Polymer Gel Electrolytes Based on 49% Methyl-Grafted Natural Rubber

(Elektrolit Gel Polimer Berasaskan 49% Metil Cangkukan Getah Asli)

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ABSTRACT

Polymer gel electrolytes (PGEs) based on 49% methyl-grafted natural rubber (MG49) were first prepared by dissolving ammonium triflate ($NH_4CF_3SO_3$) in propylene carbonate (PC) by various molar concentrations of $NH_4CF_3SO_3$ to obtain liquid electrolytes and were characterized by AC electrical impedance spectroscopy (EIS) measurements to study their conducting behaviour. The liquid electrolyte with optimum conductivity (0.7M) was then gelled with MG49 and their conductivity was also studied. The highest conductivity of liquid electrolyte was 3.6×10^{-3} Scm^{-1} and 2.9×10^{-2} Scm^{-1} for PGEs. The molecular interactions between components of $NH_4CF_3SO_3$, PC, and MG49 have been observed by ATR-FTIR spectroscopy study. The downshifting of C=O stretching frequency of PC from 1785 cm^{-1} to 1780 cm^{-1} and NH_4^+ band from 1634 cm^{-1} to 1626 cm^{-1} that has been obtained by spectroscopic data in addition of $NH_4CF_3SO_3$ confirmed the complexation occurrence. Interaction between $NH_4CF_3SO_3$ and MG49 has also been investigated. This study is focused on the interactions between components in the PGE system and relates them with their conducting behavior.

Keywords: Ammonium triflate; complexation; conductivity; MG49; polymer gel electrolyte

ABSTRAK

Elektrolit gel polimer berasaskan 49% metil cangkukan getah asli (MG49) disediakan dengan melarutkan ammonium triflat ($NH_4CF_3SO_3$) dalam propilena karbonat (PC) dengan pelbagai kepekatan molar bagi menghasilkan elektrolit cecair dan sifat kekonduksiannya diuji menggunakan alat spektroskopi impedans elektrik arus ulang-alik. Elektrolit cecair dengan kekonduksian optimum (0.7M) kemudian digel bersama MG49 dan ciri kekonduksiannya juga dikaji. Nilai kekonduksian paling tinggi bagi elektrolit cecair ialah 3.6×10^{-3} Scm^{-1} dan 2.9×10^{-2} Scm^{-1} bagi elektrolit gel polimer. Interaksi molekul antara komponen $NH_4CF_3SO_3$, PC, dan MG49 diperhatikan melalui kajian spektroskopi ATR-FTIR. Anjakan frekuensi regangan C=O PC daripada 1785 cm^{-1} ke 1780 cm^{-1} dan jalur NH_4^+ daripada 1634 cm^{-1} ke 1626 cm^{-1} dengan penambahan $NH_4CF_3SO_3$ yang diperoleh daripada data spektroskopik mengesahkan berlakunya kompleks antara PC dan $NH_4CF_3SO_3$. Interaksi antara $NH_4CF_3SO_3$ dan MG49 juga turut dikaji. Kajian ini memfokus pada interaksi antara komponen-komponen dalam sistem elektrolit gel polimer dan mengaitkan dengan sifat-sifat kekonduksiannya.

Kata kunci: Ammonium triflat; elektrolit gel polimer; kekonduksian; kompleks; MG49

INTRODUCTION

Solid polymer electrolytes (SPEs) have drawn a great attention for its potential application in electrochemical devices since Fenton et al. (1973) and Armand et al. (1978) confirmed that SPEs possessed the criteria as ionic conductor and can be used as the electrolytes for batteries. It is well known that SPEs possess lower ionic conductivity as compared to liquid electrolytes but, they have overcome the problems of liquid electrolytes (LEs) such as leakage, poor dimensional stability and internal short when it comes to battery fabrication. However, SPEs have one major drawback that was poor electrode-electrolyte interface contact. Therefore many researchers made attempts to develop new polymer electrolyte system that possessed mechanical strength as good as SPEs and ionic conductivity comparable to those LEs which led to the discovery of polymer gel electrolytes (PGEs) that fulfill those criteria. These liquid electrolytes cum polymer-based electrolytes can be used as potential substitutes for SPEs and liquid electrolytes in batteries application.

Modified natural rubber (NR) is a biomaterial-based polymer that has a low glass transition temperature, T_g and possess good elasticity and adhesion properties. Its elastomeric properties at room temperature allows it to form a free-standing film and providing good electrode-electrolyte contact (Glasse et al. 2002; Idris et al. 2001). These characteristics make MG49 a suitable polymeric gelling agent in PGE.

In this work, PGEs were obtained by gelling the $NH_4CF_3SO_3$-PC solution with MG49. The physical and electrical studies have been carried out for $NH_4CF_3SO_3$-PC-MG49 PGEs. ATR-FTIR spectroscopy study has been performed on liquid electrolyte composed of PC added various amount of $NH_4CF_3SO_3$ (0.1-1.4M) and PGEs composed of liquid electrolyte added with varying percentage by weight of MG49 (1-7%) to observe

the molecular interaction between PC-ammonium triflate, MG49-ammonium trfilate and PC-ammonium triflate-MG49 that may influence the conductivity. The conductivity of both liquid and gel system have then been correlated to the various interaction observed in ATR-FTIR spectra.

EXPERIMENTAL METHODS

Polymer gel electrolytes were obtained by first dissolving various amount of $NH_4CF_3SO_3$ (Aldrich) from 0.1-1.4 M in 10 mL PC (Aldrich) and stirred for 24 hours by magnetic stirrer to obtain liquid electrolytes. The liquid electrolyte that has optimum ionic conductivity (0.7 M) has been added with MG49 (Rubber Research Institute of Malaysia) at different weight percentage (1-7%) in tetrahydrofuran (THF; Aldrich) and stirred by magnetic stirrer for several hours until complete dissolution. The solutions were then dried in a vacuum oven at 65ºC for 48 h to remove the THF solvent. ATR-FTIR spectra were recorded using Perkin Elmer Spectrum-One spectrometer in the frequency range of 650-4000 cm^{-1} with 2 cm^{-1} resolution. The samples were placed on a crystal zinc selenide plate where total internal reflection occurred at the crystal-samples interface. The electrical impedance spectroscopy (EIS) for both liquid and gel system were conducted using Hioki 3532-50 LCR HiTESTER in the frequency range of 100 Hz to 1 MHz. The measurements were carried out by dipping stainless steel probe into the electrolytes.

RESULTS AND DISCUSSION

Infrared spectra of PC have been studied by Battisti et al. (1993) and Deepa et al. (2002, 2004), and complete assignment of the prominent peaks were given while Kumutha & Alias (2006) and Ali et al. (2008) have studied the vibrational modes of methyl-grafted natural rubber. The observation of PC and MG49 characteristic bands in this present work were assigned based on their reports. However, to the best of our knowledge, there is no report on NH_4 and MG49.

INTERACTION BETWEEN PC AND $NH_4CF_3SO_3$

The infrared spectra of PC containing ammonium triflate salt in wavenumber ranging from 1000 - 1900 and 700 - 800 cm^{-1} are presented in Figures 1 and 2, respectively. The C=O stretching mode of PC centered at 1785 cm^{-1} as in Figure 1 (ii) has been shifted to 1780 cm^{-1} upon addition of $NH_4CF_3SO_3$. The downshift of this band is due to the lone pair oxygen atom carried by C=O in PC. This lone pair electron was donated to NH_4^+ in forming complexes with the ammonium salt ($NH_4^+ \leftarrow O=C$) which have also been reported in previous works (Ali et al. 2008; Deepa et al. 2002; Kumutha & Alias 2006). The NH_4^+ band at 1634 cm^{-1} has shifted to 1626 cm^{-1} as 0.7 M of salt added as can be seen in Figure 1 (iv). The intensity of the band
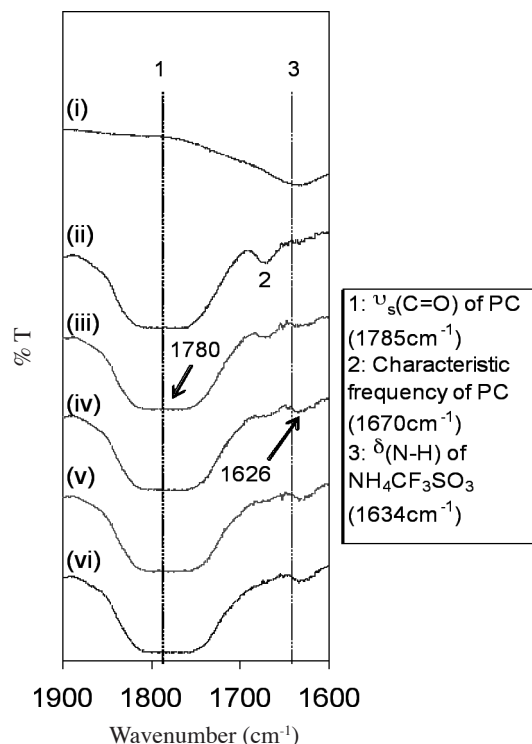

FIGURE 1. ATR-FTIR spectra of (i) pure $NH_4CF_3SO_3$, (ii) pure PC, (iii) PC+0.3 M $NH_4CF_3SO_3$, (iv) PC+0.7 M $NH_4CF_3SO_3$, (v) PC+1.1 M $NH_4CF_3SO_3$, (vi) PC+1.4 M $NH_4CF_3SO_3$ in the wavenumber region of 1600-1900cm^{-1}
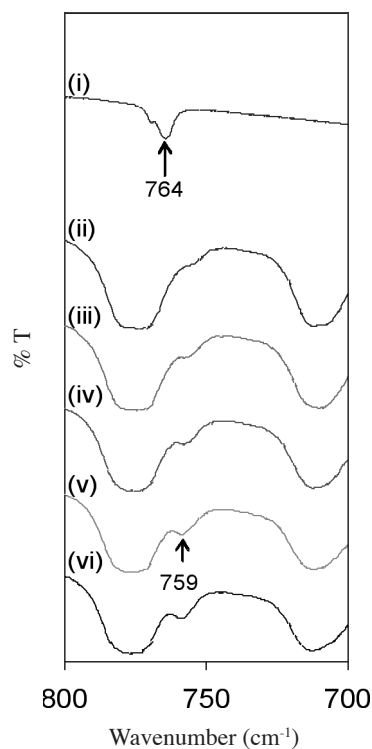
FIGURE 2. ATR-FTIR spectra of (i) pure $NH_4CF_3SO_3$, (ii) pure PC, (iii) PC+0.3 M $NH_4CF_3SO_3$, (iv) PC+0.7 M $NH_4CF_3SO_3$, (v) PC+1.1 M $NH_4CF_3SO_3$, (vi) PC+1.4 M $NH_4CF_3SO_3$ in the wavenumber region of 700-800cm^{-1}

increased as the salt concentration going higher. Another characteristic frequency of PC at 1670 cm^{-1} is observed to vanish upon addition of NH$_4$CF$_3$SO$_3$ starting at 0.3 M salt and completely disappeared when 1.4 M of ammonium triflate was added. The symmetric deformation mode CF$_3$ (δ_s (CF$_3$)) of triflate ion at 764 cm^{-1} has seen to shift to lower wavenumber at 759 cm^{-1} when 1.1 M of salt being added to PC. The shift of the band with increasing intensity to lower wavenumber indicates the presence of ion aggregates which was also reported by previous studies (Ali et al. 2008; Starkey & Frech 1997; Winie & Arof 2006).

INTERACTION BETWEEN MG49 AND NH$_4$CF$_3$SO$_3$

The infrared spectroscopy study was also performed on MG49-NH$_4$CF$_3$SO$_3$ to observe the interaction that may have occurred between the polymer and the salt. Figure 3 shows the infrared spectra of NH$_4$CF$_3$SO$_3$, MG49, and MG49+NH$_4$CF$_3$SO$_3$ with 1:1 ratio. In the spectral region of 1500 - 1900 cm^{-1} as in Figure 3 a, interaction can be seen as the N-H band at 1634 cm^{-1} is downshifted by 5

cm^{-1} to 1629 cm^{-1}. The same goes to the carbonyl band of MG49 where the C=O mode at 1725 cm^{-1} also shifted to 1720 cm^{-1}. The shift of C=O to lower wavenumber is the same case as PC-salt earlier where lone pair electron at C=O have been donated to NH$_4^+$ to form a complex (NH$_4^+$←O=C). On the other hand, the asymmetric stretch of CH$_3$ (ν_{as} (CH$_3$)) of MG49 at 1400 cm^{-1} and another prominent peak of MG49 at 1445 cm^{-1} are observed to overlap to form a broad band centered at 1435 cm^{-1} as shown in Figure 3(b) (iii). In the region of 1100 - 1350 cm^{-1} the asymmetric stretching of SO$_3$ (ν_{as} (SO$_3$)) located at 1261 cm^{-1}, symmetric stretching of CF$_3$ (ν_s (CF$_3$)) located at 1228 cm^{-1}, the C-O stretching mode at 1270 cm^{-1} and the CH$_2$ twisting mode (ρ_t (CH$_2$)) at 1239 cm^{-1} of the MG49 (Figure 3(c) (ii)) are seen to overlap to form a broad band centered at 1235 cm^{-1} as shown in Figure 3(c) (iii). Another peak at 1173 cm^{-1} assigned to υ_{as} (CF$_3$) mode (asymmetric stretching of CF$_3$) of triflate ion, is seen to merge with the CH$_2$ in plane bending (δ (CH$_2$)$_{i.p.}$) of MG49 at 1189 cm^{-1} along with the CH$_2$ twisting mode (ρ_t (CH$_2$)) at 1145 cm^{-1} of MG49 to form a broad band
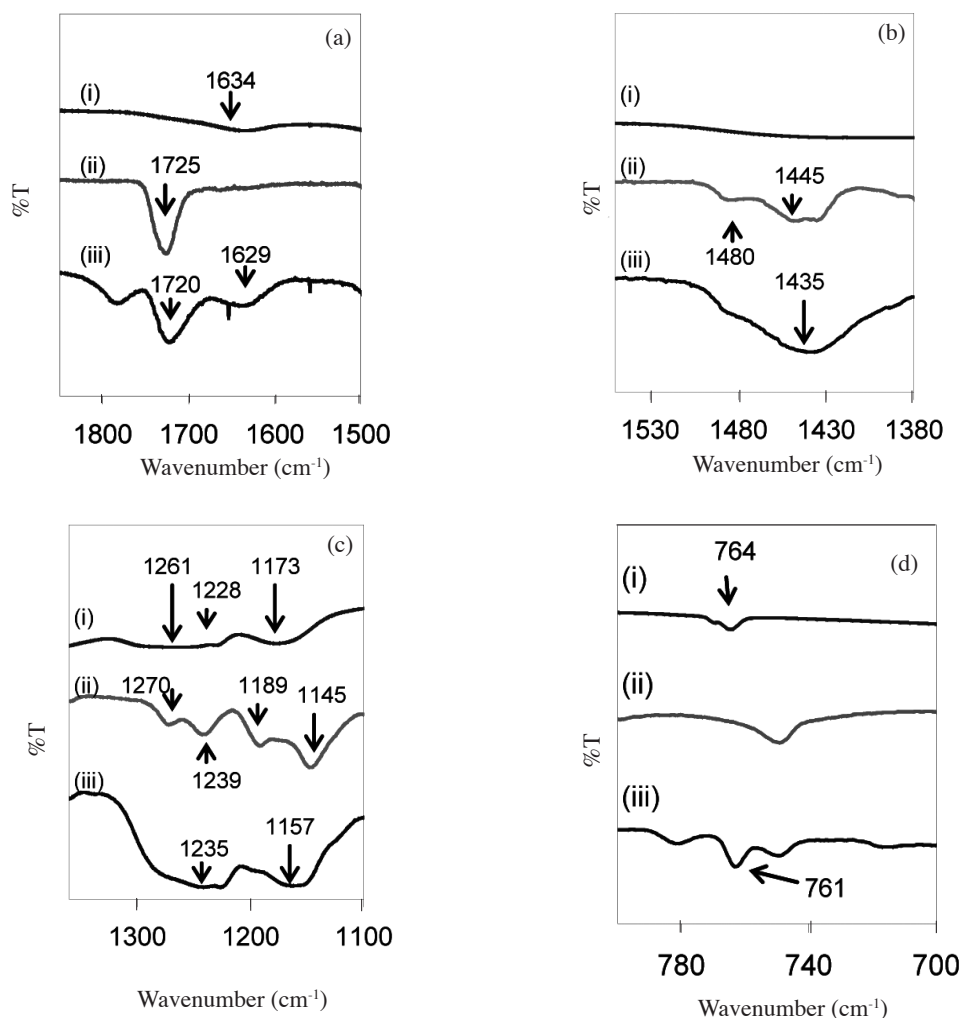

FIGURE 3. ATR-FTIR spectra of (i) pure NH$_4$CF$_3$SO$_3$, (ii) pure MG49, and (iii) MG49+ NH$_4$CF$_3$SO$_3$ (1:1)
in the wavenumber region of (a) 1500-1900, (b) 1380-1550,
(c) 1100-1350, and (d) 700-800 cm^{-1}

centered at 1157 cm^{-1}. The symmetric deformation of CF$_3$ (δ_s (CF$_3$)) of triflate ion at 764 cm^{-1} is downshifted to 761 cm^{-1} when salt was introduced to MG49. These evidences are consistent with the results reported by Ali et al. (2008) and indicate that MG49 and NH$_4$CF$_3$SO$_3$ possibly do have complexation.

INTERACTION BETWEEN MG49 AND PC

Study on plasticizer effect on polymer was also carried out to indicate any changes and differences in MG49 vibrational mode upon incorporation with PC. Depicted on Figure 4 are the infrared spectra of MG49+PC with 2:1 ratio in the 650-2000 cm^{-1} spectral region. As shown in the figure, the C=O, ν_{as} (CH$_3$) (asymmetric stretching of CH$_3$), δ_s (CH$_3$) (symmetric deformation of CH$_3$) and ρ_t (CH$_2$) (twisting mode of CH$_2$) mode of MG49 located at 1725, 1480, 1375, and 1145 cm^{-1}, respectively can be observed. The spectra show no noticeable change of the vibrational behaviour suggesting that there is no interaction between MG49 and PC.
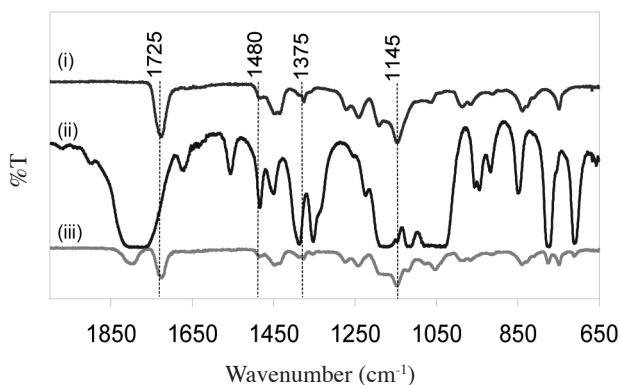
ROLE OF PC IN MG49- NH$_4$CF$_3$SO$_3$ INTERACTION

The infrared spectra in Figure 5 are assigned to PC-NH$_4$CF$_3$SO$_3$-MG49. The broad peak of C=O of PC+0.7 M salt at 1778 cm^{-1} has been narrowed with the appearance of shoulder peak between 1720-1741 cm^{-1} frequency range due to the competency of both NH$_4^+$←O=C in PC and MG49. The broad shoulder peak (1720-1741 cm^{-1}) indicates that the interaction of MG49- NH$_4$CF$_3$SO$_3$ is stronger than PC-NH$_4$CF$_3$SO$_3$ as the molecule of MG49 is bigger than PC. As can be seen in Figure 5(b) the C-O stretching (ν (C-O)) and CH$_2$ rocking (ρ_r (CH$_2$)) mode of PC [12] located at 956 cm^{-1} and 943 cm^{-1} respectively and other prominent peaks due to PC-NH$_4$CF$_3$SO$_3$ interaction at 849, 773, and 708 cm^{-1} in Figure 5(c) only reduced in intensity upon incorporation with MG49 but remain unshifted. The evidences of interaction of PC-NH$_4$CF$_3$SO$_3$-MG49 proof that the PC only penetrate to MG49 polymer chain to enhance its segmental motion that can help improve the conductivity (Frech & Chintapalli 1996) which will be discussed next.

CONDUCTIVITY MEASUREMENTS

Figure 6 shows the variation of conductivity of PC-NH$_4$CF$_3$SO$_3$ with salt concentration range of 0.1-1.4 M. It is agreed that when more salt added to the system, the conductivity goes higher. This is because, more salts means more number of NH$_4^+$ ions can complex in C=O of PC as discussed earlier. The more ions dissociate increased the number of charge carriers which results in rising the conductivity value. Region I involved salt concentration up to 0.6 M. In this region, the initial slight increase in conductivity is due to low salt concentration. Then it increases gradually due ion dissociation as more salt are being added to the system. Region II shows a slow rate of increase of conductivity mainly due to partial formation of cation-anion pairs as the concentration of salt increases. These neutral species do not take part in

FIGURE 4. ATR-FTIR spectra of (i) pure MG49, (ii) pure PC, and (iii) MG49+PC (2:1) in the wavenumber region of 650-2000 cm^{-1}

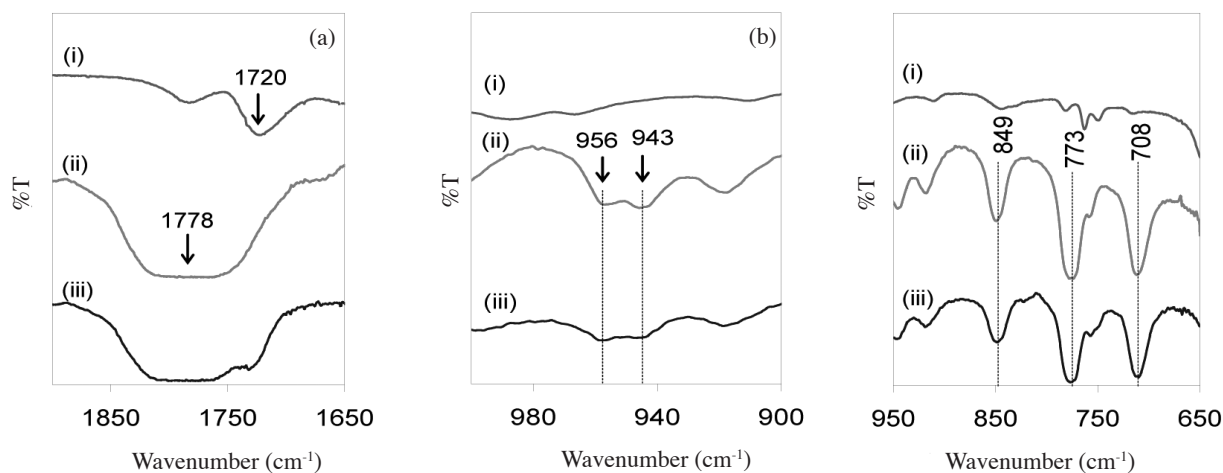FIGURE 5. ATR-FTIR spectra of (i) MG49+NH$_4$CF$_3$SO$_3$ (1:1), (ii) PC+0.7M NH$_4$CF$_3$SO$_3$, and (iii) MG49+PC+0.7M NH$_4$CF$_3$SO$_3$ in the wavenumber region of (a) 1650-1900, (b) 900-1000, and (c) 650-950 cm^{-1}

ion transport when external electric field was applied to the sample. Therefore, it is almost a 'plateau' at 0.6-0.9 M of salt concentration because the conductivity only increases very slightly. The gradual increase at higher rate compared to region II as shown in region III is resulted from the redissociation of ion-pairs to form a single or triplets ion which again take part in the ion transport and reach the maximum conductivity of 3.6×10^{-3} S cm^{-1} at 1.1 M of salt concentration. The decrease of conductivity in region IV (> 1.1 M NH$_4$CF$_3$SO$_3$ in PC) due to the formation of ion aggregate at high salt concentration which do not help in the conduction process that also concurs with the part discussed earlier. Figure 7 shows the variation of conductivity as a function of MG 49 amount in PC-0.7M NH$_4$CF$_3$SO$_3$ system. The increase in conductivity upon addition of MG49 is due to the penetration of PC into MG49 polymer chain and enhances its segmental motion. As the MG49 polymer backbone is being soften, it gives room for ammonium triflate salt to complex with MG49. Hence, more ions will be dissociated as discussed in '3.4'. 2.9×10^{-2} S cm^{-1} is the highest conductivity that the system can reach at 3 wt% of MG49 which is higher than that of liquid electrolyte and can be explained by the "Breathing Polymeric Chain" model. When polymer is added to liquid electrolyte, it increased pressure in the surrounding of the system volume as the polymer chain 'breathes' while occupying different volumes and enhancing mobility that leads to the rise in conductivity (Chandra et al. 2000). This value is much higher than reported before (Ali et al. 2006; Glasse et al. 2002; Idris et al. 2001; Mohamed et al. 208) by using methyl grafted natural rubber as the polymer host. Higher rate of ion association than ion dissociation causes the conductivity to decrease with further addition of MG49 (> 3 wt%) into the system.

CONCLUSION

Interaction between components in PC-NH$_4$CF$_3$SO$_3$-MG49 polymer gel electrolyte system has been noted through ATR-FTIR spectroscopy study. The shifting of C=O stretching of PC and NH$_4^+$ of NH$_4$CF$_3$SO$_3$ to a lower wavenumber in PC-NH$_4$CF$_3$SO$_3$ solution confirmed the complexation between PC and NH$_4$CF$_3$SO$_3$. Complexation between MG49 and NH$_4$CF$_3$SO$_3$ also noted with the downshifting of C=O of MG49 and NH$_4^+$ of NH$_4$CF$_3$SO$_3$ in MG49- NH$_4$CF$_3$SO$_3$. The interaction of MG49- NH$_4$CF$_3$SO$_3$ is stronger than PC-NH$_4$CF$_3$SO$_3$ while there is no interaction between MG49 and PC. The highest conductivity obtained through EIS for both LEs and PGEs are 3.6×10^{-3} S cm^{-1} and 2.9×10^{-2} S cm^{-1}. The data of the conductivity also concurs with the ATR-FTIR study.

ACKNOWLEDGEMENTS
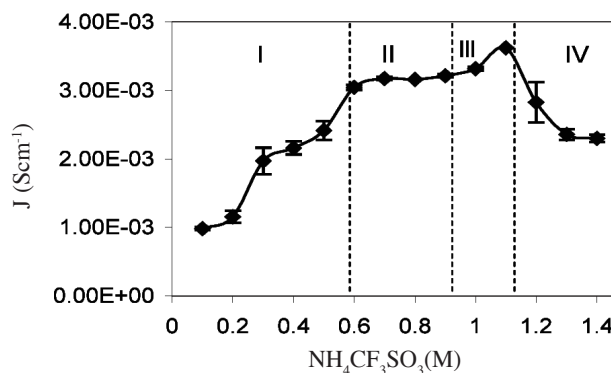
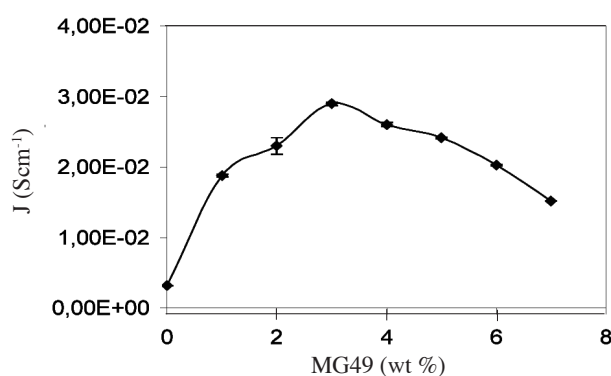FIGURE 6. Conductivity of PC-NH$_4$CF$_3$SO$_3$ as a function of salt concentration

FIGURE 7. Conductivity of PC-NH$_4$CF$_3$SO$_3$-MG49 as a function of MG49 amount

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