Conduction and thermal properties of a proton conducting polymer electrolyte based on poly (ε-caprolactone)

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A B S T R A C T
A proton conducting polymer electrolyte based on poly(ε-caprolactone) (PCL) complexed with different concentrations of ammonium thiocyanate (NH4SCN) salt has been investigated. The ionic conductivity of the solid polymer electrolyte (SPE) of pure PCL obtained at room temperature is $1.86 \times 10^{-11}$ S cm$^{-1}$. The maximum ionic conductivity achieved in the solution-cast films at room temperature is $1.01 \times 10^{-4}$ S cm$^{-1}$ for PCL incorporated with 26 wt.% NH4SCN. The calculated dielectric constant at selected frequencies follows the same trend as conductivity, concluding an increase in number density of ions with the salt content. DSC thermogram shows that the degree of crystallinity of PCL is reduced as more salt is accommodated in the PCL crystalline phase. The FTIR of asymmetric C≡N stretching mode is deconvoluted into three bands representing free ions, contact ion pairs and ion aggregates to obtain an insight on ion associations. The FTIR results show that the number of free ions become maximum at 26 wt.% NH4SCN. The correlation between free ions, ion aggregates and conductivity is obvious. The increase in ion dissociation improves conductivity, while the formation of ion aggregates reduces conductivity.

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1. Introduction

Global warming is a worrying environmental issue, which has resulted in active public movement to reduce environmental loads. The use of ‘eco-friendly’ materials as conducting polymer electrolyte (PE) can certainly contribute to the health of the planet. Since the early studies of Wright [1] and Armand [2] on polymer–salt complexes, PE has been extensively studied as all-solid-state functional devices. PE has advantages over liquid electrolyte such as light weight, improve leakage problem, mechanically stable and flexible for packaging design.

Several biodegradable polymers such as cellulose [3], starch [4] and chitosan [5,6] (natural biodegradable polymers) and also poly (vinyl alcohol) [7,8] (synthetic biodegradable polymer from petroleum sources) have been studied as conducting PEs and applied in electrochemical devices such as batteries, supercapacitors, fuel cells, solar cells and electrochromic windows.

Poly(ε-caprolactone) (PCL) is a biodegradable polymer that is nontoxic and widely used in biomedical applications [9,10]. It is a synthetic thermoplastic polymer derived from crude oil and synthesized through the polymerization of ε-caprolactone monomer by a stannous octanoate catalyzed ring opening mechanism. It has good mechanical properties [11,12] and short degradation time [13] in aqueous medium and when in contact with microorganisms [14]. PCL can be a candidate polymer host for ionic conduction because it contains a Lewis base (ester oxygen) that can coordinate cations [15]. Like polyethylene oxide (PEO), PCL also possesses low glass transition temperature (−60 °C) and therefore the polymer chain should exhibit segmental motion, enabling the ions to easily hop from one complexation site to another [16,17]. A few attempts have been made to use PCL as polymer host for different polymer–salt electrolyte systems such as PCL–lithium salts [18–20] and PEO–PCL–LiClO4 [21] ternary blend systems.

To the best of our knowledge, there has been no previous study of proton conducting solid polymer electrolyte based on PCL and ammonium salts. In this study, we investigate the relationship between conductivity and salt content through electrochemical impedance spectroscopy. The interactions between the semicrystalline PCL and ammonium thiocyanate (NH4SCN) are characterized by DSC and FTIR spectroscopy.

2. Experimental

2.1. Materials

The poly(ε-caprolactone) (PCL) with $M_w = 80$ kDa was procured from Sigma Aldrich and used as received. Ammonium thiocyanate (NH4SCN) with $M_w = 76.12$ g/mol was obtained from R&M Marketing and dried in an oven at 45 °C for 24 h prior to use as the incorporating salt. Proton conducting polymer electrolytes consisting of PCL complexed with NH4SCN in various compositions were prepared by
solution casting technique. Fig. 1 shows the structural formula for PCL and that of NH₄SCN.

2.2. Sample preparation

Desired amounts of polymer and salt with various PCL:NH₄SCN ratio in wt.% were dissolved in aprotic solvent tetrahydrofuran (THF) with purity > 99% from J.T. Baker. The mixtures were stirred continuously for several hours at room temperature to obtain homogeneous, viscous solutions. The solutions were then cast into different glass Petri dishes and maintained at 50 °C for 10 h for THF to evaporate. The films were further dried slowly at room temperature inside a dessicator for 2 weeks to remove any traces of solvent. The present system can form free standing film up to 32 wt.% of salt and beyond that is no longer mechanically stable.

2.3. Impedance spectroscopy

Impedance measurements were carried out using the HIOKI 3531 Z LCR Hi-tester within the frequency range from 50 Hz to 1 MHz. The polymer electrolyte films were cut into small discs and sandwiched between two polished stainless steel disks under spring pressure. The diameter of the stainless steel discs is 2 cm. The electrical conductivity was then calculated using the equation:

$$\sigma = \frac{d}{R_B A}$$  (1)

Here, $\sigma$ is the dc conductivity, $d$ is thickness of the electrolyte film, $A$ is the surface area of contact and $R_B$ is the bulk electrolyte resistance. $R_B$ was obtained from the Cole–Cole plot at the low frequency side of the semicircle intercept on the real impedance axis or high frequency side of the spike intercept on the real impedance axis.

2.4. Differential Scanning Calorimetry (DSC)

Thermal analyses were performed using a DSC instrument (Perkin Elmer DSC 8000). The samples were heated to 80 °C at a heating rate of 10 °C/min (isothermal hold for 10 min), cool down to −90 °C (with fast cooling rate, 150 °C/min) and then heated to 90 °C at 10 °C/min under dry nitrogen. The glass transition temperature $T_g$ (midpoint), melting temperature, $T_m$ and melting enthalpy, $\Delta H_m$ of PCL were determined from the second heating scan. The % crystallinity ($\chi_C$) of the sample can be calculated by comparing $\Delta H_m$ with that of pure PCL according to:

$$\chi_C = \frac{\Delta H_m}{\Delta H_m^{0}} \times 100\%$$  (2)

where $\Delta H_m^{0}$ is the melting enthalpy of pure PCL.

2.5. Fourier Transformation Infrared Spectroscopy (FTIR)

The IR spectra were recorded using the Thermo Scientific ( Nicolet iS10) spectrophotometer within the wave number range from 4000 to 650 cm⁻¹ operating at a resolution of 1 cm⁻¹. Each spectrum runs 32 scans in 2 s with correction against the background spectrum of air. Dry nitrogen was used for purging purposes in order to exclude the infrared active H₂O and CO₂ in the atmosphere.

3. Results and discussion

The Cole–Cole plots of PCL with different concentrations of NH₄SCN is depicted in Fig. 2.

For samples containing 5 and 10 wt.% NH₄SCN, Fig. 2(a) and (b), two well defined regions can be observed, a high frequency semicircle followed by an inclined spike at the low frequency region. The semicircle is also tilted indicating that the ions have different relaxation time. The semicircle is related to the relaxation process in the bulk polymer electrolyte and can be modeled as a parallel resistor (due to the mobile ions inside the polymer matrix) and capacitor (due to the immobile polymer chain) circuit network where the capacitance is usually of the order of nano–Farads [22]. The semicircle is also tilted indicating that the ions have different relaxation times. On the other hand, the spike should show a straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the inclination [23] and is better known as the polarization effect at electrode/electrolyte interface [24]. For samples with high salt concentrations as shown in Fig. 2(c) and (d), the semicircle part is absent.

The conductivity of the PCL–NH₄SCN system at room temperature is then calculated according to Eq. (1) and illustrated in Fig. 3. The ionic conductivity of pure PCL obtained at room temperature is 1.86 × 10⁻¹¹ S cm⁻¹. This result is of the same order of magnitude as reported by Hirai et al. [25]. The conductivity of the PCL–NH₄SCN increases to 6.31 × 10⁻⁷ S cm⁻¹ when 5 wt.% of NH₄SCN is added to pure PCL at room temperature. It can be observed that the conductivity increases with addition of salt content until a maximum is reached at 26 wt.% NH₄SCN. The maximum conductivity obtained in this solution-cast film is 1.01 × 10⁻⁴ S cm⁻¹. This is several orders of magnitude higher than other PCL–salt systems as reported in [18,21], which are 1.2 × 10⁻⁶ S cm⁻¹ for PCL–LiClO₄ and 6.3 × 10⁻⁷ S cm⁻¹ for PEO–PCL–LiClO₄ systems respectively. Table 1 lists the highest conductivity at room temperature of some other types of polymer–NH₄SCN systems [26–29]. The conductivities obtained are comparable to the present PCL–NH₄SCN system. This indicates that PCL can host proton conduction as good as other polymeric materials.

The increase in the ionic conductivity along with the increase of salt content could be understood in terms of the number density of charge carriers. In principle,

$$\sigma = \sum_i n_i z_i e \mu_i$$  (3)

where $n_i$ is the number density of charge carriers of type $i$; $z_i$ is the valency of the charge carriers on each type, $e$ is the elementary electric charge and $\mu_i$ is the ionic mobility. Fig. 3 can be divided into two regions. The increase in conductivity in Region I could be correlated to the increase in the number density of free ions due to the dissociation of salt into the polymer matrix. On the other hand, the decrease in conductivity at higher salt content in Region II (e.g. 32 wt.%) is attributed to the reassociation of ions to form ion clusters. Hence there are less mobile charge carriers and the larger size ion clusters [30] have limited relative mobility compared to the free ions. Teeters et al. [31] also observed a reduction in ionic conductivity after a maximum of around 7 × 10⁻⁴ S cm⁻¹ for PEO–LiTf system. They reported that the surfactants (free ions) would group together to form micelles (ion aggregates) after a critical salt concentration.

An important characteristic of any electrolyte, in relation to the conductivity is the number of charge carriers. In polymer electrolytes,
the charge carriers are ions and it depends upon both the dissociation energy \( U \) involved and dielectric constant \( \varepsilon' \) according to Eq. (4).

\[
n = n_0 \exp(-U/\varepsilon'kT)
\]  

(4)

The dielectric constant \( \varepsilon' \) (the real part of complex relative permittivity) can be calculated from Eq. (5).

\[
\varepsilon' = \frac{Z''}{\omega C_0(Z''^2 + Z'^2)}
\]  

(5)

Here, \( k \) is Boltzmann constant, \( T \) is absolute temperature, \( C_0 = \varepsilon_0 A/t \), \( \omega = 2\pi f \), \( \varepsilon_0 \) is permittivity of free space, \( f \) is frequency, \( Z_i \) and \( Z_r \) is the imaginary and real parts of the complex impedance, respectively.

Dielectric constant deals with a charge response induced by the applied electric field. It is a representative of stored charge in a material [32]. In addition, a detail dielectric and ac conductivity studies will provide an insight into ionic transport behavior and ion–local dipoles interaction (dipoles from ester group of PCL chains). The ionic motion could be coupled with dipole relaxation due to localized polymer segmental motion. This report will focus on the influence of the amount of free charge carriers.

Referring back to Eq. (4), an increase in \( \varepsilon' \) would reflect an increase in value of number density of charge carriers, \( n \). The dependence of the dielectric constant \( \varepsilon' \) on the salt concentration at selected frequencies is plotted in Fig. 4.

Basically, the calculated dielectric constant follows the same trend as the conductivity in Fig. 3. It can be observed that \( \varepsilon' \) increases with addition of salt content until a maximum at 26 wt.%. The increase in number density of ions at this polymer content is affirmative from dielectric constant values. This implies that the number of stored charges have increased with addition of salt content. Since the charge is due to ions, increase in charge is proof of increase in the number density of ions and hence the increase in conductivity. The reduction in dielectric constant at 26 wt.% onwards is attributed to re-association of ions. This leads to a decrease in conductivity. The reassociated ions may be neutral aggregates that do not contribute to conductivity or larger size ion aggregates with reduced mobility.

In order to understand the transport property of the polymer electrolyte, it is important to investigate the thermal properties. It has been well established that crystalline and amorphous phases co-exist in most of the polymeric materials. PCL is one of the highly crystalline polymer exhibiting both the glass transition and melting transition. At the glass transition temperature \( T_g \), a step transition of endothermic reaction will be observed. This is the characteristic of an amorphous structure, indicating a transition from disordered glassy solid (brittle amorphous) into a more rubbery solid. On the other hand, an

Fig. 2. Cole–Cole plot of PCL incorporated with different concentrations of NH4SCN at room temperature: (a) 5 wt.%, (b) 10 wt.%, (c) 20 wt.% and (d) 26 wt.% respectively.

Fig. 3. Salt concentration dependence of ionic conductivity at room temperature.

Table 1

<table>
<thead>
<tr>
<th>Systems</th>
<th>Conductivity ( \sigma ) (S cm(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 mol% PVP-20 mol% NH4SCN</td>
<td>( 1.7 \times 10^{-4} )</td>
<td>[26]</td>
</tr>
<tr>
<td>75 mol% PVAc-25 mol% NH4SCN</td>
<td>( 5.5 \times 10^{-4} )</td>
<td>[27]</td>
</tr>
<tr>
<td>PEO-NH4SCN [NH4]/[EO]=0.031</td>
<td>( 10^{-5} )</td>
<td>[28]</td>
</tr>
<tr>
<td>PEO-40 vol% PAAM-10 mol% NH4SCN</td>
<td>( 1 \times 10^{-4} )</td>
<td>[29]</td>
</tr>
</tbody>
</table>

Fig. 3. Salt concentration dependence of ionic conductivity at room temperature.
endothermic peak shall be obtained, showing the crystalline melting temperature $T_m$. This happens to a crystalline structure, it is a solid to liquid phase transition.

Fig. 5 illustrates the thermal behavior of pure PCL and of PCL containing 10, 20, 26 and 32 wt.% NH$_4$SCN.

The addition of salt to the polymer solution during the preparation stage resulted in the formation of polymer–salt complexes and a change in the crystallization nature of the sample. Fig. 5(a) shows an endothermic peak indicating melting of pure PCL at 56 °C. This is attributed to the crystalline melting of PCL that reflects the presence of uncomplexed crystalline phase. Similar result is observed by Fonseca et al. [18] with 10wt.% NH$_4$SCN. The ammonium salt complexes and a...
polymer–salt system with addition of salt. This suggests the salt has been dissolved by the polymer and incorporated into the polymer matrix.

Fig. 8 represents FTIR spectra of PCL:NH4SCN complexes at room temperature displaying carbonyl stretching regions. Two carbonyl C=O stretching modes appear around 1720 cm\(^{-1}\) (intense peak) and 1736 cm\(^{-1}\) (shoulder peak) corresponding to the absorptions of the crystalline and amorphous conformations, respectively. Upon addition of NH4SCN to PCL, both carbonyl bands increase gradually in relative intensity with little spectra shift. This could be attributed to the formation of loosely-bound hydrogen bond between polymer (carbonyl group of PCL as hydrogen bond acceptor) and salt (H atom of the NH4\(^+\) cation as hydrogen bond donor). A new shoulder peak appears at 1623 cm\(^{-1}\) which reflects the interaction between the cation and the carbonyl group of PCL. The relative intensity of this new peak increases with salt content. Chiu et al. [21] also observed little spectra shifts of the two carbonyl bands at 1724 cm\(^{-1}\) and 1734 cm\(^{-1}\) (shoulder peak) upon addition of LiClO\(_4\) to PCL and concluded that these indicate interaction between the lithium cation and the carbonyl group of PCL. This implies that although complexation occurs between the polymer host and incorporating salt (with reference to the prior DSC result), hydrogen bond is not strong enough to cause any noticeable IR spectra shift.

SCN\(^-\) is an ambident linear anion that possesses two alternative reactive sites, and can form N-bonding (CN stretching), S-bonding (CS stretching) and bridge complexes of the S and N atom (SCN bending). The FTIR spectra of SCN\(^-\) stretching mode has strong intensity and thus is a good candidate to study the effect of ion association in SPEs [46]. Fig. 9 shows the curve-fitting FTIR spectra of CN stretching modes in PCL–NH4SCN system with various salt concentrations. The overlapping complex spectra in the region 2030–2090 cm\(^{-1}\) were deconvoluted to a high sensitivity, constant base line and Gaussian Lorentzian peak type using the OMNIC software. Baseline correction was done to all spectra prior to the deconvolution. The experimental spectral envelope is described by the solid line while dotted lines represent the curve-fitting data.

According to the literature [37,46–48], the band at 2040 cm\(^{-1}\) can be attributed to free anions (SCN\(^-\)), the predominant peak centered at 2058 cm\(^{-1}\) is assigned to represent contact ion pairs (NH\(_4^+\)SCN\(^-\)) and finally the band at 2074 cm\(^{-1}\) is an indication for the formation of ion aggregates. The results of curve fitting are shown in Fig. 10, in which the area under the peak of each band is proportional to the relative concentration of different ionic species.

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**Table 2**

DSC results of PCL:NH4SCN complexes.

<table>
<thead>
<tr>
<th>PCL:NH4SCN ratio</th>
<th>(T_g(\degree C))</th>
<th>(T_m(\degree C))</th>
<th>(\Delta H_m(\text{j g}^{-1}))</th>
<th>% crystallinity ((\chi_c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>−66.0</td>
<td>56.05</td>
<td>96.38</td>
<td>100.0</td>
</tr>
<tr>
<td>90:10</td>
<td>−64.7</td>
<td>55.31</td>
<td>88.50</td>
<td>91.8</td>
</tr>
<tr>
<td>80:20</td>
<td>−64.6</td>
<td>54.99</td>
<td>79.04</td>
<td>82.0</td>
</tr>
<tr>
<td>74:26</td>
<td>−64.3</td>
<td>54.70</td>
<td>78.07</td>
<td>81.0</td>
</tr>
<tr>
<td>68:32</td>
<td>−63.9</td>
<td>55.46</td>
<td>86.33</td>
<td>89.6</td>
</tr>
</tbody>
</table>

**Table 3**

Assignments of FTIR spectra of pure NH4SCN and PCL [39–45].

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3173</td>
<td>NH stretching</td>
</tr>
<tr>
<td>2944</td>
<td>Asymmetric CH(_2) stretching</td>
</tr>
<tr>
<td>2864</td>
<td>Symmetric CH(_2) stretching</td>
</tr>
<tr>
<td>2052</td>
<td>Asymmetric C=O stretching</td>
</tr>
<tr>
<td>1720</td>
<td>Carbonyl, C=O stretching, crystalline phase</td>
</tr>
<tr>
<td>1736</td>
<td>Carbonyl, C=O stretching, amorphous phase</td>
</tr>
<tr>
<td>1619</td>
<td>Asymmetric CN stretching</td>
</tr>
<tr>
<td>1415</td>
<td>NH deformation mode</td>
</tr>
<tr>
<td>1293</td>
<td>C—O and C—C stretching in the crystalline phase</td>
</tr>
<tr>
<td>1239</td>
<td>Asymmetric COC stretching</td>
</tr>
<tr>
<td>1190</td>
<td>OC—O stretching</td>
</tr>
<tr>
<td>1170</td>
<td>Symmetric COC stretching</td>
</tr>
<tr>
<td>1157</td>
<td>C—O and C—C stretching in the amorphous phase</td>
</tr>
<tr>
<td>948</td>
<td>Symmetric SCN bending</td>
</tr>
<tr>
<td>752</td>
<td>C—S stretching</td>
</tr>
</tbody>
</table>

---

Fig. 7. FTIR spectra recorded at room temperature of (a) pure NH4SCN and complexes of PCL:NH4SCN in the weight ratio of (b) 100:0; (c) 95:5; (d) 85:15; (e) 74:26; (f) 68:32 displaying NH stretching, SCN bending and C=S stretching regions.
It can be seen that the number of free ions increase as more salt content is added until 26 wt.% and drop drastically afterwards. On the other hand, the formation of ion aggregates keeps increasing even at high salt concentration. The correlation between free ions, ion aggregates and conductivity seems clear. The increase of the ion dissociation (corresponds to number of free ions from the salt) improves the conductivity, while the formation of ion aggregates lowers the number of mobile charge carriers. Similar observations have been reported by Ramya et al. [46] in PVP-NH4SCN system and Chen-Yang et al. in PAN-LiClO4-ALA-MMT system [49]. From the above analysis, the H atom of the NH4+ from the salt is believed to interact with the oxygen in C=O of PCL via hydrogen bonding as proposed in Scheme 1.

There are two possible charge carrier species in this polymer–salt system, i.e., cation and anion. The transporting cation could be either H+ and NH3+ or NH4+. Srivastava et al. [28] has conducted coulombmetric investigation on PEO–NH4SCN system and concluded that H+ is the only cation contributing to the ionic transport. Similar results were obtained from other researchers. Hashim et al. [50], Maurya et al. [51] and Srivastava and Chandra [52] reported protonic motion due to H+ ion in different polymer–ammonium salt complexes, i.e., PEO–NH4ClO4, PEO–NH4I and PECl–NH4ClO4, respectively. Hence, the current PCL–NH4SCN complex is considered a proton conducting polymer electrolyte system. Each NH4+ cation has a tetrahedral structure [50] where one of the four hydrogen atoms is most weakly bound. It can be easily dissociated upon an applied electric field. These protons can jump from one coordinating site to adjacent site, diffuse through the polymer matrix according to the Grotthus mechanism.

Fig. 8. FTIR spectra recorded at room temperature of (a) pure NH4SCN and complexes of PCL:NH4SCN in the weight ratio of (b) 100:0; (c) 95:5; (d) 85:15; (e) 74:26; (f) 68:32 displaying carbonyl stretching regions.

Fig. 9. The curve-fitting FTIR spectra of CN stretching modes in PCL incorporated with (a) 5 wt.%, (b) 15 wt.%, (c) 26 wt.% and (d) 32 wt.% NH4SCN, respectively.
4. Conclusions

From the results obtained, the conductivity increases from addition of 5 wt.% to 26 wt.% salt. The maximum ionic conductivity achieved in the solution-cast films at room temperature is $1.01 \times 10^{-4}$ S cm$^{-1}$ for PCL complexed with 26 wt.% NH$_4$SCN. This has been attributed to the increase of the number density of conducting ions. The decrease in conductivity after the optimum salt content is due to ion association. These results are supported by dielectric constant studies and FTIR analysis. It is known in polymer electrolyte system that conductivity occurs in the amorphous phase. DSC thermogram shows that complexation has formed between the polymer host and the incorporating salt. As more salt is accommodated in the PCL crystalline phase, the crystalline phase of PCL is reduced, showing an increase in amorphousness.

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References