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# Investigating the Effect of Miscibility on the Ionic Conductivity of LiClO<sub>4</sub>/PEO/PCL Ternary Blends

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**ABSTRACT:** We demonstrate that miscibility affects the ionic conductivity of ternary polymer blends of lithium perchlorate (LiClO<sub>4</sub>), poly(ethylene oxide) (PEO), and poly( $\epsilon$ -caprolactone) (PCL). Although individually these three binary blends are fully miscible, a closed immiscibility loop exists in the ternary blend phase diagram as a result of the complicated interactions among LiClO<sub>4</sub>, PEO, and PCL. The addition of PCL suppresses the crystallization of PEO and results in higher ionic conductivity. FTIR spectroscopy studies indicate that an excess PCL content causes immiscibility, which results in PCL being excluded from the ternary blends. Consequently, the maximum ionic conductivity ( $6.3 \times 10^{-7}$  S cm<sup>-1</sup>) at ambient temperature of ternary blends having a fixed LiClO<sub>4</sub> content (25 wt %) is at a composition of 25/60/15 (LiClO<sub>4</sub>:PEO:PCL).

## Introduction

Solid polymer electrolytes (SPEs), which are complexes of solvent-free polymers and metal salts, are prepared by dissolving salts in high-molecular-weight polar polymer hosts. Polymer electrolytes have been studied extensively during the past two decades because of their potential applications, which include high-energy density batteries and fuel cells.<sup>1–5</sup> Ionic transport occurs in the amorphous regions of the polymer and very often is the result of a coupling between the ions and segmental motions of the polymer chains. Poly(ethylene oxide) (PEO)-based polymeric electrolytes are still among the most extensively studied polymer ionic conductors because their structures are beneficial for supporting fast ion transport. Unfortunately, a high content of a crystalline phase limits the conductivity of PEO-based electrolytes. Efforts to enhance the ionic conductivity of PEO-based SPEs have focused on suppressing its crystallinity by incorporating an inorganic filler, such as clay, to form composite polymeric electrolytes,<sup>6</sup> by copolymerizing PEO with macromonomers,<sup>7</sup> and by blending with other polymers into PEO-based electrolytes.<sup>8</sup> It is an important challenge to develop practical methods for preparing the SPEs that have higher ionic conductivity and dimensional stability. In this regard, the preparation of polymeric electrolytes by blending them with other appropriate polymers is of interest. Polymer blend is a quick and economical alternative method for obtaining materials that have optimized properties and for the easy control of their physical properties by compositional change.

PEO/PCL (poly( $\epsilon$ -caprolactone)) blends are miscible over their entire range of compositions.<sup>9</sup> The existence of strong interaction between PEO and PCL tends to suppress the crystallinity of PEO. Furthermore, because PCL possesses low  $T_g$  ( $-60$  °C), PEO/PCL blend systems generally maintain the polymer chain mobility and flexibility. Nevertheless, the immiscible phenomenon occurs upon the addition of certain compositions of

lithium perchlorate (LiClO<sub>4</sub>) into a ternary LiClO<sub>4</sub>/PEO/PCL blend system, even though any pair of its components is miscible. Amorphous PEO complexes with LiClO<sub>4</sub> are suitable for achieving reasonably high and stable conductivity.<sup>1,10,11</sup> Because the addition of PCL into an electrolyte system based on LiClO<sub>4</sub>/PEO tends to retard or inhibit the PEO crystallization, we expected that this ternary blend, LiClO<sub>4</sub>/PEO/PCL, would have higher ionic conductivity than previously reported electrolyte systems based on LiClO<sub>4</sub>/PEO binary blends.

To our knowledge, there has been no previous study of the influence of the miscibility behavior and interaction mechanism on the variation of ionic conductivity in polymer electrolytes. In this study, we employed differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), solid-state <sup>7</sup>Li NMR spectroscopy, and alternating current (ac) impedance to investigate the miscibility and related conductivity behaviors of this LiClO<sub>4</sub>/PEO/PCL ternary blend system. Furthermore, we have presented a more convenient method to suppress the crystalline phase of PEO and obtain a higher ionic conductivity by adding PCL in LiClO<sub>4</sub>/PEO-based electrolyte system.

## Experimental Section

**Materials.** The poly(ethylene oxide) (PEO) with  $M_n = 10\,000$  and poly( $\epsilon$ -caprolactone) (PCL) with  $M_n = 65\,000$  were purchased from Aldrich Co. Lithium perchlorate (LiClO<sub>4</sub>, Aldrich) was dried in a vacuum oven at 80 °C for 24 h and stored in a desiccator prior to use. Acetonitrile was distilled at a suitable temperature under a nitrogen atmosphere prior to use.

**Sample Preparations.** Polymer electrolytes of LiClO<sub>4</sub>/PEO/PCL in various ternary blend compositions were prepared by solution casting. Desired amounts of PEO, PCL, and LiClO<sub>4</sub> salt were dissolved in dry acetonitrile and stirred continuously for 24 h at 60 °C. The solution was cast onto a Teflon dish and maintained at 50 °C for an additional 24 h to remove the solvent, and then the dish was further dried under vacuum at 80 °C for 2 days. To prevent its contact with the air and moisture, the polymer electrolyte was transferred to a glovebox under a nitrogen atmosphere.

**Differential Scanning Calorimetry (DSC).** Thermal analyses were performed using a DSC instrument (DuPont TA

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2010). The sample was heated from  $-100$  to  $150$  °C under dry nitrogen. The glass transition temperature ( $T_g$ ) was obtained as the inflection point of the heat capacity jump recorded at a scan rate of  $20$  °C/min.

#### Fourier Transformation Infrared Spectroscopy (FTIR).

The conventional potassium bromide (KBr) disk method was employed to measure the infrared spectra of the blend films. All polymer films were prepared under a N<sub>2</sub> atmosphere. The acetonitrile solution was cast onto a KBr disk, from which the solvent was evaporated under vacuum at  $70$  °C for  $48$  h. All IR spectra were obtained within the range of  $4000$ – $400$  cm<sup>-1</sup> using a Nicolet AVATR 320 FTIR spectrometer (Nicolet Instruments, Madison, WI) operating at a resolution of  $1$  cm<sup>-1</sup>.

**Solid-State NMR Spectroscopy.** The solid-state <sup>7</sup>Li magic angle spinning (MAS) NMR spectra were recorded at  $300$  K on a Bruker DSX-400 NMR spectrometer equipped with a  $7$  mm double-resonance probe, operating at  $400.13$  MHz for <sup>1</sup>H nucleus and  $155.27$  MHz for <sup>7</sup>Li nucleus. Typical experimental conditions used to obtain the solid-state NMR spectra:  $\pi/2$  duration,  $2$   $\mu$ s; recycle delay,  $8$  s; <sup>1</sup>H decoupling power,  $65$  kHz; spinning speed,  $2$  kHz. A  $1$  M aqueous LiCl solution was used as an external chemical shift reference ( $0$  ppm).

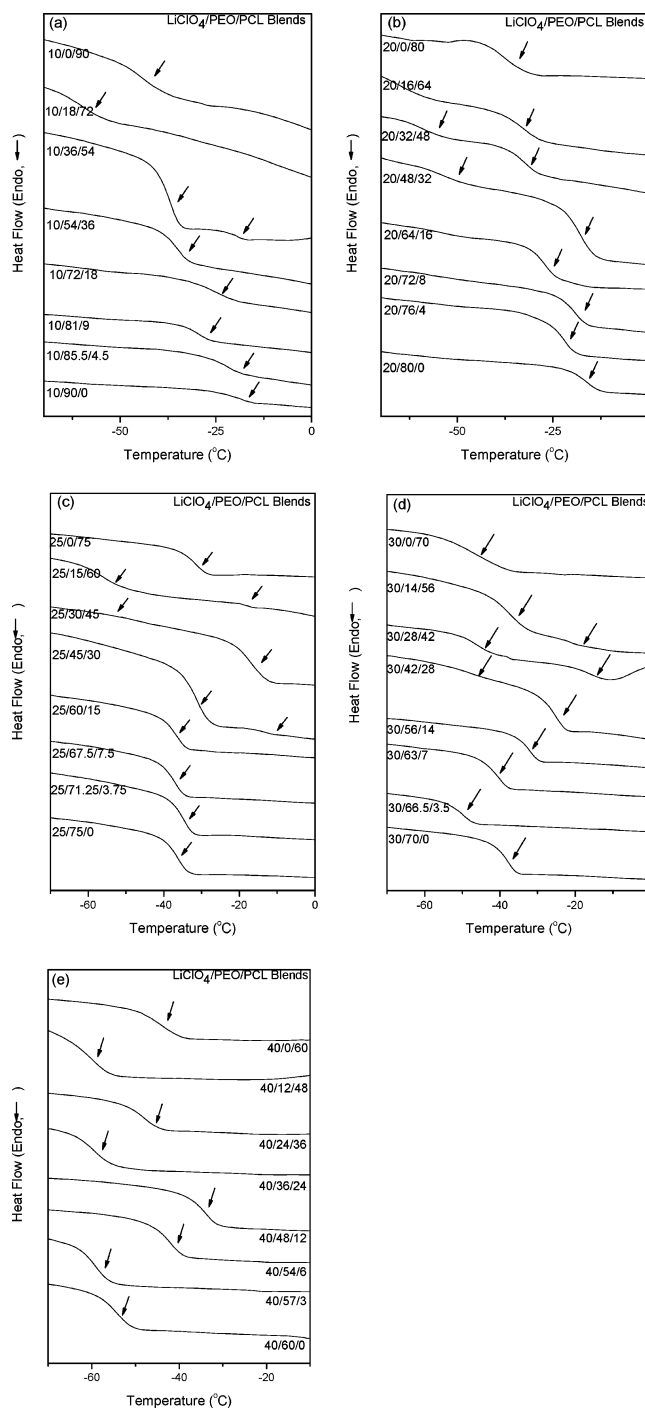
**Conductivity Measurements.** Ionic conductivity measurements with alternation current were conducted on an AUTOLAB designed by Eco Chemie within the frequency range from  $10$  MHz to  $10$  Hz. The electrolyte film was sandwiched between stainless steel blocking electrodes (diameter:  $1$  cm). The specimen thickness varied from  $0.8$  to  $1.2$  mm; the impedance response was gauged over the range from  $20$  to  $120$  °C. The bulk resistance was derived from the Cole–Cole plot of the complex impedance data of the blend where the imaginary impedance is zero.<sup>12–14</sup> Conductivity was calculated from the bulk resistance according to the equation

$$\sigma = L/A \times R_b$$

where  $\sigma$  is the conductivity,  $L$  is the thickness of the electrolyte film,  $A$  is the section area of the stainless steel electrode, and  $R_b$  is the bulk resistance.

## Results and Discussion

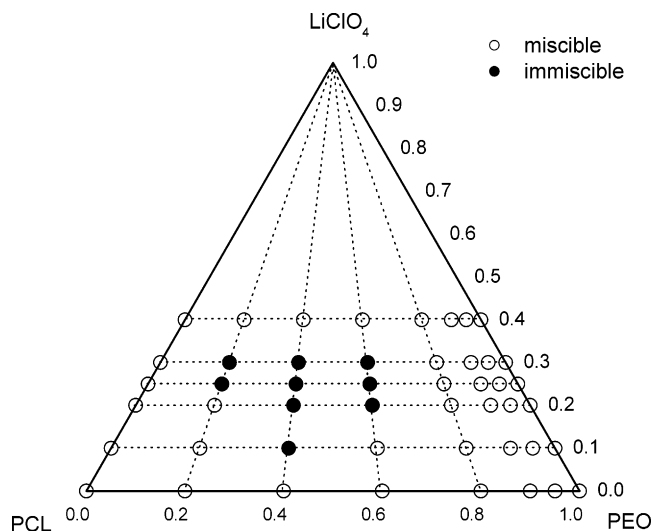
**DSC Studies.** The DSC analysis is one of the most convenient methods for determining the miscibility in polymer blends.  $T_g$ s of the pure polymers used in this study, PEO and PCL, are both ca.  $-60$  °C. Figure 1 presents the conventional second-run DSC thermograms of various LiClO<sub>4</sub>/PEO/PCL ternary blends. Each system (Figure 1a–e) contains a fixed fraction of lithium perchlorate, but the PEO/PCL ratios vary; either single  $T_g$  or two  $T_g$ 's are identified in all blends. A single  $T_g$  strongly suggests that these blends are fully miscible and exist as a homogeneous amorphous phase. Meanwhile, a ternary blend with two  $T_g$ 's implies is considered immiscible or partially miscible in the amorphous phase. In PEO/PCL binary blends, however, a single  $T_g$  or two  $T_g$ 's cannot be identified from the DSC thermograms because  $T_g$ s of PEO and PCL are so close. Therefore, the miscibility between PEO and PCL cannot be determined simply on the basis of the appearance of one or two  $T_g$ 's in the DSC thermogram. Kuo et al. have reported,<sup>9</sup> however, that the binary blends of PEO/PCL at various ratios are miscible in their amorphous phase. Therefore, the phase diagram of this ternary LiClO<sub>4</sub>/PEO/PCL blend system at room temperature based on its DSC analyses is present in Figure 2. A closed-loop, phase-separated region exists in this three-component phase diagram. This observed phenomenon indicates that these complicated interactions, which can be grouped into LiClO<sub>4</sub>/PEO, LiClO<sub>4</sub>/PCL, and PEO/PCL pairs, exist in this ternary blend system and that these interactions compete with each other. Interestingly,



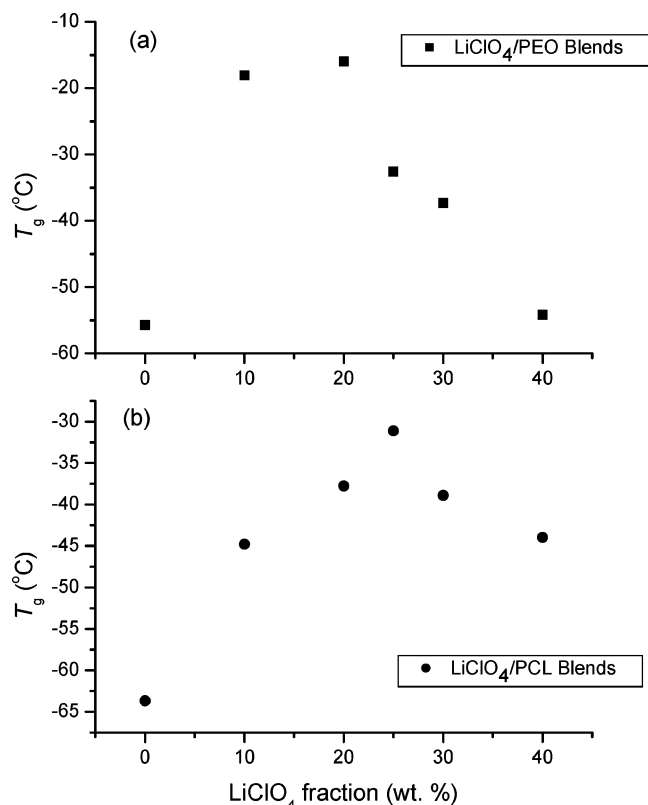
**Figure 1.** DSC thermograms of ternary blends of LiClO<sub>4</sub>/PEO/PCL containing a constant composition of LiClO<sub>4</sub>: (a) 10, (b) 20, (c) 25, (d) 30, and (e) 40 wt %.

even though these three individual binary blends (LiClO<sub>4</sub>/PEO, LiClO<sub>4</sub>/PCL, and PEO/PCL) are all miscible in the amorphous phase, immiscibility exists within certain compositions of the ternary system.

Figure 3 displays the effect that the LiClO<sub>4</sub> content has on the glass transition temperatures of (a) LiClO<sub>4</sub>/PEO and (b) LiClO<sub>4</sub>/PCL blends. In both of these systems, the  $T_g$ s increase upon increasing the LiClO<sub>4</sub> content, but they tend to decrease for concentrations of LiClO<sub>4</sub> above  $20$ – $25$  wt %. It has been suggested that the initial increase in  $T_g$  is due to the interaction between the polymer chains and the salt whereas the decrease is due to the repulsion between the free anions or the dilution effect of salt aggregation.<sup>15,16</sup> Within the



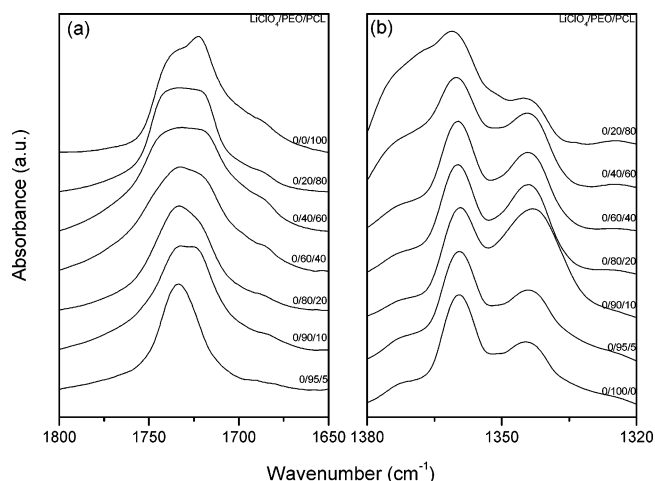
**Figure 2.** Ternary phase diagram of the  $\text{LiClO}_4$ /PEO/PCL system. The open circles represent a miscible ternary blend, and the full circles represent an immiscible ternary blend.



**Figure 3.** Effect of  $\text{LiClO}_4$  content on the glass transition temperatures of (a)  $\text{LiClO}_4$ /PEO and (b)  $\text{LiClO}_4$ /PCL.

range of 10–20 wt % of  $\text{LiClO}_4$ , the  $T_g$  increment of the  $\text{LiClO}_4$ /PEO system is greater than that of the  $\text{LiClO}_4$ /PCL system, implying that the interaction between  $\text{LiClO}_4$  and PEO is stronger than that between  $\text{LiClO}_4$  and PCL.

When we look at the changes in  $T_g$  (Figure 3) on the molar basis, though the two  $T_g$  elevation patterns look similar, the elevation maximum in  $\text{LiClO}_4$ /PEO takes place at Li/O mole ratio of 1/9.7, whereas in  $\text{LiClO}_4$ /PCL it occurs at Li/ester group = 1/2.8. It is understandable because PEO interacts stronger with lithium ions than that of PCL. Moreover, the distance between ether oxygens in PEO is shorter than that between ester groups in PCL. It has been suggested that the lithium



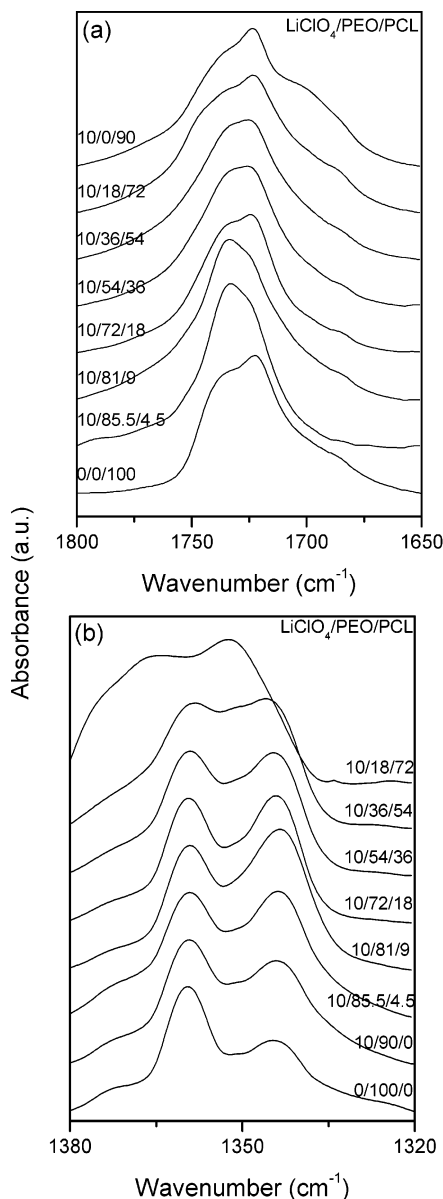
**Figure 4.** Infrared spectra of binary blends of PEO/PCL, recorded at room temperature, displaying (a) the carbonyl stretching and (b)  $\text{CH}_2$  wagging regions.

ion is able to coordinate with more functional groups of the polymer chain in PEO than that in PCL. As a result, higher content of  $\text{LiClO}_4$  salt is needed to achieve maximum  $T_g$  in the  $\text{LiClO}_4$ /PCL system.

**FT-IR Spectroscopy.** Figure 4 shows infrared spectra recorded at room temperature, displaying the bands representing the carbonyl stretching (a) and  $\text{CH}_2$  wagging (b) of a series of PEO/PCL binary blends. As shown in Figure 4a, two carbonyl stretching bands appear for the pure PCL at 1734 and 1724  $\text{cm}^{-1}$ ; these bands correspond to the absorptions of the amorphous and crystalline conformations, respectively. The relative peak area of the crystalline conformation of PCL (1724  $\text{cm}^{-1}$ ) decreases upon increasing the PEO content in this binary PEO/PCL blend system. Figure 4b shows infrared spectra of the  $\text{CH}_2$  wagging vibration, in the region 1320–1380  $\text{cm}^{-1}$ , of the pure PEO and various PEO/PCL binary blends. The pure PEO has two bands, at 1360 and 1343  $\text{cm}^{-1}$ , that represent its crystalline phase.<sup>17</sup> The crystalline conformation of PEO is partially destroyed when the PCL content in this binary blend is increased. As a result, we confirm that the interaction between PEO and PCL tends to decrease the fraction of the crystalline phases of both PEO and PCL.

Figure 5 presents Infrared spectra recorded at room temperature, which display the carbonyl stretching (a) and  $\text{CH}_2$  wagging (b) regions of a series of ternary  $\text{LiClO}_4$ /PEO/PCL blends containing the  $\text{LiClO}_4$  content fixed at 10 wt %. In the carbonyl group vibration region (Figure 5a), the spectrum of the blend  $\text{LiClO}_4$ /PCL = 10/90 possesses a shoulder band at 1700  $\text{cm}^{-1}$ , which reflects the interaction between the lithium cation and the carbonyl group of PCL. This shoulder peak disappears upon the addition of PEO, even at a content of as low as 18 wt %, indicating that the interaction between  $\text{Li}^+$  cation and PEO is much stronger than that between  $\text{Li}^+$  and PCL. The crystalline phase of PCL nearly disappears at low PCL concentration (compositions of  $\text{LiClO}_4$ /PEO/PCL = 10/85.5/4.5 and 10/81/9; Figure 5a). By comparing these spectra with those in Figure 4a, the fraction of the crystalline PCL phase in this ternary blend is relatively higher than that in the binary blend at the same PEO/PCL ratio. The addition of  $\text{LiClO}_4$  in PEO/PCL binary blend tends to promote PCL's phase separation and crystallization; the lithium perchlorate prefers to coordinate with PEO rather than with PCL. The bands of crystalline PEO still exist in the ether



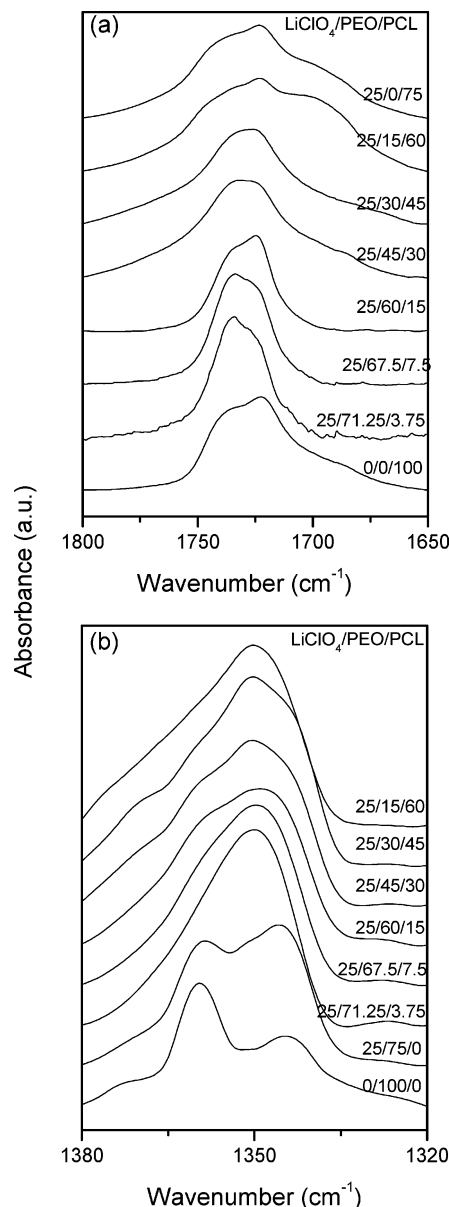


**Figure 5.** Infrared spectra of ternary blend of LiClO<sub>4</sub>/PEO/PCL containing a constant composition (10 wt %) of LiClO<sub>4</sub>, recorded at room temperature, displaying (a) the carbonyl stretching and (b) CH<sub>2</sub> wagging regions.

group vibration region displayed in Figure 5b, which suggests that the crystalline phase of PEO is only partially destroyed because of the relatively lower content of LiClO<sub>4</sub> (10 wt %) in these ternary blends.

Figure 6 shows infrared spectra of these LiClO<sub>4</sub>/PEO/PCL ternary blends containing a fixed and relatively higher lithium perchlorate content (25 wt %). We observe the same trends with respect to the appearance of the carbonyl group vibration as appear in Figure 5a, but Figure 6b indicates that the crystalline PEO phase disappears totally when the PEO content is 71.25 wt % or less. This finding implies that at a high LiClO<sub>4</sub> content (25 wt %) in these ternary blends LiClO<sub>4</sub> interacts with or complexes to essentially all of the available PEO, which, thus, retards its crystal formation.

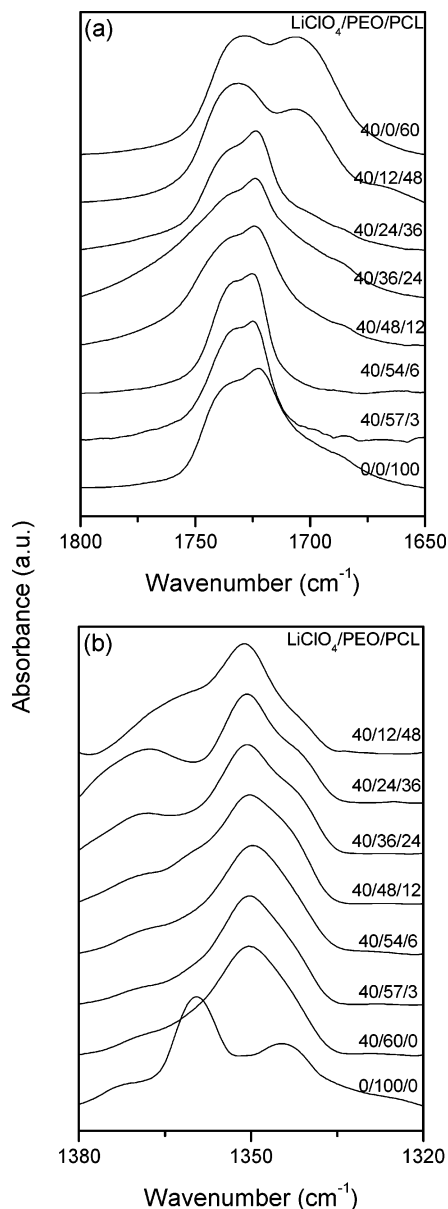
Infrared spectra recorded an even higher LiClO<sub>4</sub> content (40 wt %) are shown in Figure 7. At compositions of 40/12/48 and 40/0/60 (Figure 7a), the spectra of the bands representing the carbonyl group indicate that



**Figure 6.** Infrared spectra of ternary blend of LiClO<sub>4</sub>/PEO/PCL containing a constant composition (25 wt %) of LiClO<sub>4</sub>, recorded at room temperature, displaying (a) the carbonyl stretching and (b) CH<sub>2</sub> wagging regions.

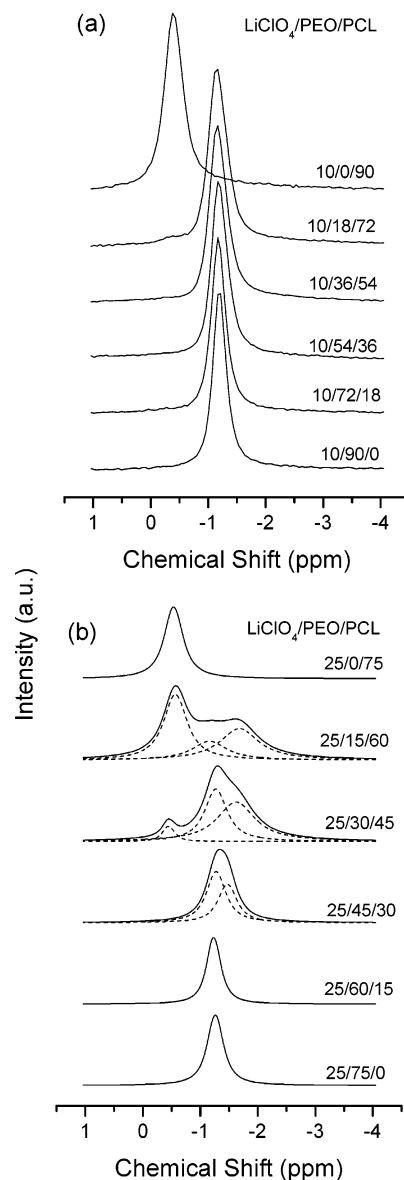
the crystalline PCL phase is destroyed completely while a strong shoulder peak appears at 1700 cm<sup>-1</sup>, which corresponds to the interaction between the lithium cation and the carbonyl group of the PCL. This content of LiClO<sub>4</sub> (40 wt %) is high enough to interact with essentially all of the PEO, and a portion of the PCL, in the 40/12/48 blend. Upon further addition of the PEO component to 24 wt % or more, the peak at 1700 cm<sup>-1</sup> disappears completely while the crystalline phase of PCL appears. In other words, no free PEO or free LiClO<sub>4</sub> salt is left and available to interact with PCL, and this situation results in the PCL's phase separation and crystallization. Figure 7b shows that PEO is totally amorphous at all compositions in these ternary blends containing 40 wt % LiClO<sub>4</sub>, indicating that excess LiClO<sub>4</sub> tends to coordinate with all of the PEO present.

**<sup>7</sup>Li MAS NMR Spectroscopy.** Solid-state <sup>7</sup>Li NMR spectroscopy has been used widely to study the interaction between the lithium ions and the polymer hosts<sup>18–20</sup> since the strong receptivity of the Li<sup>+</sup> ion makes it a



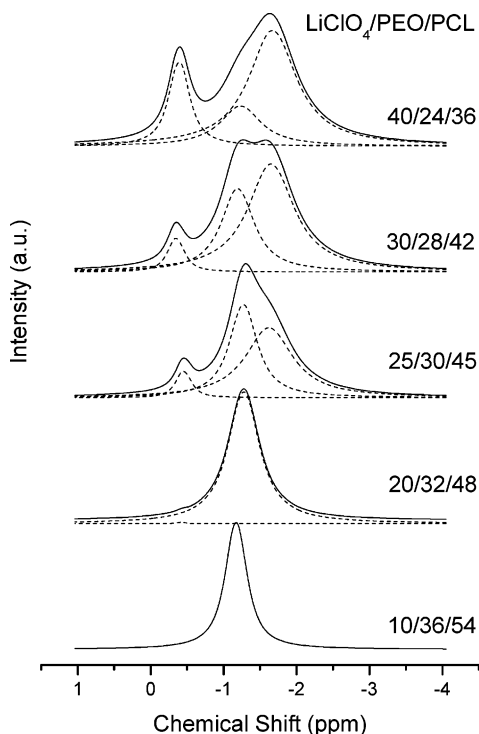
**Figure 7.** Infrared spectra of ternary blend of LiClO<sub>4</sub>/PEO/PCL containing a constant composition (40 wt %) of LiClO<sub>4</sub>, recorded at room temperature, displaying (a) the carbonyl stretching and (b) CH<sub>2</sub> wagging regions.

very attractive analytical tool. Figure 8a shows the <sup>7</sup>Li NMR spectra, recorded at 300 K, of ternary LiClO<sub>4</sub>/PEO/PCL blends having a LiClO<sub>4</sub> concentration at fixed 10 wt %. One single peak appears for all of the blends at this low LiClO<sub>4</sub> concentration. The peak at high field (ca. -1.1 ppm) is assigned as the interaction between PEO and Li cation, whereas the peak at low field (ca. -0.4 ppm) is assigned to the coordination of Li<sup>+</sup> with PCL; the latter peak appears only at a composition of 10/0/90, i.e., where PEO is absent. This result indicates that the lithium cation coordinates much more preferably with PEO than with PCL. This result also demonstrates that the ability of PCL to donate its electron to Li<sup>+</sup> is significantly poorer than that of PEO. Figure 8b displays the <sup>7</sup>Li MAS NMR spectra of various LiClO<sub>4</sub>/PEO/PCL ternary blends containing a fixed LiClO<sub>4</sub> content of 25 wt %. Unlike the spectra displayed in Figure 8a, there is no longer only a single peak in each <sup>7</sup>Li NMR spectrum; a new shoulder single is present at compositions of 25/45/30, 25/30/45, and 25/15/60. After



**Figure 8.** Solid-state <sup>7</sup>Li proton-decoupled MAS NMR spectra of ternary blends of LiClO<sub>4</sub>/PEO/PCL containing constant LiClO<sub>4</sub> concentrations of (a) 10 and (b) 25 wt %.

curve fitting, a new peak appears at ca. -1.6 ppm (peak III) in addition to two peaks mentioned above (peak I at ca. -0.4 ppm and peak II at ca. -1.1 ppm). Peak III has been assigned as representing the ion pairs of the lithium salt or its aggregates.<sup>19,21</sup> The relative intensity of peak III increases as the PCL content increases. Because PEO tends to interact with PCL, as a result of the strong miscibility between PEO and PCL, there is not enough free PEO available to dissolve the LiClO<sub>4</sub>, and thus, the Li<sup>+</sup> ion recoordinates with its counterion (ClO<sub>4</sub><sup>-</sup>) or the salt aggregates. Upon further addition of PCL, a decrease in the relative intensity of peak III accompanies an increase in the relative intensity of peak I; these observations result from the dissolution of LiClO<sub>4</sub> salt in PCL. As Figure 8 indicates, peak III appears only under two conditions: (1) at a high LiClO<sub>4</sub> salt concentration (25 wt % or higher) and (2) in the ternary blends LiClO<sub>4</sub>/PEO/PCL having a fixed LiClO<sub>4</sub> concentration and various compositions of PEO/PCL = 60/40, 40/60, or 20/80. Nevertheless, peak III does not appear in binary blends of LiClO<sub>4</sub>/PEO and LiClO<sub>4</sub>/PCL.

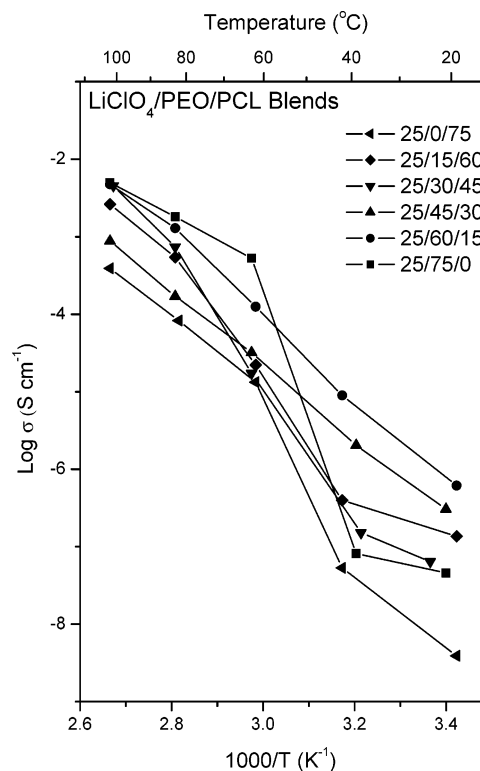


**Figure 9.** Solid-state  $^7\text{Li}$  proton-decoupled MAS NMR spectra of ternary blends of  $\text{LiClO}_4$ /PEO/PCL having a fixed PEO/PCL ratio of 40/60.

Figure 9 shows the  $^7\text{Li}$  MAS NMR spectra of  $\text{LiClO}_4$ /PEO/PCL ternary blends recorded at a constant PEO/PCL ratio (40/60), but with varying  $\text{LiClO}_4$  content. Peaks I–III appear simultaneously when the concentration of  $\text{LiClO}_4$  is 25 wt % or higher because the excess of  $\text{LiClO}_4$  interacts simultaneously with both PCL and PEO. The relative intensities of peaks I and III increase as the  $\text{LiClO}_4$  content increases. This phenomenon suggests a relative decrease in PEO content in these ternary blends such that eventually no PEO is left and available to interact with PCL; in this situation, PCL can interact only with the  $\text{LiClO}_4$ , resulting in the increased intensity of peak I. Discussing Figure 9 on the molar basis, the salt aggregation is formed whenever  $\text{Li}/\text{O}$  is greater than  $1/4$  regardless of PCL content due to stronger interaction between  $\text{Li}^+$  and PEO than that between  $\text{Li}^+$  and PCL. An excess content of  $\text{LiClO}_4$  tends to self-aggregate, which is consistent with the DSC studies.

Three pairs of interactions are present in these ternary  $\text{LiClO}_4$ /PEO/PCL blends: between  $\text{LiClO}_4$  and PEO,  $\text{LiClO}_4$  and PCL, and PEO and PCL. The combination of these mutually competitive interactions dictates the final miscibility of these ternary blends and also the mobility of the  $\text{Li}^+$  cation within the polymer chains. From the solid-state NMR spectra, we conclude that an excess content of  $\text{LiClO}_4$  tends to result in aggregation and increase the mobility of the polymer chains due to the dilution effect.

**Ionic Conductivity.** Figure 10 presents plots of the Arrhenius ionic conductivity as a function of temperature for  $\text{LiClO}_4$ /PEO/PCL ternary blend-based electrolyte systems containing a constant  $\text{LiClO}_4$  salt concentration (25 wt %). From DSC data, we know that the  $T_g$ s of PEO and PCL are similar (ca.  $-60^\circ\text{C}$ ), but the ionic conductivity of  $\text{LiClO}_4$ /PCL is ca. 1–2 orders lower than that of  $\text{LiClO}_4$ /PEO. In addition to the chain mobility of the polymer matrix, we must also consider



**Figure 10.** Arrhenius ionic conductivity plots as a function of temperature for  $\text{LiClO}_4$ /PEO/PCL ternary blend-based electrolyte systems containing constant  $\text{LiClO}_4$  concentration (25 wt %).

the ability of the  $\text{Li}^+$  cation to coordinate to the polar groups present in the polymer matrix. According to the information we obtained from the solid-state  $^7\text{Li}$  NMR spectra, the  $\text{Li}^+$  cation has a much greater preference for coordination with PEO rather than with PCL. Therefore, the  $\text{LiClO}_4$ /PEO system has a higher ionic conductivity than that of the  $\text{LiClO}_4$ /PCL system. Figure 10 indicates, however, that the maximum ionic conductivity occurs for the ternary blend  $\text{LiClO}_4$ /PEO/PCL = 25/60/15. The addition of PCL into the  $\text{LiClO}_4$ /PEO or PEO into the  $\text{LiClO}_4$ /PCL binary blend increases their ionic conductivities at lower temperature of  $20^\circ\text{C}$ . The FTIR spectra clearly reveal that the crystalline phases of PEO and PCL still exist in both the  $\text{LiClO}_4$ /PEO and  $\text{LiClO}_4$ /PCL binary blends, respectively. The addition of the third component (PCL or PEO) to these binary blends tends to retard or destroy the crystalline phase and results in higher ionic conductivity as a result of the strong miscibility between PEO and PCL. In addition, the crystalline phase can be reduced or inhibited and higher conductivity occurs upon raising the temperature, as is expected. If we consider, for example, a composition of 25/75/0, we observe that its ionic conductivity increases drastically when the temperature is raised from  $40$  to  $60^\circ\text{C}$ . Nevertheless, further addition of the third component results in a decrease in ionic conductivity because phase separation (immiscibility) occurs, which causes  $\text{LiClO}_4$  to aggregate in these ternary blends. As a result, the maximum ionic conductivity occurs at the composition at which phase separation begins. The addition of PCL tends to retard or inhibit PEO crystallization, while the excess content of PCL tends to be excluded. In fact, a slight PCL phase separation promotes the ionic conductivity.

## Conclusions

We have investigated the miscibility behavior, interaction mechanism, and ionic conductivity of LiClO<sub>4</sub>/PEO/PCL ternary blend-based electrolyte systems by the use of DSC, FTIR, solid-state <sup>7</sup>Li NMR spectroscopy, and ac impedance measurements. Although each of the three individual binary pairs is fully miscible, a closed-loop immiscibility region exists in the ternary blend's phase diagram. Lithium cation more preferably coordinates with the ether oxygen atom of PEO rather than with the carbonyl group of PCL. When LiClO<sub>4</sub> is added to the PEO/PCL binary blend, the PCL component tends to be excluded, which causes phase separation of these ternary blends. The presence of a small PCL content in the PEO phase is able to retard or inhibit crystallization because PEO and PCL are fully miscible at all compositions. This factor is responsible for the observed increase in ionic conductivity of the LiClO<sub>4</sub>/PEO/PCL blend. The maximum ionic conductivity ( $6.3 \times 10^{-7}$  S cm<sup>-1</sup>) of the ternary blend at room temperature occurs at the LiClO<sub>4</sub>/PEO/PCL composition of 25/60/15.

## References and Notes

- (1) Cheradame, H.; Le Nest, J. F. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier: Amsterdam, 1987/1989; Vols. 1 and 2.
- (2) Scrosati, B. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: New York, 1993.
- (3) Armand, M. B. *Solid State Ionics* **1983**, 9–10, 745.
- (4) Murata, K.; Izuchi, S.; Yoshihisa, Y. *Electrochim. Acta* **2000**, 45, 1501.
- (5) Lee, I. J.; Song, G. S.; Lee, W. S.; Suh, D. H. *J. Power Sources* **1994**, 89, 47.
- (6) Chen, H. W.; Chiu, C. Y.; Wu, H. D.; Shen, I. W.; Chang, F. C. *Polymer* **2002**, 43, 5011.
- (7) Xia, D. W.; Smid, J. *J. Polym. Sci., Polym. Lett.* **1984**, 22, 617.
- (8) Li, J.; Khan, I. M. *Macromolecules* **1993**, 26, 4544.
- (9) Kuo, S. W.; Lin, C. L.; Chang, F. C. *Macromolecules* **2002**, 35, 278.
- (10) Berthier, C.; Forecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, 11, 91.
- (11) Wright, P. V. *Br. Polym. J.* **1975**, 7, 39.
- (12) MacDonald, J. R. *J. Chem. Phys.* **1974**, 61, 3977.
- (13) Watanabe, M.; Ohashi, S.; Sanui, K.; Ogata, N.; Kobayashi, T.; Ohtaki, Z. *Macromolecules* **1985**, 18, 1945.
- (14) Li, J.; Khan, I. M. *Macromol. Chem.* **1991**, 192, 3043.
- (15) Chen, H. W.; Chiu, C. Y.; Chang, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **2002**, 40, 1342.
- (16) Kim, J. H.; Min, B. R.; Won, J.; Kang, Y. S. *J. Phys. Chem. B* **2003**, 107, 5901.
- (17) Chintapalli, S.; Frech, R. *Macromolecules* **1996**, 29, 3499.
- (18) Fu, R.; Ma, Z.; Zheng, J. P.; Au, G.; Plichta, E. J.; Ye, C. *J. Phys. Chem. B* **2003**, 107, 9730.
- (19) Wang, H. L.; Kao, H. M.; Wen, T. C. *Macromolecules* **2000**, 33, 6910.
- (20) Dai, Y.; Wang, Y.; Greenbaum, S. G.; Bajue, S. A.; Golodnitsky, D.; Ardel, G.; Strauss, E.; Peled, E. *Electrochim. Acta* **1998**, 43, 1557.
- (21) Liang, W. J.; Kuo, P. L. *Macromolecules* **2004**, 37, 840.

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