# Miscibility Behavior and Interaction Mechanism of Polymer Electrolytes Comprising LiClO$_4$ and MPEG-*block*-PCL Copolymers

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*Received April 25, 2005*

ABSTRACT: We have used DSC, FTIR spectroscopy, and ac impedance techniques to investigate in detail the miscibility behavior, interaction mechanism, and ionic conductivity of polymer electrolytes composed of lithium perchlorate (LiClO$_4$) and monomethoxypoly(ethylene glycol)-*block*-poly($\epsilon$-caprolactone) (MPEG−PCL) diblock copolymer. The existence of the PCL phase in the MPEG−PCL block copolymer tends to retard the crystallinity of MPEG and results in a higher ionic conductivity for the LiClO$_4$/MPEG−PCL based polymer electrolyte. DSC analyses indicate that the phase separation occurs for some compositions of the LiClO$_4$/MPEG−PCL blends. In addition, FTIR spectroscopy studies reveal the complicated interactions that occur within the LiClO$_4$/MPEG−PCL blend system upon varying the LiClO$_4$ content and increasing the temperature. For the LiClO$_4$/MPEG−PCL blend system, the relative intensity of the "complexed" carbonyl stretching band of the PCL block tends to increase when either the LiClO$_4$ concentration or the length of the PCL block increases. For some compositions of LiClO$_4$/MPEG−PCL, when the temperature is increased from 120 to 180 °C, the relative intensity of the "complexed" C=O group increases; this phenomenon is different from that observed for the LiClO$_4$/PCL homopolymer blend.

## Introduction

A polymer electrolyte may be defined generally as a membrane having transport properties that are comparable with those of the common liquid ionic solutions.[1−5] These systems are of technological interest due to their applications as solid electrolytes in electrochemical devices, such as energy conversion units (batteries, fuel cells), smart windows, components in solid-state sensors, and solid-state transistors.[6−9] Consequently, the lithium salt-based electrolytes have been the focus of a wide variety of fundamental and application-oriented studies. However, Li$^+$-based polymer electrolytes exhibit several disadvantages that affect the commercialization of such cells; for example, one major drawback is the low ionic conductivity of the electrolyte at ambient temperatures.[10] Thus, it is of great importance to optimize their performance through a detailed understanding of the fundamental ionic interactions that occur within polymeric electrolytes.

Poly(ethylene oxide) (PEO) exhibits good complexation properties and high flexibility and retains good mechanical stability at temperatures up to its melting point, but its relatively high degree of crystallinity limits the ionic conductivity of these PEO-based electrolytes.[1−3,11] Extensive research efforts have been devoted toward lowering the temperature of operation of the PEO-based electrolytes into the ambient region.[12−15]

Monomethoxypoly(ethylene glycol)-*block*-poly($\epsilon$-caprolactone) (MPEG−PCL) diblock copolymer is a desirable polymer electrolyte because the existence of strong interaction between the PEO and PCL units tends to suppress the crystallization of PEO.[16] In a previous study,[17] we reported that the addition of PCL into an electrolyte system based on LiClO$_4$/PEO tends to retard or inhibit the crystallization of PEO and subsequently increases the ionic conductivity. Thus, we became interested in studying polymer electrolytes composed of LiClO$_4$ and the MPEG−PCL diblock copolymer. It

seemed reasonable to us to expect that MPEG−PCL may be more miscible than the PEO/PCL binary blend when considering our previous studies in which we compared the miscibility between block copolymers and blends.[18] Therefore, we expected that this salt/block copolymer blend system, LiClO$_4$/MPEG-PCL, would possess higher ionic conductivity than those of previously reported electrolyte systems based on LiClO$_4$/PEO binary blends.

Previous reports have described blend systems of PEO-containing block copolymers doped with a range of inorganic salts.[19,20] These studies, however, involved the use of amphiphilic block copolymers, such as poly(ethylene oxide)-*block*-polyisoprene (PEO−PI), and concentrated mainly on the morphologies, phase behavior, and thermal and mechanical properties of these block copolymer/salt mixtures. To the best of our knowledge, there have been no studies on the influences that the miscibility behavior and interaction mechanism have on the variation of ionic conductivity in polymer electrolytes comprising LiClO$_4$ and block copolymers possessing two LiClO$_4$-miscible blocks. In this study, we employed differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and alternating current (ac) impedance to investigate the miscibility and related conductivity behavior of LiClO$_4$/MPEG−PCL blend systems.

## Experimental Section

**Materials.** Monomethoxypoly(ethylene glycol) having a molecular weight of 5000 (MPEG-5K) was obtained from Aldrich and dried by an azeotropic distillation with dry toluene. $\epsilon$-Caprolactone ($\epsilon$-CL, from Acros) was purified by vacuum distillation over CaH$_2$. The fraction collected at room temperature (5 mmHg) was used for polymerization. Tin(II) 2-ethylhexanoate [stannous octoate, Sn(Oct)$_2$] and acetonitrile, both from Aldrich, were used as received. Lithium perchlorate (LiClO$_4$, Aldrich) was dried in a vacuum oven at 80 °C for 24 h and stored in a desiccator prior to use.

**Synthesis of Monomethoxypoly(ethylene glycol)-*block*-poly($\epsilon$-caprolactone) (MPEG−PCL).**[21] Block copolymers are readily prepared through the ring-opening polymerization of

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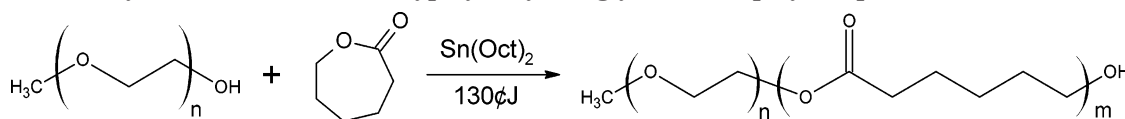
**Scheme 1.  Synthesis of Monomethoxypoly(ethylene glycol)-*block*-poly(ε-caprolactone) (MPEG−PCL)**



**Table 1. Compositions and Molecular Weights of MPEG−PCL Block Copolymers**

| copolymer MPEG−PCL | EO/CL in feed | EO/CL[a] in product | $\overline{DP}_{MPEG}$[b] | $\overline{DP}_{PCL}$[a] | $M_n$[a] | $M_n$[c] | $M_n/M_w$[c] | MPEG/PCL (wt %) |
|---|---|---|---|---|---|---|---|---|
| EO$_{114}$−CL$_{42}$ | 2.85 | 2.71 | 114 | 42 | 9 800 | 8 900 | 1.22 | 51/49 |
| EO$_{114}$−CL$_{111}$ | 1.14 | 1.03 | 114 | 111 | 17 650 | 13 400 | 1.29 | 28/72 |
| EO$_{114}$−CL$_{247}$ | 0.49 | 0.46 | 114 | 247 | 33 200 | 29 800 | 1.38 | 15/85 |
| EO$_{114}$−CL$_{516}$ | 0.23 | 0.22 | 114 | 516 | 63 900 | 57 000 | 1.43 | 8/92 |

[a] Calculated by using the integration ratio of resonances due to MPEG blocks at 3.60 ppm (−O−CH$_2$−CH$_2$−) and to PCL blocks at 4.01 ppm [(−CO)−O−CH$_2$−] in the $^1$H NMR spectra. [b] Degree of polymerization of MPEG = 5000/44 = 114. [c] Obtained from GPC.

CL and MPEG in the presence of stannous octoate as a catalyst (Scheme 1). The reaction mixture was prepared by introducing, under a nitrogen atmosphere, a known volume of ε-caprolactone monomer into a silanized flask containing a preweighted amount of MPEG. One drop of Sn(Oct)$_2$ was added into the mixture. The flask was connected to a vacuum line, evacuated, sealed off, and heated at 130 °C. After 24 h, the resulting block copolymer was dissolved in methylene chloride, precipitated in an excess of cold hexane, and dried at 40 °C under vacuum. Diblock copolymers having different degrees of polymerization (DP) of PCL were obtained upon adjusting the feed ratio of CL to MPEG. The results of these polymerizations are summarized in Table 1.

**Characterizations.** The molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) using *N,N*-dimethylformamide (DMF) as an eluent at 50 °C, and poly(ethylene oxide) standards were employed for column calibration.

$^1$H NMR spectra of the copolymers were recorded in deuterated chloroform (CDCl$_3$) solutions at 25 °C using a Varian UNITY INOVA-400 NMR spectrometer. The molecular weights and MPEG/PCL ratios of the various types of copolymers were evaluated from these $^1$H NMR spectra and compared with the corresponding values obtained by GPC.

**Sample Preparations.** Polymer electrolytes of LiClO$_4$/MPEG−PCL in various blend compositions were prepared by solution casting. The desired amounts of MPEG−PCL and LiClO$_4$ salt were dissolved in 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; then the dish was further dried under vacuum at 80 °C for 2 days. To prevent its contact with air or moisture, the polymer electrolyte film was transferred to a glovebox under a nitrogen atmosphere.

**Differential Scanning Calorimetry (DSC).** Thermal analyses were performed using a DSC instrument (DuPont TA 2010). The sample was heated from −110 to 150 °C under an atmosphere of dry N$_2$. 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$_2$ 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 4000−400 cm$^{-1}$ using a Nicolet AVATAR 320 FTIR spectrometer (Nicolet Instruments, Madison, WI) operating at a resolution of 1 cm$^{-1}$.

**Conductivity Measurements.** Ionic conductivity measurements with alternation current were conducted on an AUTOLAB designed by Eco Chemie within a 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 0.08 to 0.12 mm; the impedance response was gauged over the range from 20 to 100 °C. The conductivity was calculated from the bulk resistance

according to the equation[22,23]

$$\sigma = L/AR_b$$

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

**Synthesis of MPEG−PCL.** The ring-opening polymerization of ε-caprolactone was initiated with MPEG in the presence of stannous octoate as catalyst (Scheme 1). We performed the polymerization in the bulk at 130 °C for 24 h and varied the concentration of ε-caprolactone to obtain copolymers having a range of PCL block lengths. Table 1 summarizes the data of the polymers characterized by $^1$H NMR spectroscopy and GPC.

**DSC Studies.** According to the results of a previous study,[24] ionic aggregation may have a dramatic effect on the miscibility and thermal properties of a polymer/salt blend. First of all, we carried out thermal analyses to determine whether the properties of these systems are affected by the addition of the lithium salt. Figure 1 shows the typical second-run DSC analyses of various LiClO$_4$/MPEG−PCL blends. The composition of each system (Figure 1a−d) varies with the content of the lithium salt; 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 blend having two $T_g$s is considered to be immiscible or partially miscible in the amorphous phase. Kuo et al. have reported[16] that the binary blends of poly(ethylene oxide) (PEO) and PCL at various ratios are miscible in their amorphous phase. Thus, the MPEG−PCL diblock copolymer, regardless of the length of its PCL block, is expected to be miscible in the amorphous phase. However, blending MPEG−PCL block copolymers with LiClO$_4$ salt results in phase separation. Figure 1a−c displays two $T_g$s at lower LiClO$_4$ contents. Moreover, Figure 1d suggests that no phase separation appears at any composition of the LiClO$_4$/EO$_{114}$−CL$_{516}$ blend system. These results can be interpreted as arising from a complicated set of interactions occurring between LiClO$_4$ and both blocks of MPEG and PCL. Our previous study indicated that the interaction between LiClO$_4$ and PEO is stronger than that between LiClO$_4$ and PCL.[17] Figure 1a−d shows DSC thermograms of LiClO$_4$/MPEG−PCL blends containing varying lengths of the PCL block in the block copolymer (i.e., different molecular weight ratios of MPEG and PCL). For the LiClO$_4$/EO$_{114}$−CL$_{42}$ blend system, which contains a shorter length of PCL block,
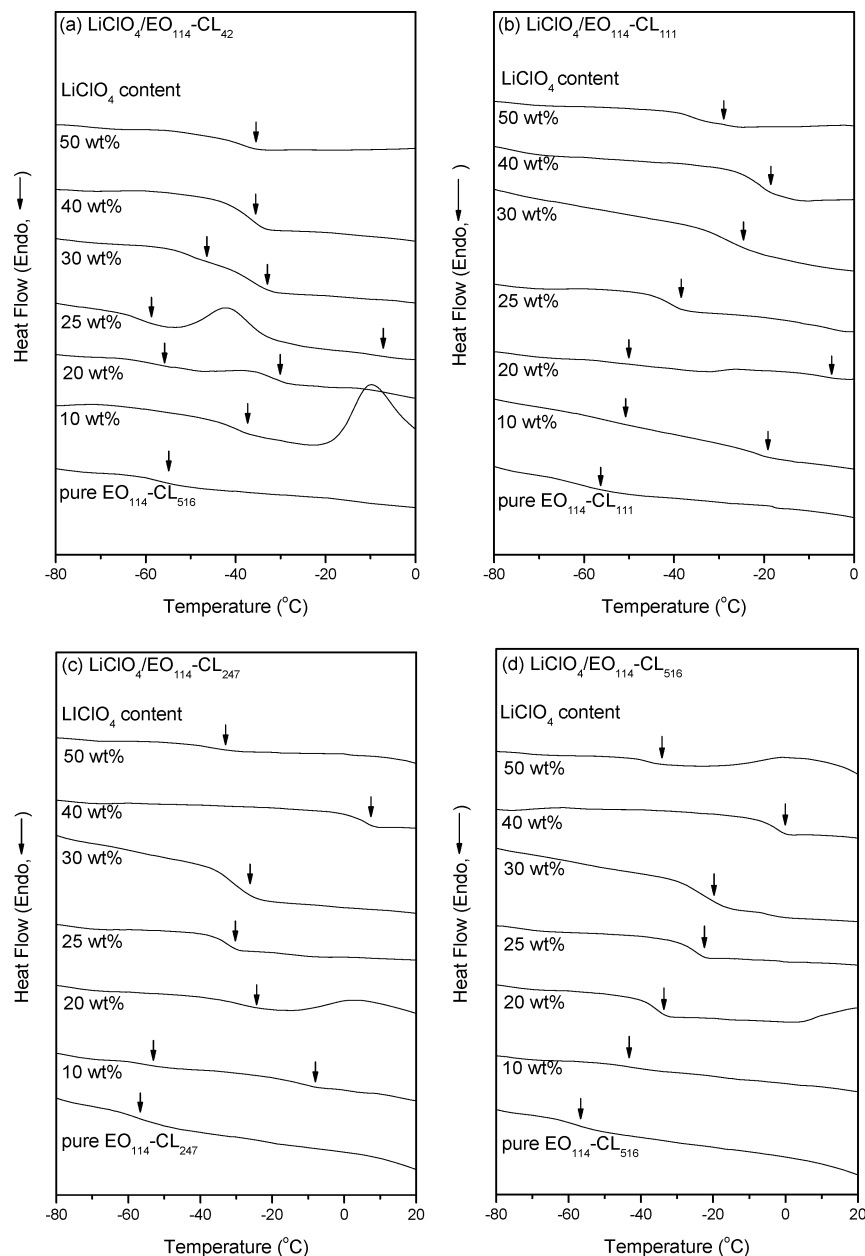
**Figure 1.** DSC thermograms of LiClO$_4$/MPEG−PCL blend with various LiClO$_4$ salt content: (a) EO$_{114}$−CL$_{42}$, (b) EO$_{114}$−CL$_{111}$, (c) EO$_{114}$−CL$_{247}$, (d) EO$_{114}$−CL$_{516}$. Variations of melting temperature ($T_m$) and melting enthalpy ($\Delta H_m$) of LiClO$_4$/EO$_{114}$−CL$_{516}$ blends with various LiClO$_4$ content.

the observed phase separation (nonhomogeneity) is caused by the exclusion of the PCL block. This phase separation disappears upon increasing the molecule weight of the PCL block. The higher PCL content is allowed to interact simultaneously with both the MPEG block and LiClO$_4$, which, thus, results in single phase in their amorphous phase. In addition, increasing the concentration of the LiClO$_4$ salt also tends to increase miscibility.

Interestingly, the glass transition temperature (Figure 1b−d) increases continuously upon increasing the content of LiClO$_4$, even when the salt content is as high as 40 wt %. In contrast, the value of $T_g$ of the LiClO$_4$/PEO blend system tends to achieve its maximum at a LiClO$_4$ content of 20 wt %;[17] the excess LiClO$_4$ tends to self-aggregate and causes the $T_g$ of LiClO$_4$/PEO to decrease owing to the dilution effect.[25,26] As a result, the MPEG−PCL block copolymer is able to accommodate higher LiClO$_4$ salt content in the LiClO$_4$/

MPEG−PCL blend system than can the PEO matrix in LiClO$_4$/PEO blend systems. It is understandable that because blends of PEO and PCL are miscible in the amorphous region, the incorporation of PCL block into the PEO domain tends to retard PEO crystallization. As a result, the greater fraction of the amorphous PEO is able to coordinate with LiClO$_4$ salt. Figure 1d shows that $T_g$ of the LiClO$_4$/MPEG−PCL blend system tends to decrease by increasing the LiClO$_4$ content up to 50 wt %.

Figure 2 shows the variations of melting temperature ($T_m$) and melting enthalpy ($\Delta H_m$) obtained form DSC analyses of LiClO$_4$/EO$_{114}$−CL$_{516}$ blends with various LiClO$_4$ contents. It is well-known that the value of $\Delta H_m$ correlates to the degree of crystallization. In the LiClO$_4$/EO$_{114}$−CL$_{516}$ blend system, the addition of LiClO$_4$ reduces the degree of crystallization. Eventually, the melting peak disappears when the LiClO$_4$ content salt is increased to 25 wt %. However, two melting peaks
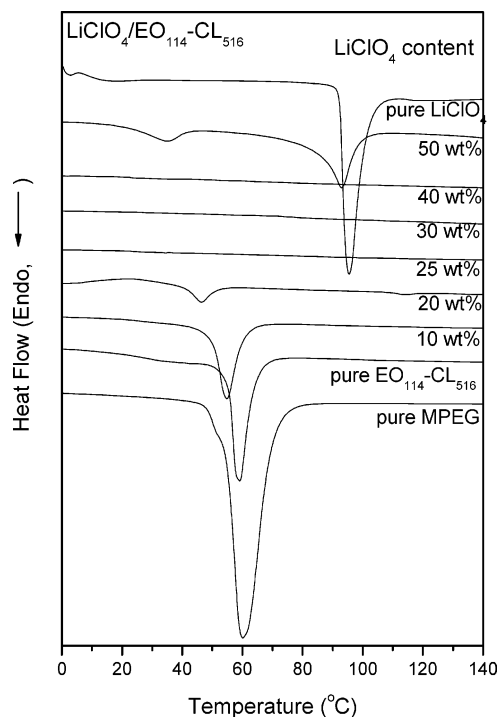
**Figure 2.** Infrared spectra of MPEG−PCL block copolymers with various EO/CL ratios, recorded at room temperature, displaying (a) the carbonyl stretching and (b) CH$_2$ wagging regions.

appear at 35 and 93 °C when the salt content is at 50 wt %. The lower-temperature peak is assigned as the melting peak of the diblock copolymer EO$_{114}$−CL$_{516}$, while the higher-temperature peak corresponds to that of the LiClO$_4$ salt. Excess LiClO$_4$ tends to aggregate and causes the crystallization of both the EO$_{114}$−CL$_{516}$ diblock copolymer and the LiClO$_4$ salt. The results of thermal properties of the blends obtained from DSC measures are listed in Table 2; a similar trend is observed for each system. When comparing all of the MPEG−PCL blends which contain LiClO$_4$ content fixed at 50 wt %, $T_m$ and $\Delta H_m$ of the LiClO$_4$ salt increase with increasing the length of PCL block; this situation arises because the longer PCL chain is more miscible with the MPEG block, and thus, a lower amount of free MPEG is available to dissociate the lithium perchlorate ion pair.[17] As a result, LiClO$_4$ salt tends to crystallize at a relatively lower MPEG content.

**FT-IR Spectroscopy.** Figure 3 presents infrared spectra recorded at room temperature, displaying the bands representing the carbonyl stretching (a) and CH$_2$ wagging (b) of a series of MPEG−PCL block copolymers. As observed in Figure 3a, the carbonyl stretching for the PCL block is split into two bands: absorptions of the amorphous and the crystalline conformations at 1734 and 1724 cm$^{-1}$, respectively.[27,28] The relative intensity of the crystalline conformation of PCL block (1724 cm$^{-1}$) is lowest for EO$_{114}$−CL$_{111}$ block copolymer; the relative intensity of the crystalline conformation of the PCL block increases when the length of the PCL block is increased, i.e., for EO$_{114}$−CL$_{247}$ and EO$_{114}$−CL$_{516}$. Furthermore, Figure 3b shows IR spectra of the CH$_2$ wagging vibration, in the region 1380−1320 cm$^{-1}$, of the pure MPEG-5K and various MPEG−PCL block copolymers. The pure MPEG-5K exhibits two bands, at 1360 and 1343 cm$^{-1}$, that represent its crystalline phase.[16] The crystallinity of MPEG is gradually destroyed when the length of the PCL block is increased.

**Table 2. DSC Results of LiClO$_4$/MPEG−PCL Blends**

| copolymer MPEG−PCL | LiClO$_4$ content (wt %) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) |
|---|---|---|---|---|
| MPEG-5K$^a$ | 0 | −58.5 | 60.2 | 185.6 |
| EO$_{114}$−CL$_{42}$ | 0 | −56.9 | 56.8 | 120.6 |
| | 10 | −39.1 | 58.5 | 64.0 |
| | 20 | −58.5, −32.0 | 59.3 | 37.2 |
| | 25 | −61.7, −10.8 | 59.4 | 32.6 |
| | 30 | −49.7, −36.3 | | |
| | 40 | −36.7 | | |
| | 50 | −38.5 | 42.2, 80.2$^b$ | 11.2, 24.0 |
| EO$_{114}$−CL$_{111}$ | 0 | −59.2 | 54.1 | 104.2 |
| | 10 | −54.6, −21.2 | 58.4 | 51.4 |
| | 20 | −54.8, −6.8 | 55.1 | 36.0 |
| | 25 | −40.8 | 48.2 | 5.8 |
| | 30 | −28.6 | | |
| | 40 | −20.4 | | |
| | 50 | −35.9 | 28.9, 88.4 | 2.0, 40.8 |
| EO$_{114}$−CL$_{247}$ | 0 | −57.5 | 59.2 | 91.5 |
| | 10 | −55.7, −13.1 | 57.2 | 65.2 |
| | 20 | −28.3 | 53.9 | 37.1 |
| | 25 | −32.3 | | |
| | 30 | −31.5 | | |
| | 40 | −5.9 | | |
| | 50 | −38.7 | 42.1, 89.8 | 20.5, 56.4 |
| EO$_{114}$−CL$_{516}$ | 0 | −57.2 | 59.1 | 89.4 |
| | 10 | −43.5 | 54.9 | 45.6 |
| | 20 | −35.2 | 46.4 | 9.7 |
| | 25 | −24.5 | | |
| | 30 | −23.7 | | |
| | 40 | −2.3 | | |
| | 50 | −38.2 | 34.7, 93.0 | 12.5, 58.4 |

$^a$ The macroinitiator of ring-opening of $\epsilon$-caprolactone in the synthesis of MPEG−PCL. $^b$ The melting point of pure LiClO$_4$ is at ca. 95 °C.
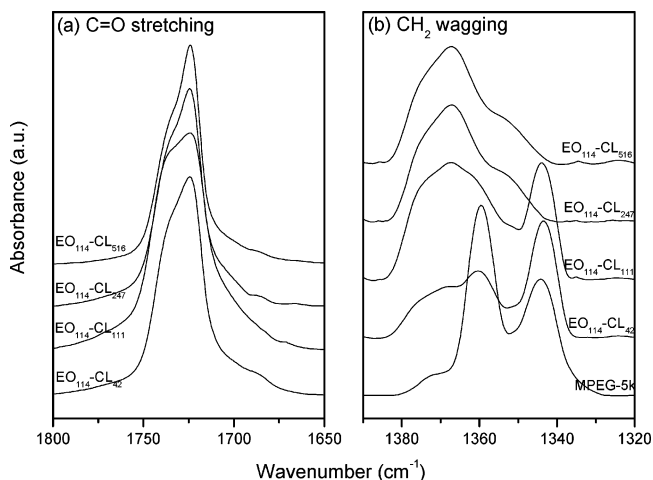


**Figure 3.** Carbonyl group stretching region of IR spectra recorded at room temperature for MPEG−PCL block copolymers having different EO/CL ratios after blending with 20 wt % LiClO$_4$: (a) EO$_{114}$−CL$_{111}$, (b) EO$_{114}$−CL$_{247}$, (c) EO$_{114}$−CL$_{516}$.

Therefore, we confirm that the interaction between MPEG and PCL tends to decrease the fraction of the crystalline phases of both MPEG and PCL.

Since the carbonyl group (C=O) is an electron donor within the PCL-based polymer electrolyte, the Li$^+$ ion tends to coordinated with oxygen atom of the carbonyl group. Infrared spectroscopy is a powerful tool to monitor such ionic interaction. Thus, we focus on the change of the carbonyl group within the PCL block of the MPEG−PCL diblock copolymer and determine the strengths of the ionic interactions between Li$^+$ and the EO and CL blocks of MPEG−PCL. Figure 4 presents the infrared spectra (carbonyl stretching region) re-
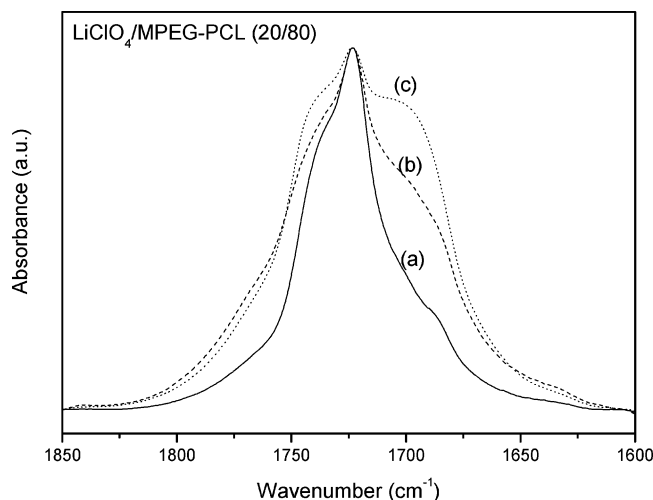
**Figure 4.** Carbonyl group stretching region of the IR spectra recorded at 120 °C for $LiClO_4$/MPEG−PCL blends having different $LiClO_4$ contents: (a) $EO_{114}$−$CL_{42}$, (b) $EO_{114}$−$CL_{111}$, (c) $EO_{114}$−$CL_{247}$, (d) $EO_{114}$−$CL_{516}$.

corded at room temperature of the MPEG−PCL diblock copolymers having different EO/CL ratios and blended with 20 wt % $LiClO_4$. When the $LiClO_4$ salt is added, a shoulder at ca. 1704 cm$^{-1}$ appears in Figure 4, corresponding to the interaction between the C=O group and Li$^+$. It is clearly observed in Figure 4 that the relative intensity of the shoulder at ca. 1704 cm$^{-1}$ increases upon increasing the length of PCL block at a fixed $LiClO_4$ concentration. From Figure 3 we conclude that the crystalline conformation of MPEG in $EO_{114}$−$CL_{247}$ tends to be destroyed due to the strong miscibility between MPEG and PCL. No free MPEG block is available to coordinate with Li$^+$ ion while the length of the PCL block is increased; thus, more Li$^+$ ion is able to coordinate with the PCL.

**Effect of $LiClO_4$ Salt Content.** Figure 5 illustrates the carbonyl stretching region (1800−1650 cm$^{-1}$) of IR spectra recorded at 120 °C for various $LiClO_4$/MPEG−PCL blends containing a range of $LiClO_4$ contents. The PCL crystalline phase tends to be destroyed at 120 °C; thus, the IR spectrum shows a single peak at ca. 1734 cm$^{-1}$ corresponding to the amorphous PCL. The addition of $LiClO_4$ salt causes the appearance of an absorption band at 1704 cm$^{-1}$, assigned as the interaction between Li$^+$ and carbonyl group, i.e., "complexed" C=O. In Figure 5a, the absorption band of the "complexed" carbonyl group only appears when the composition of $LiClO_4$/$EO_{114}$−$CL_{42}$ is at 50/50. Nevertheless, upon increasing the length of PCL block, as shown in Figure 5b−d, the "complexed" C=O band at 1704 cm$^{-1}$ clearly appears at a relatively lower content of the $LiClO_4$. To further clarify the effect of $LiClO_4$ content on the charge environment surrounding the carbonyl group of PCL block in MPEG−PCL block copolymer, relative fractions of "free" and "complexed" C=O sites have been quantified by decomposing the C=O stretching band into two Gaussian peaks[29−31] and summarized in Table 3. At a lower concentration of PCL in the MPEG−PCL copolymer, the absorption band of "complexed" C=O appears until the $LiClO_4$ content is increased to 40−50 wt %. Besides, no "complexed" C=O appears for any composition of the MPEG−PCL block copolymer system at lower $LiClO_4$ content (10 wt %). These results suggest that MPEG is preferred to interact with Li$^+$ cation than PCL does. The coordination between Li$^+$ ion and the carbonyl

group of PCL in the $LiClO_4$/MPEG−PCL blend system will occur at a higher concentration of $LiClO_4$ salt or when PCL is present at a relatively higher content relative to MPEG.

**Effect of Temperature.** Figure 6a indicates the carbonyl group vibration region of FTIR spectra recorded at different temperatures by blending 25 wt % $LiClO_4$ with PCL homopolymer. As mentioned above, the "complexed" C=O band is located at 1704 cm$^{-1}$, while the "free" C=O band is located at 1734 cm$^{-1}$. The relative intensity of the "free" carbonyl vibration band increases at the expense of the "complexed" C=O band with the increase of temperature, implying that the fraction of the "complexed" carbonyl group decreases accordingly. The "complexed" C=O band arises from the interaction between Li$^+$ ion and carbonyl group; it is well-known that the strength of such ionic interaction tends to decrease upon raising the temperature.[32] Figure 6b presents the absorption peaks of the ether groups (C−O−C) recorded at different temperatures by blending 25 wt % $LiClO_4$ with PEO homopolymer. The band centered at around 1103 cm$^{-1}$ is attributed to the stretching of the "free" ether group, while the band at about 1080 cm$^{-1}$ is assigned to the coordination between Li$^+$ with ether groups, i.e., "complexed" ether group.[33,34] The relative intensity of the "free" ether group vibration band increases with increasing the temperature. These changes indicate that the ionic interaction between Li$^+$ cation and the ether group on PEO weakens as the temperature is increased,[35] which is similar to the trend observed in Figure 6a. The IR spectra with different temperatures of $LiClO_4$/$EO_{114}$−$CL_{42}$ (30/70) recorded in both regions of carbonyl group stretching and ether group stretching are shown in parts a and b of Figure 7, respectively. In Figure 5a and Table 3, no "complexed" carbonyl band is observed for $LiClO_4$/$EO_{114}$−$CL_{42}$ (30/70) in the IR spectra recorded at 120 °C. Figure 7a shows, however, that the relative intensity of the "complexed" C=O band increases gradually when the temperature is raised from 120 to 180 °C. In addition, Figure 7b displays that the relative intensity of the "free" ether stretching band at ca. 1103 cm$^{-1}$ increases with the increase of the temperature. It is interesting to notice that the ion−dipole interaction between Li$^+$ ion and the carbonyl group increases, but the interaction between Li$^+$ ion and the ether group decreases upon increasing the temperature of the $LiClO_4$/$EO_{114}$−$CL_{42}$ (30/70) blend system. Furthermore, the $LiClO_4$/$EO_{114}$−$CL_{111}$ (30/70) blend system also exhibits the same behavior in its IR spectra by varying the temperature from 120 to 180 °C (Figure 8). The relative intensity of "complexed" ether stretching band decays but that of "complexed" carbonyl stretching band increases when the temperature is increased. Since Li$^+$ cation is capable of coordinating with both the ether group of the MPEG block and carbonyl group of the PCL block in the $LiClO_4$/MPEG−PCL blend system, it is reasonable to assume that there exist two different ion−dipole interactions, representing two interaction parameters, $k_E$ (between Li$^+$ and ether group) and $k_C$ (between Li$^+$ and carbonyl group), as depicted in Scheme 2. Both of these interaction parameters, $k_E$ and $k_C$, are dependent on the temperature, and their values decrease with increasing the temperature. Making a summary form Figures 6−8, $k_E$ decreases more rapidly than $k_C$ at the temperature range from 120 to 180 °C.[36] The Li$^+$ cation prefers to coordinate with PEO rather than PCL; hence, at the
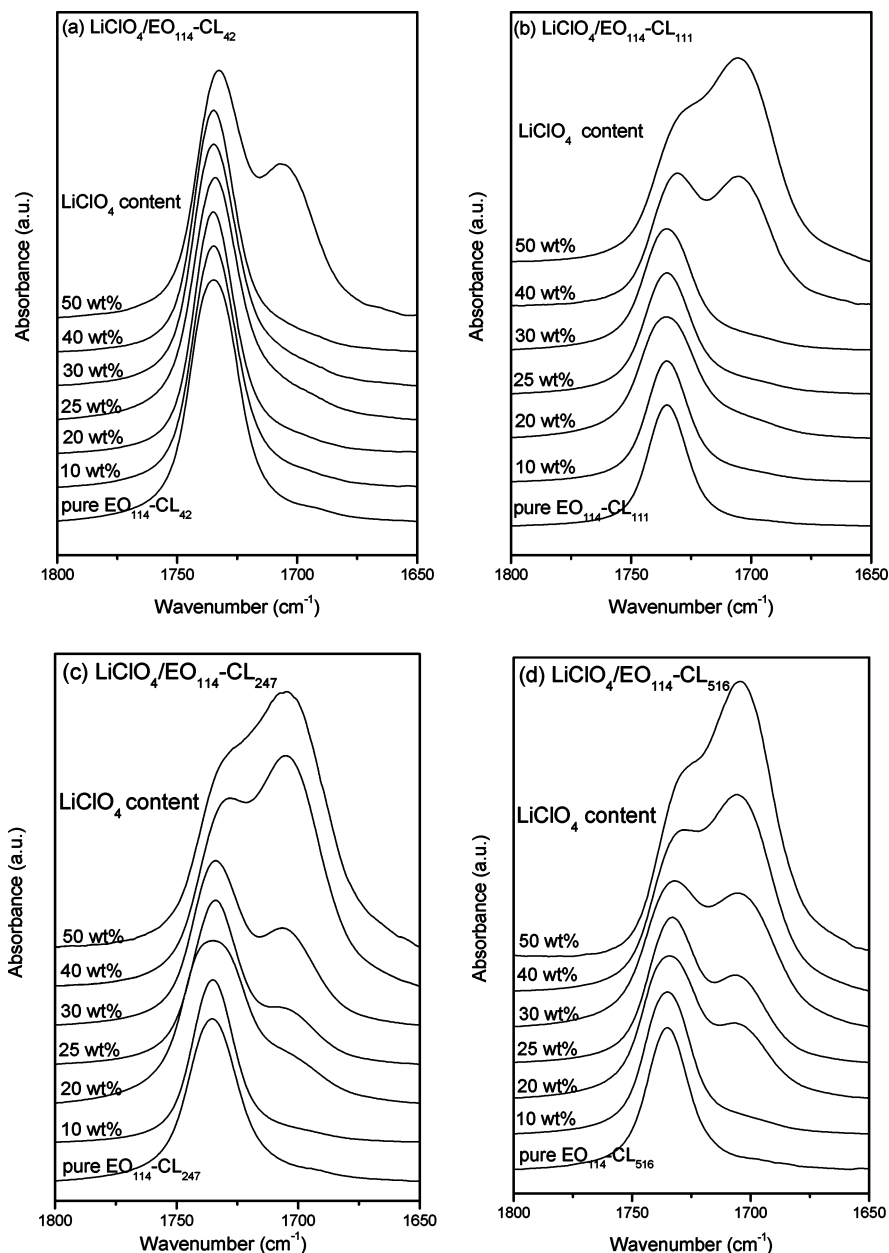
**Figure 5.** FTIR spectra recorded at temperatures from 120 to 180 °C of blends of (a) LiClO₄/PCL homopolymer (25/75), displaying the carbonyl group vibration region, and (b) LiClO₄/MPEG-5K homopolymer (25/75), displaying the ether group stretching region.

beginning of the addition of lithium perchlorate, LiClO₄ is preferable to enter the MPEG phase at lower temperature. The ion−dipole interaction between Li⁺ and the ether group weakens upon increasing the temperature, and the dissociated Li⁺ cation turns to coordinate with the carbonyl group (Figures 7a and 8a). As a result, the relative intensity of the "complexed" C=O stretching band increases by raising the temperature. However, there are two factors as below controlling the variation of the relative intensity of the "complexed" C=O stretching band upon increasing the temperature: (1) the ion−dipole interaction weakens as the temperature increases, and (2) the dissociated Li⁺ cation from MPEG turns to interact with carbonyl group, causing the absorption of the "complexed" C=O group to increase. Therefore, the trend of the relative intensity of the "complexed" C=O stretching band is somewhat unexpected. Figure 9 indicates the carbonyl (a) and ether (b) group stretching regions of the IR spectra of LiClO₄/EO₁₁₄−CL₁₁₁ (40/60) recorded at temperatures from 120

to 180 °C. The variation of the intensity of the "complexed" C=O stretching band has no order while the temperature increases (Figure 9a) because of factors mentioned above. Nevertheless, the relative intensity of "complexed" ether stretching band always decreases (Figure 9b) due to the weakening of the ion−dipole interaction at elevated temperature.

**Ionic Conductivity.** Figure 10 presents the Arrhenius ionic conductivities plotted as a function of temperature for LiClO₄/MPEG−PCL blend-based electrolyte systems containing a constant LiClO₄ salt concentration (25 wt %). From the DSC data, we know that the crystallinity of PEO decreases upon increasing the length of PCL block. Furthermore, previous studies have stated that the LiClO₄/PEO system has a higher ionic conductivity than that of the LiClO₄/PCL system because the Li⁺ cation has a much greater preference for coordination with PEO rather than it does with PCL. This factor is responsible for the observed increase in ionic conductivity of the LiClO₄/MPEG−PCL blend.
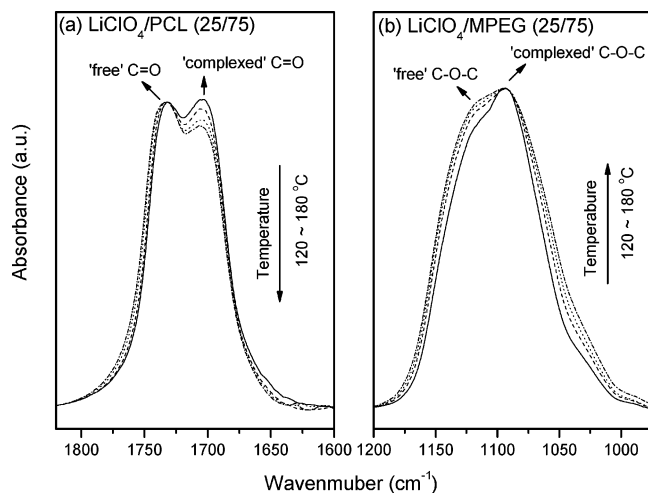
**Figure 6.** FTIR spectra of LiClO$_4$/EO$_{114}$–CL$_{42}$ (30/70) recorded at temperatures from 120 to 180 °C displaying both the (a) carbonyl group stretching and (b) ether group stretching regions.

**Table 3. Curve-Fitting Results of Infrared Spectra of C=O Group Stretching Region Recorded at 120 °C for the LiClO$_4$/MPEG–PCL Blends with Various LiClO$_4$ Salt Content**

| copolymer MPEG–PCL | LiClO$_4$ content (wt %) | free C=O | | complexed C=O | |
|---|---|---|---|---|---|
| | | $\nu_f$ (cm$^{-1}$) | $A_f$ (%) | $\nu_c$ (cm$^{-1}$) | $A_c$ (%) |
| EO$_{114}$–CL$_{42}$ | 0 | 1734.9 | | | |
| | 10 | 1734.3 | | | |
| | 20 | 1734.4 | | | |
| | 25 | 1733.5 | | | |
| | 30 | 1733.9 | | | |
| | 40 | 1734.1 | | | |
| | 50 | 1733.4 | 53.59 | 1705.3 | 46.41 |
| EO$_{114}$–CL$_{111}$ | 0 | 1734.7 | | | |
| | 10 | 1734.6 | | | |
| | 20 | 1734.2 | | | |
| | 25 | 1734.5 | | | |
| | 30 | 1734.4 | | | |
| | 40 | 1732.7 | 40.90 | 1704.7 | 59.10 |
| | 50 | 1731.8 | 28.04 | 1704.7 | 71.96 |
| EO$_{114}$–CL$_{247}$ | 0 | 1735.0 | | | |
| | 10 | 1734.8 | | | |
| | 20 | 1734.8 | 81.96 | 1702.0 | 18.04 |
| | 25 | 1734.1 | 73.36 | 1703.5 | 26.64 |
| | 30 | 1734.4 | 58.12 | 1705.1 | 41.88 |
| | 40 | 1732.4 | 32.46 | 1704.4 | 67.54 |
| | 50 | 1732.8 | 25.12 | 1704.7 | 74.88 |
| EO$_{114}$–CL$_{516}$ | 0 | 1734.4 | | | |
| | 10 | 1734.6 | | | |
| | 20 | 1734.7 | 65.81 | 1704.0 | 34.19 |
| | 25 | 1733.7 | 59.34 | 1704.7 | 40.66 |
| | 30 | 1734.1 | 45.44 | 1703.5 | 54.56 |
| | 40 | 1732.7 | 32.66 | 1705.0 | 67.34 |
| | 50 | 1731.9 | 21.28 | 1704.8 | 78.72 |

Although the LiClO$_4$/EO$_{114}$–CL$_{247}$ (25/75) and LiClO$_4$/EO$_{114}$–CL$_{512}$ (25/75) blends have lower crystallinity than LiClO$_4$/EO$_{114}$–CL$_{111}$ (25/75), Figure 10 indicates that the maximum ionic conductivity at room temperature occurs for the LiClO$_4$/EO$_{114}$–CL$_{111}$ at a fixed LiClO$_4$ content of 25 wt %.

## Conclusions

This paper describes the miscibility behavior, interaction mechanism, and ionic conductivity of LiClO$_4$/MPEG–PCL blend-based electrolyte systems using DSC, FTIR spectroscopy, and ac impedance measurements. The presence of PCL in the MPEG–PCL block copolymer tends to suppress the crystallinity of MPEG
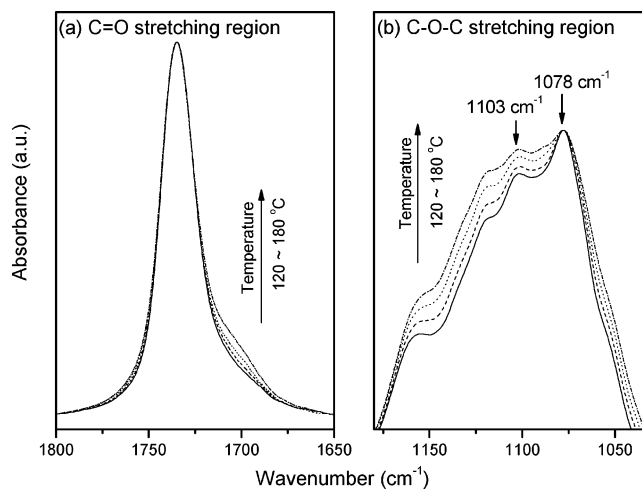


**Figure 7.** FTIR spectra of LiClO$_4$/EO$_{114}$–CL$_{111}$ (30/70) recorded at temperatures from 120 to 180 °C displaying both the (a) carbonyl group stretching and (b) ether group stretching regions.
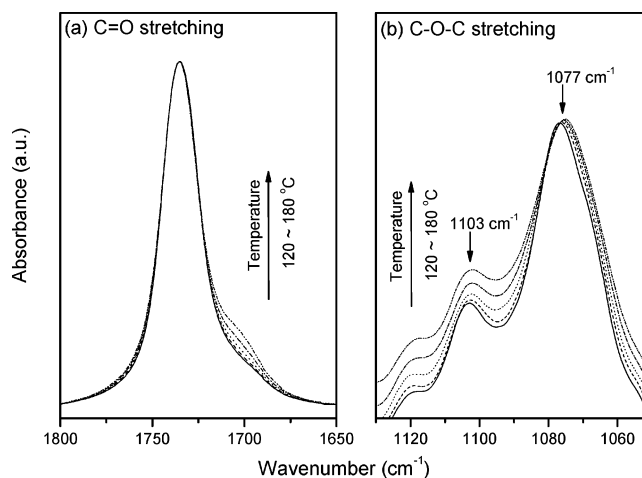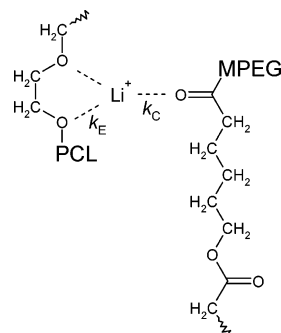


**Figure 8.** FTIR spectra of LiClO$_4$/EO$_{114}$–CL$_{111}$ (40/60) recorded at temperatures from 120 to 180 °C displaying both the (a) carbonyl group stretching and (b) ether group stretching regions.

**Scheme 2. Ionic Interactions of Li$^+$ Cation with Ether and Carbonyl Groups**



as a consequence of the miscibility between MPEG and PCL. Thus, the ionic conductivity of the LiClO$_4$/MPEG–PCL blend system at room temperature is higher than that of the LiClO$_4$/MPEG-based polymer electrolyte. Lithium cation coordinates more preferably with the ether oxygen atom of PEO rather than with the carbonyl group of PCL. Although the MPEG–PCL diblock copolymers are miscible over their entire range of compositions, the addition of LiClO$_4$ salt in a blend with MPEG–PCL results in a distinct phase separation,
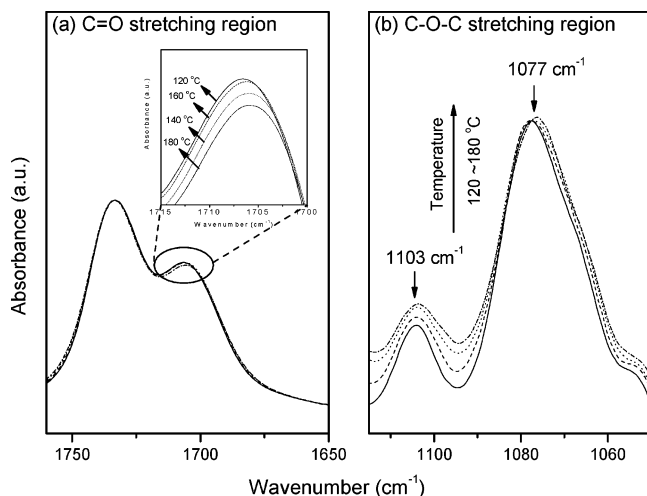
**Figure 9.** Arrhenius ionic conductivities plotted as a function of temperature for LiClO$_4$/MPEG−PCL blend-based electrolyte systems containing a constant LiClO$_4$ concentration (25 wt %).
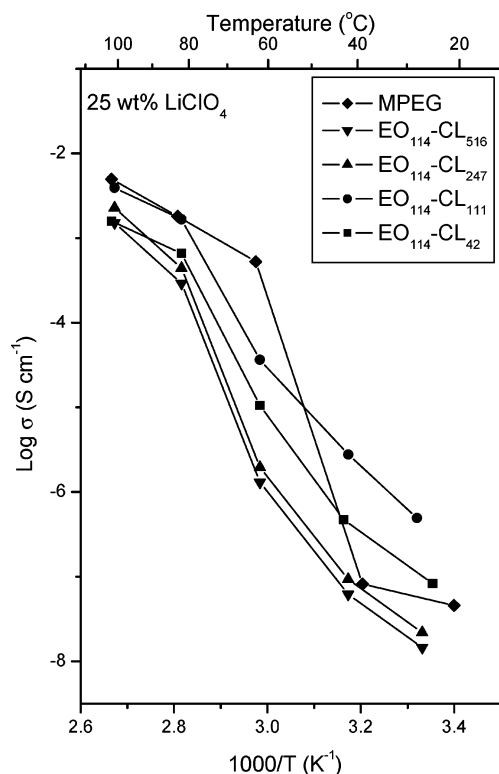


**Figure 10.** Arrhenius ionic conductivities plotted as a function of temperature for LiClO$_4$/MPEG−PCL blend-based electrolyte systems containing a constant LiClO$_4$ concentration (25 wt %).

which causes the maximum ionic conductivity of the LiClO$_4$/MPEG−PCL blend system occurring at LiClO$_4$/EO$_{114}$−CL$_{111}$(25/75). Besides, raising the concentration of LiClO$_4$ salt or increasing the length of the PCL block in the LiClO$_4$/MPEG-PCL blend increases the relative intensity of stretching band for the "complexed" carbonyl

group in IR spectra. However, the relative intensities of the "complexed" carbonyl and "complexed" ether stretching groups tend to be changed in different directions for some compositions of the LiClO$_4$/MPEG−PCL blend system when the temperature is increased.

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