

Highly Conductive Polymer Electrolytes Containing Rigid Polymers

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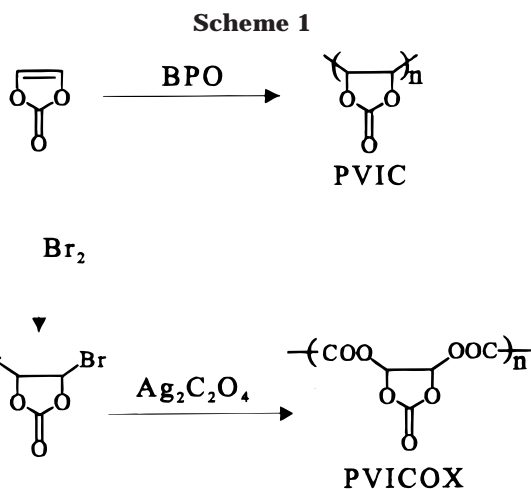
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Introduction. Polymer electrolytes are the newest area of solid-state ionic conductors to receive wide attention. They are of interest from the fundamental standpoint of ion transport mechanism and their applications in electrochemical devices such as batteries and electrochromic windows.¹ Generally, polymer electrolytes are mixtures of salts with soft polar polymers such as poly(ethylene oxide) (PEO) and poly(bis(methoxyethoxyethoxy)phosphazene) (MEEP). Since their discovery in the 1970s,^{2,3} the polymer electrolytes have been intensively studied.^{1,4–10} It is generally agreed that ion transport above T_g in polymer electrolytes is strongly coupled to the polymer segmental motion.^{1,5–8} To increase the segmental motion and thereby conductivity of polymer electrolytes, a variety of polymers with low T_g values have been developed.^{1,4–6,9,10} At present, the highest room-temperature conductivity for this type of polymer electrolyte is around 10^{-5} S cm⁻¹. Furthermore, many avenues to low T_g materials have been explored, so the prospects are not encouraging for the development of polymers with a T_g low enough to obtain a room-temperature conductivity of 10^{-3} S cm⁻¹, an often cited goal for practical application in high energy density batteries.¹¹ Moreover, low T_g results in poor mechanical properties, which complicates the design of batteries and fuel cells. New materials with unconventional conduction mechanism are clearly needed.

Conventional polymer electrolytes, at low temperatures, are thought to conduct ions by thermally activated ion hopping.^{7,8,12} Recently, a room-temperature conductivity of $10^{-5.5}$ S cm⁻¹ was obtained from a very rigid polymer/salt system in which the polymer has a T_g of 315 °C.¹³ These developments encouraged us to search for new rigid polymers that can provide pathways for ion hopping. This line of reasoning led us to



investigate two rigid polymer systems, poly(vinylene carbonate) (PVIC) and poly((1,3-dioxolan-2-one-4,5-diyl oxalate) (PVICOX), which display both favorable conductivity and mechanical properties. These systems were selected because they can be easily synthesized (Scheme 1) and because they contain a high density of coordinating sites, which is necessary to dissolve salts. In addition, the high density of the polar groups should reduce the activation energy for ion hopping from one polar site to the next. Of these two polymers, PVICOX is more irregular, and we hypothesize that this property will frustrate close packing and thereby increase static free volume and conductivity.

Experimental Section. Measurements. Powdered samples were pressed into pellets at a pressure of 2.7×10^8 Pa. The density of the PVIC pellet is 1.38 g/cm³ and the PVICOX pellet density is 1.15 g/cm³. Impedance spectroscopy was performed with a HP 4192A impedance analyzer or a Solartron 1250 analyzer. The conductivity cell was airtight and loaded under dry nitrogen. Temperature control was achieved with a Sun Systems environmental chamber. DSC data were collected on a Perkin-Elmer Pyris 1 DSC.

Materials. Poly(vinylene carbonate) was synthesized by bulk polymerization under nitrogen in a sealed tube employing 0.3% benzoyl peroxide.¹⁴ Dibromoethylene carbonate was synthesized according to a literature method.¹⁵ PVICOX was synthesized by reaction of $\text{Ag}_2\text{C}_2\text{O}_4$ and dibromoethylene carbonate in DMF/H₂O at room temperature.

Preparation of Polymer Electrolytes. Weighed amounts of polymer and lithium triflate were dissolved in solvents (DMF for PVIC system, H₂O for PVICOX system), and the solvent was removed under vacuum. The polymer electrolytes were further dried under high vacuum (ca. 10^{-5} Torr) for at least 4 days (at 70 °C for PVIC-based polymer electrolytes and at 60 °C for PVICOX-based polymer electrolytes).

Results and Discussion. The new polymer electrolytes are identified here by the abbreviation of the

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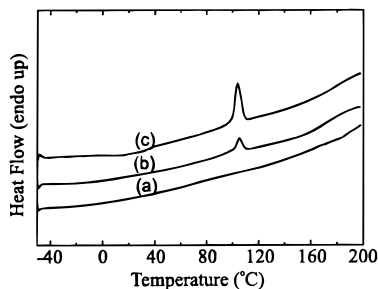


Figure 1. DSC curves of (a) PVIC, (b) PVIC2, (c) PVIC1.

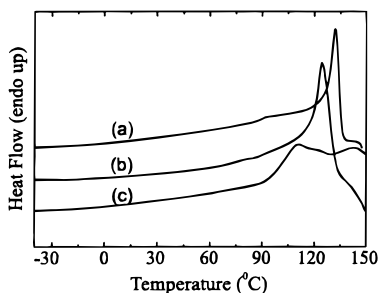


Figure 2. DSC curves of (a) PVICOX, (b) PVICOX5, (c) PVICOX1/2.

polymer followed by a number, which represents the mole ratio of the repeating unit of the polymer to lithium triflate, LiCF_3SO_3 . For example, PVIC10 represents a polymer electrolyte which contains poly(vinylene carbonate) and lithium triflate, with a molar ratio of 10 repeating units of poly(vinylene carbonate) to one of lithium triflate.

Thermal Properties. DSC data of these two new systems are presented in Figures 1 and 2. For PVIC, PVIC10, and PVIC5, no T_g (glass transition temperature) or T_m (melting temperature) was detected up to 200 °C, while PVIC2 and PVIC1 exhibit a T_m around 100 °C. These phenomena also occur with other rigid polymer systems. For example, the poly(parabanic acid)– LiBF_4 system exhibits no T_m for the pure polymer over a range from room temperature to 400 °C, but addition of a large amount of salt results in a T_m of 220 °C.¹³ These seemingly puzzling observations may result from high-temperature-induced crystallization or may represent the formation of a eutectic mixture. For the PVICOX system, the pure polymer exhibits a T_m of 132 °C. X-ray diffraction indicates crystallinity for both the pure polymer and the polymer salt complexes. Addition of lithium triflate shifts the T_m to lower temperatures. This behavior is similar to that of poly(vinyl alcohol)–lithium salts systems in which T_m decreases with increasing salt concentration.¹³ For conventional polymer electrolytes, the addition of salt generally stiffens the polymers with an increase in T_g and/or T_m ,^{1,16,17} but for the new polymer electrolytes, addition of salt softens the polymers and lowers both T_m and T_g .¹³

Conductivity. Conductivity data are presented in Figures 3 and 4, and these are comparable to or higher than most conventional polymer electrolytes. The highest conductivity observed at room temperature is 10^{-4} S cm^{-1} . The salt concentration which provides optimum conductivity is much higher than that in conventional

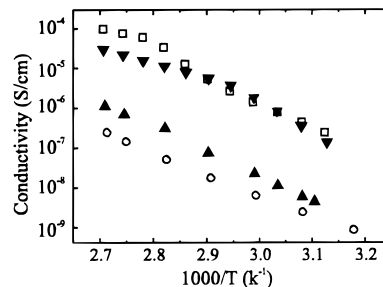


Figure 3. Temperature dependence of the conductivity for the PVIC– LiCF_3SO_3 composite: PVIC10 (▲), PVIC5 (○), PVIC2 (▼), PVIC1 (□).

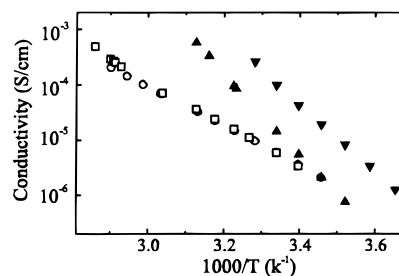


Figure 4. Temperature dependence of the conductivity for the PVICOX– LiCF_3SO_3 composite: PVICOX5 (□), PVICOX2 (▲), PVICOX1 (▼), PVICOX1/2 (○).

polymer electrolytes. For the PVICOX-based electrolytes, the maximum conductivity occurs at 1:1 molar ratio (repeating unit of polymer to lithium triflate). In conventional polymer electrolytes, the conductivity reaches a maximum conductivity at a much lower salt concentration (typically around 4:1 molar ratio).^{1,5,18,19}

The conductivities of PVIC2 and PVIC1 are much higher than those of PVIC10 and PVIC5, suggesting a structural change. Indeed, DSC data show that PVIC2 and PVIC1 display a T_m of around 100 °C, while PVIC10 and PVIC5 exhibit no T_m or T_g up to 200 °C. The conductivities of PVICOX system are about 2–4 orders of magnitude higher than those of PVIC system. We believe this is due to the larger free volume of PVICOX system. In fact, the PVICOX pellet density is about 20% lower than PVIC, indicating that PVICOX has larger free volume.

One interesting feature of these new polymer electrolytes is that crystalline phases do not appear to suppress ion transport. In conventional polymer electrolytes, ion transport in crystalline phases is generally lower than that in amorphous phases,^{1,20} because reduced segmental motion in the crystalline phases generally decreases conductivity and ion transport is generally facilitated by the segmental motion. We conclude that ion transport is decoupled from the segmental motion in these new rigid polymer electrolytes.

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