymer electrolyte film, and A is the surface area of electrode. The thickness of the GPEs was controlled between 150 and 200 μm.

3. Results and discussion

3.1. Characterization of the copolymers

The polymer matrix poly(AN-co-GMA-IDA) was synthesized by free radical copolymerization of AN and GMA-IDA according to Scheme 1. Fig. 1 shows the FT-IR spectra of the polymers PAN, AG1, AG2, and AG3. The spectra feature characteristic signals at $\nu = 2900$, 1730, and 2240 cm^{-1}, attributable to the common groups of –CH$_3$, carbonyl ester, and –C≡N, respectively, in the copolymers. Furthermore, the absorbance peaks at $\nu = 3430$ and 1670 cm^{-1} can be ascribed to the –OH and –COO$^-$ groups in the copolymers. The intensities of the –OH and –COO$^-$ stretching bands increase with increasing GMA-IDA content. Table 1 lists the results of elemen-
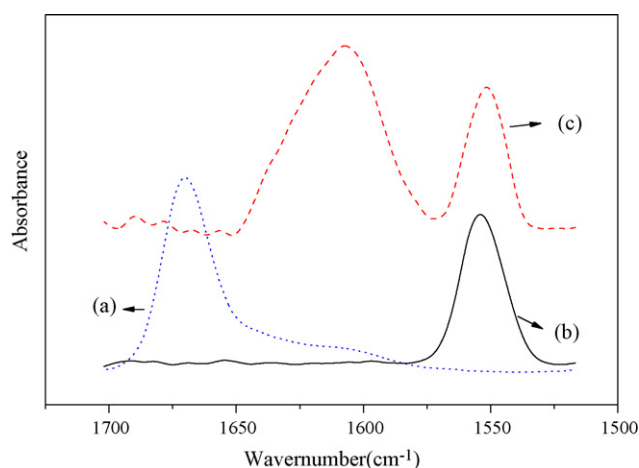

Fig. 2. FT-IR spectra in the C=O stretching region of –COO$^-$ group in: (a) AG2, (b) EC and (c) AG2 + EC.

tal analyses of these copolymers. The FT-IR spectra and elemental analyses confirmed that the copolymer, poly(AN-co-GMA-IDA), had been successfully synthesized and accurately identified.

3.2. Characterization of the plasticized polymer

The plasticized copolymer was prepared by mixing poly(AN-co-GMA-IDA) with ethylene carbonate (EC). The effect of GMA-IDA on the plasticized copolymer was investigated by FT-IR, solid-state NMR, XRD, and DSC.

The interaction of GMA-IDA with EC in the plasticized polymer was confirmed by FT-IR. Fig. 2 presents the IR spectra in the region of the C=O stretching absorption of the –COO$^-$ group for the copolymer (Fig. 2(a)), the plasticizer (Fig. 2(b)), and the plasticized polymer (Fig. 2(c)). The frequency of the peak shifts downward when the copolymer is mixed with EC to form the plasticized polymer. This shift is caused by the interaction of EC with the lithium ion of –COO$^-$Li$^+$. As shown in Scheme 2, the interaction between this lithium ion and EC causes the C=O bond of the –COO$^-$ group to tend towards single-bond character, reducing the frequency of the C=O absorption. Additionally, the mobility of this lithium ion increases with the amount of plasticizer added, improving the conductivity. Fig. 3 shows the FT-IR spectra of the C=O stretching bands of EC and the ester group in GMA-IDA. The C=O band of EC is split in the spectra, because of the Fermi resonance of the C=O stretching mode with an overtone of the ring-breathing mode and the existence of short-range ordering of the molecular orientation, which originates from the dipole–dipole coupling of the EC molecule [10,11]. However, as the GMA-IDA content in the plasticized polymer is increased, the width of the bands increases, as shown in Fig. 3. The C=O band of EC can be deconvoluted into five components. Fortunato et al. [12] observed and assigned the peak 1 (1750 cm^{-1}), peak
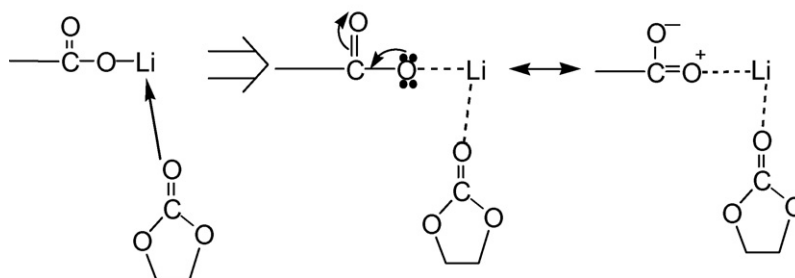
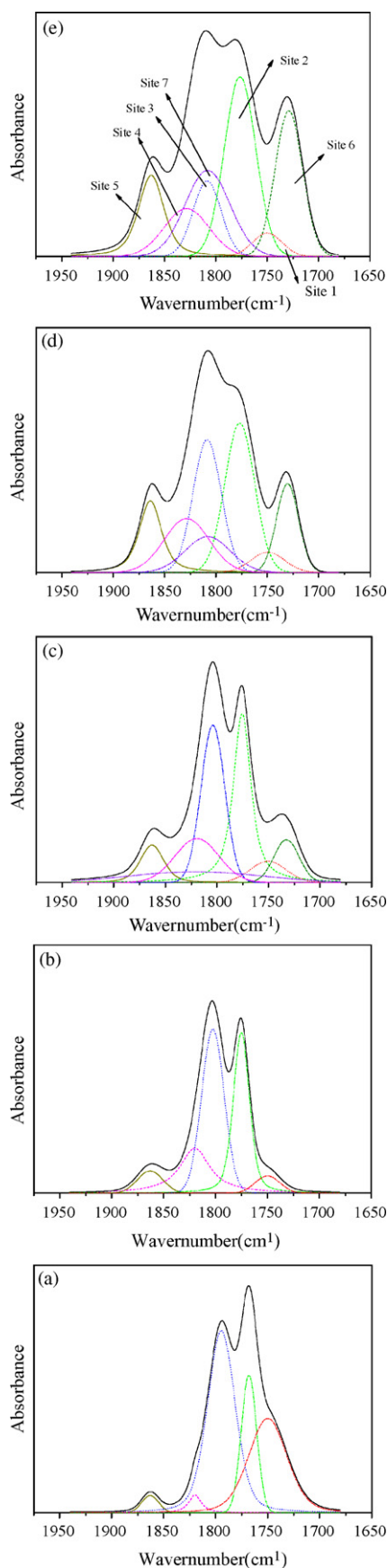**Scheme 2.** Schematic representation of interaction between –COO$^-$Li$^+$ group and EC.

Fig. 3. Deconvolution of C=O of EC stretching region for (a) pure EC at solid state and polymer/EC 50:50 wt.%: (b) PAN, (c) AG1, (d) AG2 and (e) AG3.
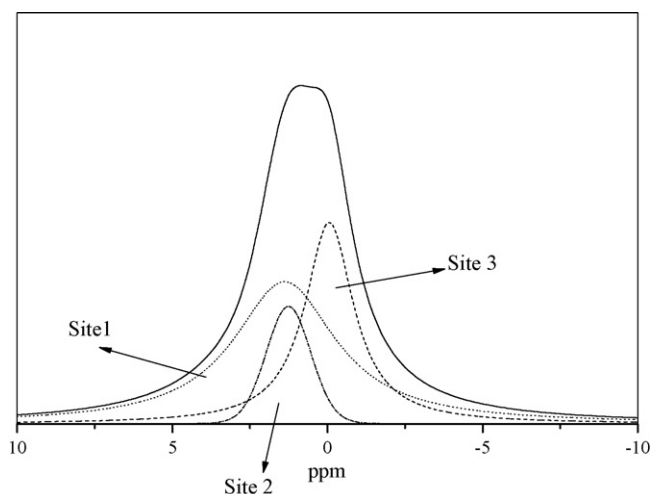

Fig. 4. ^{7}Li MAS NMR spectra of AG3/EC 50:50 wt.% at 213K.

4 (1820 cm^{-1}), and peak 5 (1863 cm^{-1}) bands. Peak 6 corresponds to the C=O band of the ester group in GMA-IDA. Peak 7 was assigned for the hydrogen-bond between C=O of EC and OH of the GMA-IDA unit. The other two bands, corresponding to peak 2 and peak 3 at 1769 and 1795 cm^{-1}, respectively, are related to the C=O symmetric stretching. These peaks show some interesting changes in the plasticized polymers. First, as the GMA-IDA content is increased, the relative intensities of peak 2, peak 3, peak 4, peak 5 and peak 7 clearly change. Second, the width of peak 2 increases with increasing GMA-IDA content. Thirdly, the positions of peak 2 and peak 3 shift to ν = 1776 and 1809 cm^{-1}, respectively, as the polymer is added. Therefore, the changes in these peaks unambiguously indicate the interaction between the lithium ion of –COO$^-$Li$^+$ and the C=O groups of the EC molecules and the hydrogen-bond between C=O of EC and OH of the GMA-IDA unit. Therefore, the results indicated that GMA-IDA can hinder the ordering of the EC molecular orientation.

Fig. 4 shows the ^{7}Li MAS NMR spectrum of AG3/EC 50:50 wt.% without the lithium salt at 213 K. Following deconvolution, Site 1, Site 2, and Site 3 are observed, and their linewidths may be compared by reference to the literature [13–15]. Site 1 is associated with the –COO$^-$Li$^+$ groups of the GMA-IDA unit. Site 2 is associated with coordination between the nitrogen atoms of the GMA-IDA units and lithium ions that are dissociated from the –COO$^-$Li$^+$ groups of the GMA-IDA. Site 3 is related to coordination between EC and lithium ions that are derived from the copolymer. The presence of lithium ions in different environments is diagnostic of the interaction between EC and the lithium ions of the –COO$^-$Li$^+$ groups of the GMA-IDA in the plasticized copolymer. This result also confirms the aforementioned FT-IR results.

To briefly sum-up our key finding, this study has established that the lithium ion of the –COO$^-$Li$^+$ group can interact with the C=O group of EC.

EC is an electrolyte; it has a high dielectric constant and a high donor number. However, it exists in the solid state at room temperature, thus reducing the mobility of lithium ions in the electrolytes. According to the above paragraph, the lithium ions of the –COO$^-$Li$^+$ groups can interact with the C=O groups of EC, and as a result the crystallization behavior of EC in the GPEs can be expected to be changed. Hence, DSC has been further applied to elucidate the thermal behavior of the plasticized polymer in this study. Table 2 contains the endothermic peaks of EC in the plasticized polymers. With a composition of polymer/EC 40:60 wt.%, the endothermic heat of EC decreases as the GMA-IDA content is increased. Moreover, at 50:50 wt.%, no crystalline state is detected for EC in the plasti-

Table 2
The endothermic heat ΔH ($J\,g^{-1}$ EC) for the polymer with various wt.% of EC.

EC (wt.%)	Polymer			
	PAN	AG1	AG2	AG3
50	19.96	–	–	–
60	97.60	35.97	29.77	17.28

Table 3
The endothermic heat ΔH ($J\,g^{-1}$ EC) for the Polymer/EC 40:60 wt.% for various concentration of $LiClO_4$.

Polymer/EC 40:60 wt.%	$LiClO_4$ (mmol g^{-1} polymer)				
	0.25	0.5	1.0	2.0	3.0
PAN	68.72	33.90	0.38	–	–
AG1	4.30	–	–	–	–
AG2	2.73	–	–	–	–
AG3	2.50	–	–	–	–

cized polymer containing the GMA-IDA unit. The results indicate that GMA-IDA can hinder the crystallization of EC in the plasticized polymer owing to the interaction between the EC and GMA-IDA, which was confirmed by FT-IR. Additionally, the added lithium ions also hindered the crystallization of EC in polymer/EC 40:60 wt.% system, as the results of DSC (Table 3).

XRD experiments were performed on plasticized polymer samples with the compositions polymer/EC 40:60 and 50:50 wt.%, as presented in Fig. 5, to confirm the aforementioned DSC results. Obviously, for the polymer/EC 40:60 wt.% composition, the intensity of the peaks due to EC (Fig. 5(I) (a)) decreases as the GMA-IDA content is increased (Fig. 5(I) (b)–(d)). Moreover, the diffraction peaks due to EC [16] (Fig. 5(II) (a)) are not found in the diffractograms of the plasticized polymers containing GMA-IDA (Fig. 5(II) (b)–(d)). The DSC and XRD results confirm that the

GMA-IDA unit in the copolymer can hinder the crystallization of EC.

3.3. Lithium ions in the plasticized polymers

The copolymer, the plasticizer EC, and the lithium salt are mixed together to form the gel polymer electrolyte. The form of the lithium ions in the GPE critically affects the conductivity. The presence of ion aggregation $\{Li^+ClO_4^-\}_n$ reduces the number of charge carriers, lowering the conductivity of the GPE. In this study, FT-IR has been used to study the form of the lithium ions in the GPEs. According to the literature [17,18], the free perchlorate anion exhibits four fundamental bands, υ_1 (symmetrical stretching) ≈ 931 cm^{-1}, υ_2 (symmetrical bending) ≈ 462 cm^{-1}, υ_3 (asymmetrical stretching) ≈ 1102 cm^{-1}, and υ_4 (asymmetrical bending) ≈ 624 cm^{-1}. Of these, υ_3 and υ_4 are IR-active; however, υ_3 is overlapped by the peaks of the polymer and the plasticizer. Therefore, υ_4 has been used to probe the existence of aggregated ions in the GPE. Fig. 6(I) shows the FT-IR spectral region of the υ_4 band for polymer/EC 50:50 wt.% with $LiClO_4$ at 3 mmol g^{-1} polymer. As the GMA-IDA content in the copolymer is increased, the band becomes more symmetrical. In the literature [19,20], it has been reported that when ion aggregation is present, a shoulder appears at 640 cm^{-1}. Deconvolution of the peak yielded Fig. 6(II), which shows the spectral region for free "ClO_4^-". The fraction of the free "ClO_4^-" increases as the GMA-IDA content is increased, indicating that GMA-IDA can improve the dissociation of the lithium salt and reduce the ion aggregation.

3.4. Ionic conductivity

The ionic conductivity of the gel polymer electrolytes was measured using two stainless steel electrodes, in order to study the
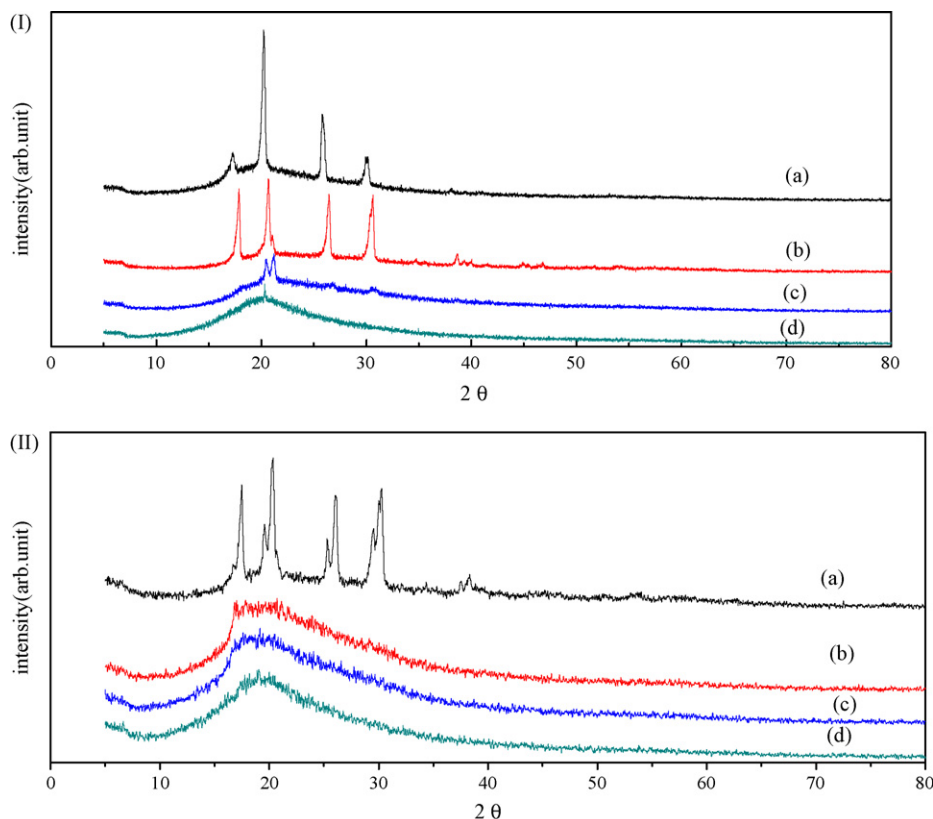

Fig. 5. (I) XRD spectra of polymer/EC 40:60 wt.%: (a) PAN, (b) AG1, (c) AG2 and (d) AG3; (II) polymer/EC 50:50 wt.%: (a) PAN, (b) AG1, (c) AG2 and (d) AG3.
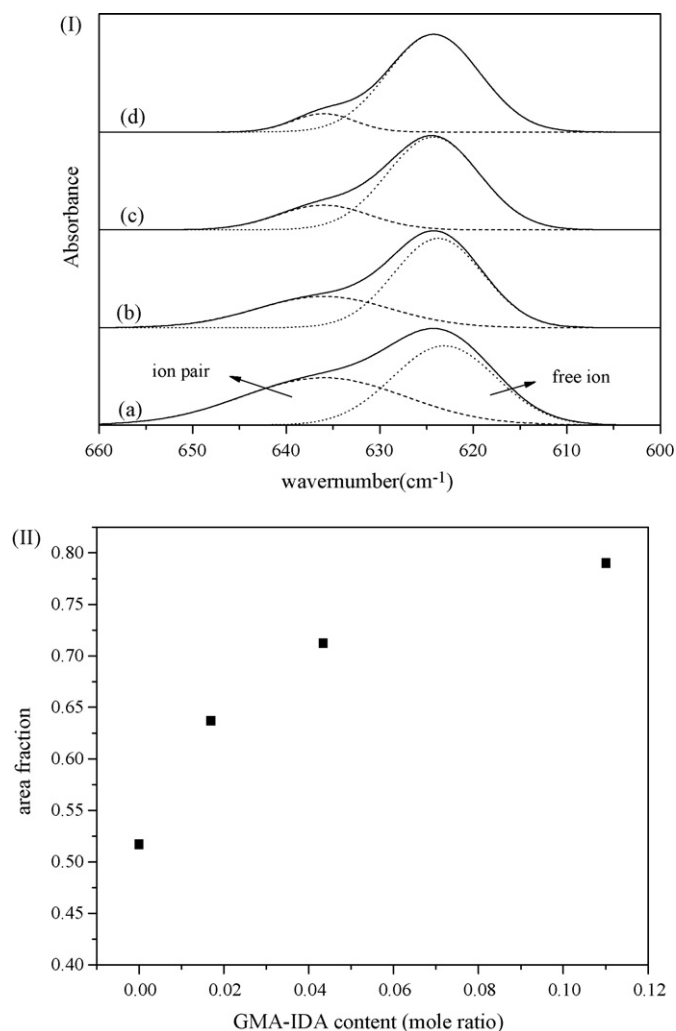
Fig. 6. (I) FT-IR spectra of free perchlorate anion υ_4 band in polymer/EC 50:50 wt.% with LiClO$_4$ (3 mmol g^{-1} polymer): (a) PAN, (b) AG1, (c) AG2 and (d) AG3. (II) Fraction of free "ClO$_4^-$" versus GMA-IDA content for (I).

Fig. 7. Ionic conductivity vs. LiClO$_4$ concentration for (I) polymer/EC 50:50 wt.% and (II) polymer/EC 40:60 wt.%: (■) PAN, (○) AG1, (△) AG2 and (▽) AG3.

effect of the copolymer composition on this parameter. Fig. 7 shows plots of the conductivity of polymer/EC 50:50 and 40:60 wt.% as a function of lithium salt content at 30 °C. The conductivity is seen to increase with increasing salt concentration. Fig. 7 shows higher ionic conductivity of polymer/EC 40:60 wt.% in comparison with polymer/EC 50:50 wt.%. In the GPEs, the EC is similar to the general plasticizer, the increase of it in the GPEs increase the distance between the polymer chains and so increase the movement of the free EC molecules. Moreover, the higher EC content in the GPEs increases the dissociation of lithium salt and reduces the aggregation of ions in the GPEs. Hence, the number of charge carriers in the GPE increases, improving the ionic conductivity. Unfortunately, crystallization of EC reduces the mobility of Li$^+$ and so decreases the ionic conductivity. In this study, the crystallization of EC exist in the polymer/EC 40:60 wt.% system. However, the added lithium ion also hindered the crystallization of EC in polymer/EC 40:60 wt.% system, as the results of Table 3. Consequently, these effects determine the ionic conductivity of polymer/EC 40:60 wt.% system is higher than that of polymer/EC 50:50 wt.% system. Additionally, the conductivities of the GPEs increase with increasing GMA-IDA content in the copolymer. Some of the GPEs containing the GMA-IDA unit have a conductivity that is one order of magnitude greater than that of the PAN system with same composition, for which three reasons may be cited. (1) The GMA-IDA unit can hinder the crystallization of EC
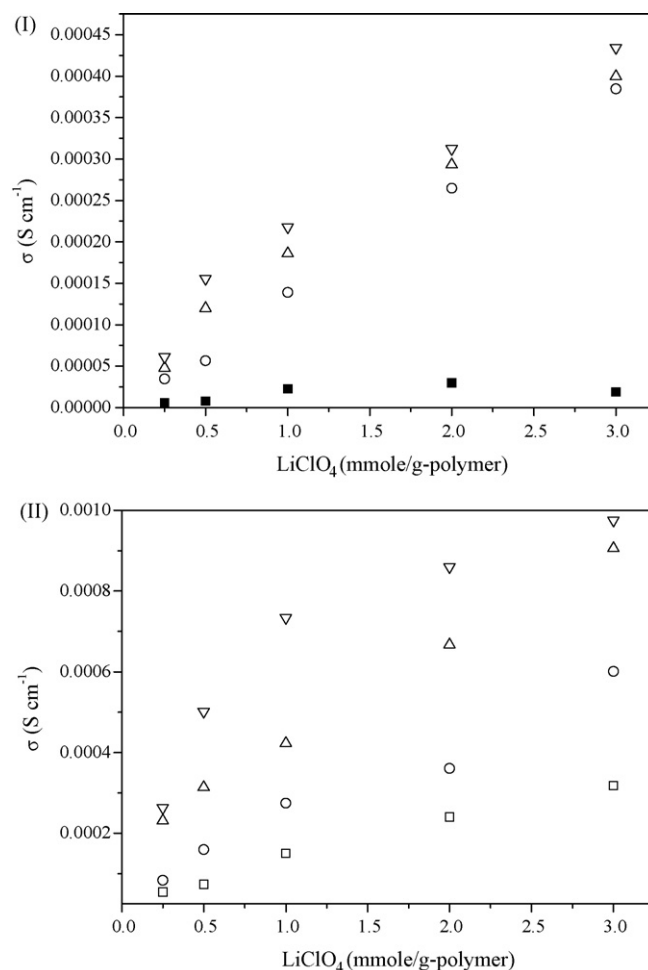
in the GPEs, as confirmed by DSC and XRD analyses. (2) According to the FT-IR and solid-state NMR results, the mobility of Li$^+$ in –COO$^-$Li$^+$ increases with the amount of EC added. Hence, the number of charge carriers in the GPE increases, improving the ionic conductivity. (3) The GMA-IDA unit increases the dissociation of the lithium salt and reduces the aggregation of ions in the GPEs, as confirmed by FT-IR analysis. Therefore, AG3/EC 40:60 wt.% with LiClO$_4$ at 3 mmol g^{-1} polymer displayed the highest conductivity of 9.75×10^{-4} S cm^{-1}. This level of ionic conductivity approaches that of the PAN/PC 20:80 wt.% system (1.90×10^{-3} S cm^{-1}). Fig. 8 shows the conductivities of AG3/EC 50:50 wt.%, AG3/EC/PC 50:40:10 wt.%, PAN/EC/PC 50:40:10 wt.%, and AG3/PC 50:50 wt.% with various concentrations of the lithium salt. The GMA-IDA-containing gel polymer electrolytes with EC as the plasticizer show greater conductivity than those with mixed EC/PC as plasticizer. Mixed-liquid electrolytes are usually used to prevent the crystallization of EC, but the properties of the mixed-liquid electrolytes are not as good as those of EC alone. Accordingly, copolymerization with a GMA-IDA unit represents a better approach than using mixed-liquid electrolytes as plasticizers to suppress the crystallization of EC.

Notably, the AG3/EC 40:60 wt.% system (Young's modulus = 0.76 MPa, toughness = 666.25 MPa) has good conductivity – close to 1×10^{-3} S cm^{-1} – and has better mechanical properties than the PAN/PC 20:80 wt.% system (Young's modulus = 0.18 MPa, toughness = 4.30 MPa). Therefore, in this work, the AG3/EC 40:60 wt.% system has been shown to provide a polymer electrolyte that displays good conductivity and good mechanical strength.
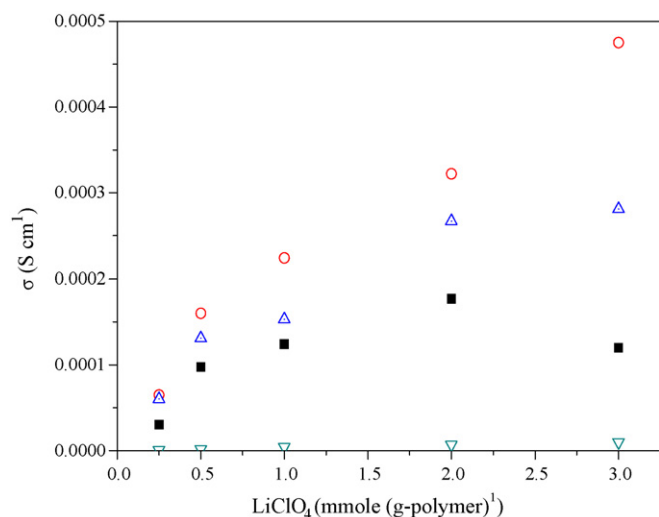
Fig. 8. Ionic conductivity vs. LiClO$_4$ concentration for (○) AG3/EC 50:50 wt.%; (△) AG3/EC/PC 50:40:10 wt.%; (■) PAN/EC/PC 50:40:10 wt.%; (▽) PAN/EC 50:50 wt.%.

4. Conclusion

A plasticized polymer has been synthesized from AN and GMA-IDA, with EC as a plasticizer. Analytical results have revealed a significant interaction between the GMA-IDA and EC. This interaction gives rise to three effects. (1) The GMA-IDA unit hinders the crystallization of EC in the GPEs. (2) The mobility of Li$^+$ in the $-COO^-Li^+$ units increases with the amount of EC added, and hence the number of charge carriers in the GPE increases, improving the ionic conductivity. (3) The GMA-IDA unit increases the dissociation of the lithium salt and reduces the ion aggregation in the GPEs. Consequently, the maximum conductivity measured in this work exceeds that of a typical PAN-based system of similar composition.

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