



Ion-Conductive and Thermal Properties of a Synergistic Poly(ethylene carbonate)/Poly(trimethylene carbonate) Blend Electrolyte

Zhenguang Li, Ronnie Mogensen, Jonas Mindemark, Tim Bowden, Daniel Brandell,* and Yoichi Tominaga*

Electrolytes comprising poly(ethylene carbonate) (PEC)/poly(trimethylene carbonate) (PTMC) with lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) are prepared by a simple solvent casting method. Although PEC and PTMC have similar chemical structures, they are immiscible and two glass transitions are present in the differential scanning calorimetry (DSC) measurements. Interestingly, these two polymers change to miscible blends with the addition of LiTFSI, and the ionic conductivity increases with increasing lithium salt concentration. The optimum composition of the blend electrolyte is achieved at PEC₆PTMC₄, with a conductivity as high as 10^{-6} S cm⁻¹ at 50 °C. This value is greater than that for single PEC- and PTMC-based electrolytes. Moreover, the thermal stability of the blend-based electrolytes is improved as compared to PEC-based electrolytes. It is clear that the interaction between C=O groups and Li⁺ gives rise to a compatible amorphous phase of PEC and PTMC.

PEO host.^[8–11] These PEO-based electrolytes have poor Li⁺ transference properties and ionic conductivities compared to liquid electrolytes, primarily because of the ion-transport mechanism in complex-formed polymer electrolytes.^[12–14] To overcome these problems, novel polymers such as poly(vinyl alcohol), poly(acrylonitrile), and poly(urea-sulfonyl imide) have been investigated as host polymers for electrolytes,^[15–18] but further improvement is still necessary.

Polycarbonates have recently been studied as a new class of host polymer which has very different ion-conductive properties from typical PEO-based electrolytes. In the case of poly(ethylene carbonate) (PEC), the conductivity and Li⁺ transference number (t_{Li^+}) increases with increasing lithium salt concentration.^[19]

Unfortunately, PEC-based electrolytes have low thermal stability and weak mechanical properties.^[20] In contrast, poly(trimethylene carbonate) (PTMC)-based electrolytes have good electrochemical properties and thermal stability.^[21,22] The conductivity and t_{Li^+} of PTMC-based electrolyte are nevertheless lower than for PEC-based electrolytes. Polymer blending is a feasible and cost-effective technique for developing SPEs having excellent properties. It may be possible to use blend systems to prepare SPEs, based on previous successes.^[23–25] The objective of the present study is to combine PTMC with PEC so as to prepare polycarbonate-based electrolytes having superior ion-conductive properties, thermal stability, and mechanical properties.

1. Introduction

Solid polymer electrolytes (SPEs) are of great interest for their possible deployment in next-generation secondary batteries.^[1–3] SPEs are more promising than liquid and gel electrolytes because of their light weight, nonflammability, customisability, and flexibility properties.^[4–6] Poly(ethylene oxide) (PEO)–metal salt complexes were first reported by Fenton et al. in 1973,^[7] and there has since been much SPE studies on polymer design, salt solubility, filler composites, and other properties using the

Z. Li, Prof. Y. Tominaga
Graduate School of Bio-Applications and Systems Engineering
Tokyo University of Agriculture and Technology
2-24-16, Naka-cho, Koganei, Tokyo 184-8588, Japan
E-mail: ytominaga@cc.tuat.ac.jp

R. Mogensen, Dr. J. Mindemark, Dr. T. Bowden, Prof. D. Brandell
Department of Chemistry – Ångström Laboratory
Uppsala University
SE-75121 Uppsala, Sweden
E-mail: daniel.brandell@kemi.uu.se

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/marc.201800146>.

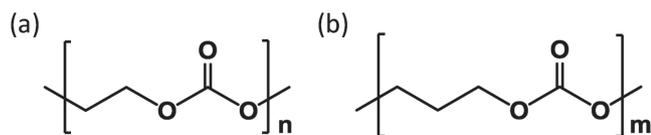
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2. Results and Discussion

2.1. Thermal Properties

As shown in **Scheme 1**, PEC and PTMC have similar chemical structure, and have the same carbonate unit (O–C(=O)–O) in the main chain. The differential scanning calorimetry (DSC) curves of the second heating runs for neat PEC and PTMC, and for PEC–PTMC blends, are shown in **Figure 1a**. On the DSC traces of the neat polymers, a single glass transitions is clearly observed for each polymer without any further transition above this temperature, which implies that PEC and PTMC are both amorphous polymers. The glass transition temperatures (T_g) for neat PEC and PTMC are around 10 and –15 °C, respectively, whereas the PEC and PTMC blends have two transitions which



Scheme 1. Chemical structures of a) PEC and b) PTMC.

appeared at values around $-18\text{ }^{\circ}\text{C}$ for PTMC and $20\text{ }^{\circ}\text{C}$ for PEC (Figure 1a). A small phase separation, based on the appearance of the blend sample (see photograph of $\text{PEC}_6\text{PTMC}_4$ in Figure S1a in the Supporting Information) has thus been confirmed. This tells us that neat PEC and PTMC are basically incompatible, even though they have very similar chemical structures.

Figure 1b shows DSC results at the second heating scan for PEC, PTMC, and $\text{PEC}_6\text{PTMC}_4$ with addition of LiTFSI. The values of T_g are also summarized in Table 1. The values

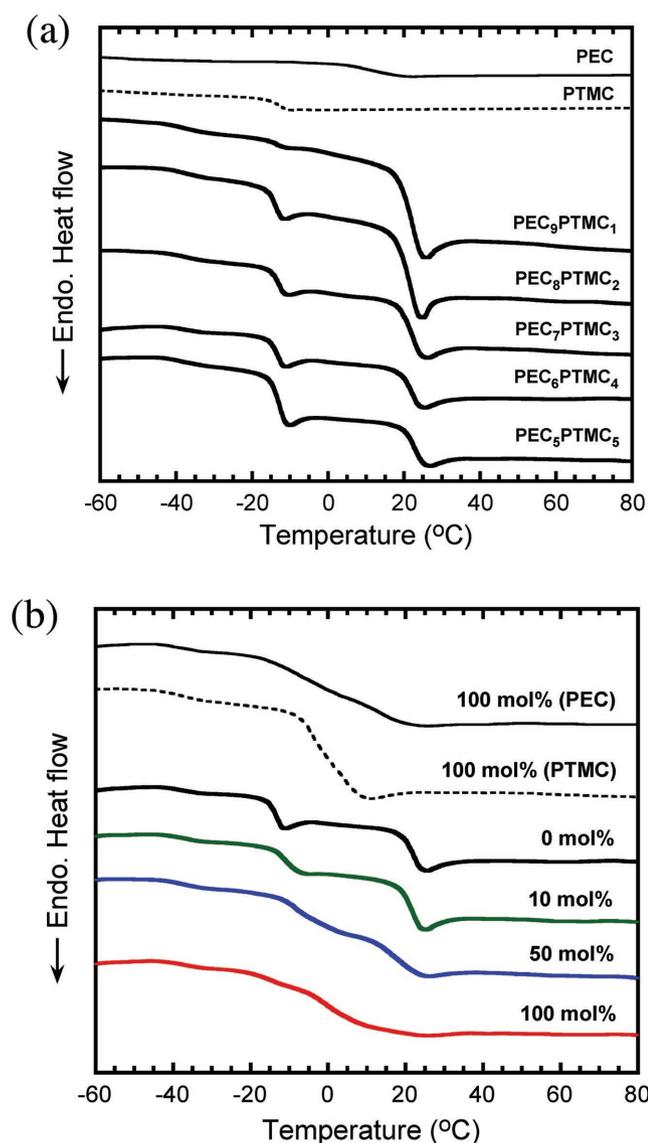


Figure 1. DSC traces of a) neat PEC, PTMC and single $\text{PEC}_x\text{PTMC}_y$ blends and b) their electrolytes (PEC-LiTFSI 100 mol%, PTMC-LiTFSI 100 mol%, and $\text{PEC}_6\text{PTMC}_4$ -LiTFSI n mol%).

Table 1. DSC and TGA results for PEC, PTMC, and $\text{PEC}_6\text{PTMC}_4$ electrolytes with LiTFSI.

| Sample | T_g [$^{\circ}\text{C}$] | | T_{d5} [$^{\circ}\text{C}$] |
|--|------------------------------|--------------|---------------------------------|
| | PEC derived | PTMC derived | |
| PEC-LiTFSI 100 mol% | -8 | - | 159 |
| PTMC-LiTFSI 100 mol% | - | -4 | 207 |
| $\text{PEC}_6\text{PTMC}_4$ -LiTFSI 0 mol% | -13 | 22 | - |
| $\text{PEC}_6\text{PTMC}_4$ -LiTFSI 10 mol% | -10 | 22 | 160 |
| $\text{PEC}_6\text{PTMC}_4$ -LiTFSI 50 mol% | -8 | 16 | 167 |
| $\text{PEC}_6\text{PTMC}_4$ -LiTFSI 100 mol% | -6 | | 169 |

of T_g for PEC and PTMC electrolytes with 100 mol% LiTFSI are lower than that of PEC neat polymer, but higher for PTMC. As seen in the blend without LiTFSI (0 mol%), the glass transitions deriving from PEC and PTMC are clearly visible separately. Interestingly, addition of LiTFSI to the blend gives rise to changes in the glass transition temperature. These PEC- and PTMC-derived glass transitions become weaker relative to the corresponding single polymer systems. Moreover, T_g for PTMC converge to the T_g of PEC with further addition of LiTFSI. As 100 mol% LiTFSI was added into the $\text{PEC}_6\text{PTMC}_4$ mixture, the two glass transitions from PTMC and PEC disappeared and merged into a single curve. This has also been observed from other blend compositions (see Figure S2 in the Supporting Information). These changes suggest that the addition of LiTFSI causes PEC and PTMC to be compatible, and the dissolved ions act as physical cross-linkers between the two carbonate polymers.

Furthermore, the thermal stability of these electrolytes was determined by thermogravimetry, and the results are shown in Figure 2. The values of 5 wt% weight-loss temperatures are also summarized in Table 1. The onset temperatures for degradation of PEC-LiTFSI 100 mol% and PTMC-LiTFSI 100 mol% are ≈ 150 and $200\text{ }^{\circ}\text{C}$, respectively. The first- and second-stage degradation reactions occurring at around $150\text{--}300$ and $300\text{--}400\text{ }^{\circ}\text{C}$ are due

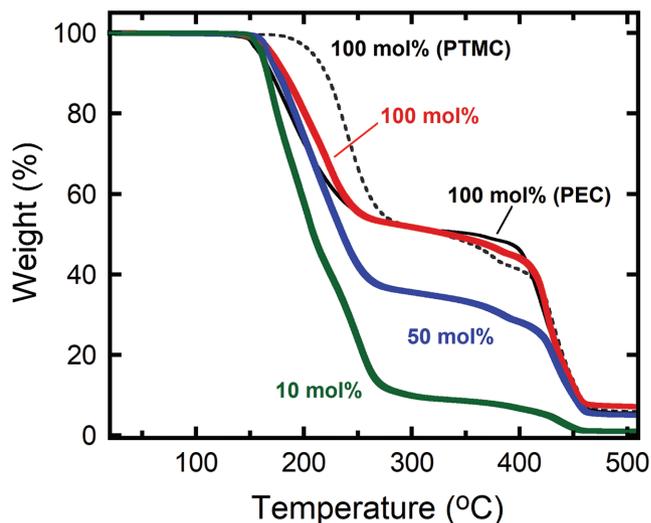


Figure 2. TGA curves of PEC-LiTFSI 100 mol%, PTMC-LiTFSI 100 mol%, and $\text{PEC}_6\text{PTMC}_4$ -LiTFSI electrolytes with different salt concentrations.

to thermal degradation of the polymer and of LiTFSI, and these values are consistent with previous studies.^[20,21] Based on the thermogravimetric analysis (TGA) curves, it was observed that the value of T_{d5} for PEC₆PTMC₄-LiTFSI electrolytes increased slightly with increasing salt concentration. This may be due to the increase in compatibility of PEC and PTMC with the addition of LiTFSI, which improves the interaction between the two polymers. Moreover, the addition of PTMC improves the T_{d5} value of blend electrolytes relative to that of the PEC-based electrolytes (see Figure S3 and Table S1 in the Supporting Information).

2.2. Ion-Conductive Properties

The ionic conductivity was measured for all PEC/PTMC electrolytes with LiTFSI 100 mol% (see also Figure S4 in the Supporting Information). All electrolytes measured showed reasonable variations of conductivity that were smooth and essentially nonlinear curves with respect to $1/T$. This behavior can be seen in the typical amorphous polymer electrolyte system. **Figure 3a** shows the dependence on PEC content of the conductivity for PEC_xPTMC_y-LiTFSI 100 mol% electrolytes at 50 °C. The conductivity increases with increasing PEC content until the value reaches a maximum and then decreases, matching a previous study.^[26] The PEC₆PTMC₄-LiTFSI 100 mol% electrolyte displayed the highest conductivity of all blend electrolytes, as high as 10^{-6} S cm⁻¹. For this sample the ionic conductivity is higher than for other blend electrolytes at all temperatures (see also Figure S4 in the Supporting Information). Furthermore, these blend electrolytes have slightly higher conductivities than those of single PEC- and PTMC-based electrolytes. This is probably due to the good combination of the two polymers and LiTFSI.^[26,27] The temperature dependence of the conductivity for the PEC₆PTMC₄-LiTFSI electrolytes with different salt concentration is shown in Figure 2b. The conductivity of the PEC₆PTMC₄-LiTFSI electrolytes increases with increasing LiTFSI concentration. When the concentration increases at 100 mol%, the conductivity reaches $\approx 10^{-4}$ S cm⁻¹ at 80 °C, which is more than one order of magnitude greater than the 10 mol% electrolyte. The PEC/PTMC blends become compatible and the existence of interactions between host matrix and Li⁺ upon adding LiTFSI can explain the increase in conductivity. This matches the fact that the conductivity was improved by the addition of Li salts into the PEO/PTMC blend system.^[28] A further reason is that PEC can dissolve a large amount of Li salts and cause the conductivity to increase with increasing salt concentration.^[19,27,29]

2.3. FT-IR Analysis

The formation of complexes between blend polymers (PEC/PTMC) and LiTFSI can be studied by fourier transform infrared (FT-IR) spectroscopic measurement. For the polycarbonate-based electrolytes, interaction is clearly observed between C=O groups and Li⁺, useful information for the ion-conductive behavior. **Figure 4** shows the FT-IR spectra of the C=O stretching vibration region for the pure polymer blend (PEC₆PTMC₄) and the electrolytes containing various concentrations

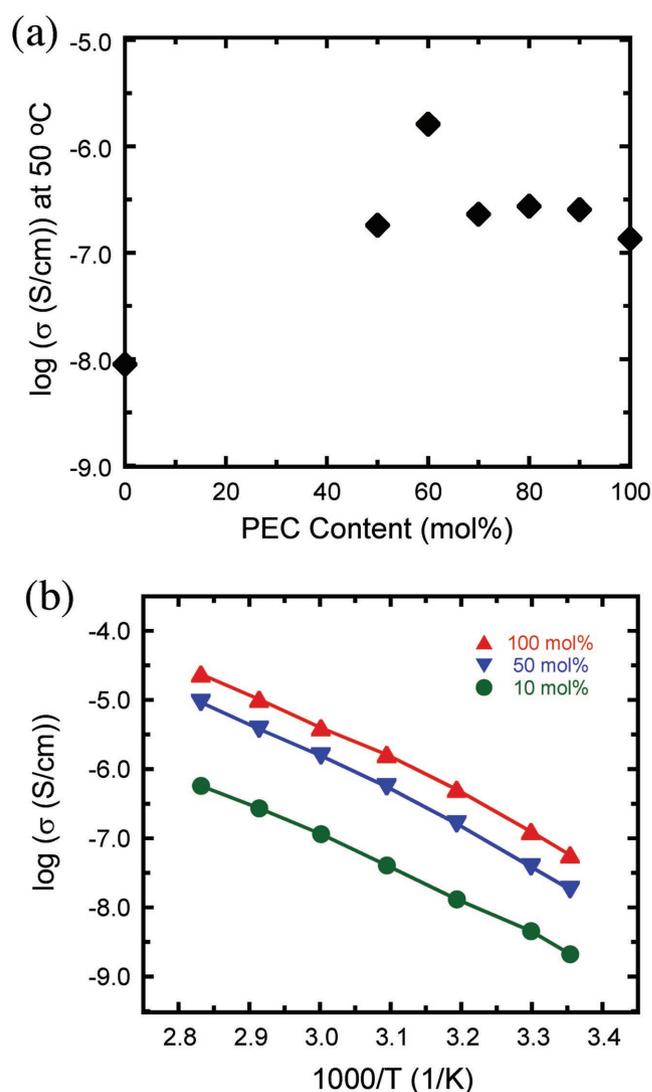


Figure 3. a) PEC content dependence of the ionic conductivity for PEC_xPTMC_y-LiTFSI 100 mol% at 50 °C, and b) temperature dependence of the ionic conductivity for PEC-LiTFSI 100 mol%, PTMC-LiTFSI 100 mol%, and PEC₆PTMC₄-LiTFSI electrolytes with differing salt concentrations.

of LiTFSI. It is known that the band of free C=O groups appears at around 1740 cm⁻¹, and the band corresponding to C=O groups interacting with Li ions (C=O...Li⁺) shifts to lower wavenumbers around 1720 cm⁻¹.^[20,30,31] The pure PEC/PTMC blend (0 mol%) clearly showed a strong free C=O band at around 1735 cm⁻¹, and the band shifted slightly to lower wavenumber with the addition of LiTFSI. For the blend with higher concentration (50 and 100 mol%) of LiTFSI, a new band appeared around 1716–1722 cm⁻¹. This new band may be due to interaction between C=O groups and Li⁺ in both PEC and PTMC phases. In fact, the interaction bands for both PEC- and PTMC-LiTFSI 100 mol% were observed at 1723 and 1717 cm⁻¹, respectively. If there is only one interaction between C=O of PEC and Li⁺, the band should appear only at 1723 cm⁻¹. The band between 1716–1722 cm⁻¹ of the interacting C=O in the blend electrolytes suggests that a compatible amorphous phase of PEC and PTMC was induced by dissolved ions such as Li⁺.

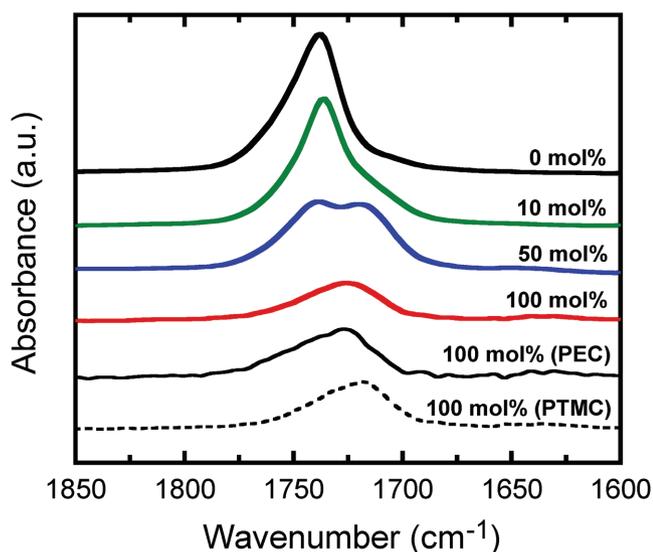


Figure 4. FT-IR spectra of polymer electrolytes (PEC-LiTFSI 100 mol%, PTMC-LiTFSI 100 mol%, and PEC₆PTMC₄-LiTFSI *n* mol%) in the stretching vibration region of the free and interacting C=O groups.

3. Conclusion

In this study, a simple blend electrolyte consisting of amorphous PEC and PTMC with LiTFSI was successfully prepared for the first time. PEC and PTMC are immiscible with each other even though they have similar chemical structures. DSC measurements were carried out in order to observe the compatibility of PEC/PTMC blends without Li salt, and it was confirmed that there are two T_g values for all blend compositions. An interesting result is that the immiscible blends of PEC and PTMC changed to a miscible system upon adding LiTFSI. According to the DSC results for the blend electrolytes, the glass transition became weaker, and merged with further addition of LiTFSI. In case of PEC₆PTMC₄ with 100 mol% of LiTFSI, the glass transitions merged into a single curve. Similarly, the ionic conductivity of PEC₆PTMC₄-LiTFSI electrolytes increased with increasing LiTFSI concentration, to a value as high as 10^{-6} S cm⁻¹ at 50 °C. Simultaneously, the value of T_{d5} for PEC₆PTMC₄-LiTFSI electrolyte increased slightly with increasing LiTFSI. It is clear that the interaction between C=O groups and Li⁺ gives rise to a compatible amorphous phase of PEC and PTMC.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

lithium batteries, poly(ethylene carbonate), poly(trimethylene carbonate), polymer blends, solid polymer electrolytes

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