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## Communications

### Hybrid Organic–Inorganic Polymer: A New Approach for the Development of Decoupled Polymer Electrolytes

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Two general types of polymer electrolyte have been investigated: polymer–salt complexes and polyelectrolytes. A typical polymer–salt complex consists of a coordinating polymer in which a salt is dissolved, and both anions and cations can be mobile. In contrast, polyelectrolytes contain charged groups, either cations or anions, covalently attached to the polymer with only counterions being mobile. Moreover, it is well-known that ionic transport above  $T_g$  (glass transition temperature) in typical polymer electrolytes is strongly coupled to segmental motions of the polymer chain, resulting in a VTF ionic conduction behavior (after Vogel, Tamman, and Fulcher).<sup>1</sup> However, different classes of polymer electrolytes have recently been reported in which the ionic conductivity is not coupled to the segmental motion of the polymer chain<sup>2–4</sup> (i.e., a material in which the ions

move independently of viscous flow).<sup>1</sup> The approach used in the development of segmental motion-decoupled polymer is the synthesis of hard polymers (e.g., liquid crystalline materials<sup>2</sup> and polyester structures).<sup>3,4</sup> The development of a segmental motion-decoupled polymer system is an alternative way to increase ionic conductivity in polymer electrolytes.<sup>1</sup>

In a previous paper, we described the synthesis, thermal properties, and ionic conductivity of hybrid organic–inorganic polymer electrolytes with interesting mechanical properties.<sup>5</sup> The polymer electrolyte discussed in that paper was based on the formation of a Si and citric acid (CA) complex subsequently polymerized by means of a polyesterification reaction with ethylene glycol (EG). However, an excessive amount of EG and CA was used, resulting in a material composed of two different amorphous phases. The resulting solid material became ionically conductive when  $\text{Li}_2\text{CO}_3$  was dissolved in the structure during its synthesis. Due to the acidic conditions of the synthesis, the dissociation of  $\text{Li}_2\text{CO}_3$  occurred (according to the reaction:  $\text{Li}_2\text{CO}_3 + 2\text{H}_3\text{O}^+ \rightarrow 2\text{Li}^+ + \text{CO}_2(\text{g})\uparrow + 3\text{H}_2\text{O}$ ), resulting in  $\text{Li}^+$ . In fact,  $\text{Li}^+$  ion (acting as Lewis acid) was expected to be mobile, and the counterion is composed of carboxyl groups (acting as Lewis base) that are present in the polymer chain, leading to a polyelectrolytic material, according to the definition of a polyelectrolyte described in the previous paragraph. Even that two-phase material presented an Arrhenius-type behavior above  $T_g$ , suggesting a segmental motion-decoupled polymer system. This result motivated us to synthesize a single-phase hybrid organic–inorganic polymer that can result in a new segmental motion-decoupled material with superior ionic conductivity.

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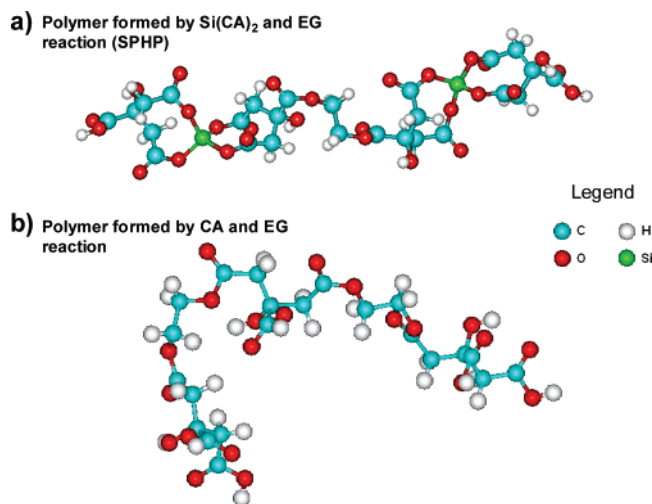
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Scheme 1



According to our study,<sup>6</sup> tetraethyl orthosilicate (TEOS—Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and CA (HO<sub>2</sub>CCH<sub>2</sub>C(OH)(CO<sub>2</sub>H)CH<sub>2</sub>CO<sub>2</sub>H) are expected to become complexed in ethanol, according to the following equation:



The Si complexation process involves the terminal carboxyl group of CA. From <sup>13</sup>C NMR results,<sup>6</sup> it was verified that the central carboxyl group is not used during the formation of Si—CA complex. Thus, this carboxyl group can be used in a subsequent reaction with EG, resulting in a polymer network produced through a polyesterification reaction. Scheme 1 shows the structures of the polymer originating from the reaction between Si—CA complex and EG (Scheme 1a) and CA and EG (Scheme 1b). These structures were determined by a quantum mechanical calculation using an ab initio method<sup>7</sup> and by NMR spectroscopy.<sup>6</sup> On the basis of the structure and stoichiometry of the Si—CA complex, the material was synthesized in order to obtain single-phase Si—CA complex.

Single-phase hybrid organic—inorganic polymer electrolyte was synthesized by a derivative in situ polymerizable method (a nonhydrolytic sol—gel process) that we described in detail elsewhere.<sup>5,6</sup> In this synthesis, a CA/Si (molar) ratio of 2:1 and a Si—CA complex/EG mass ratio of 77:23 were used. For the Si—CA complex synthesis, TEOS was used as the Si source. The Si—CA complex and polymerization reaction were performed in an ethanol solution at 40 °C under constant magnetic stirring. A hybrid polymer with an excess of CA and EG (Si:CA = 3:1 and CA:EG = 60:40) was also synthesized, using an experimental procedure described previously.<sup>5</sup> In the preparation of the polymer electrolyte,

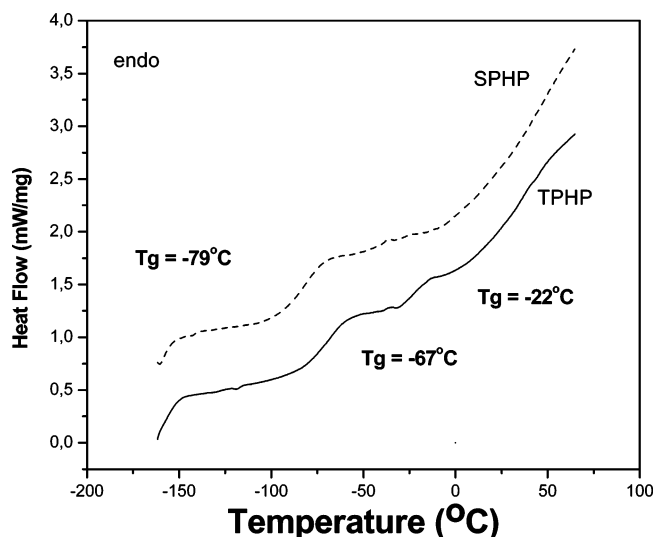


Figure 1. DSC curves of SPHP and TPHP.

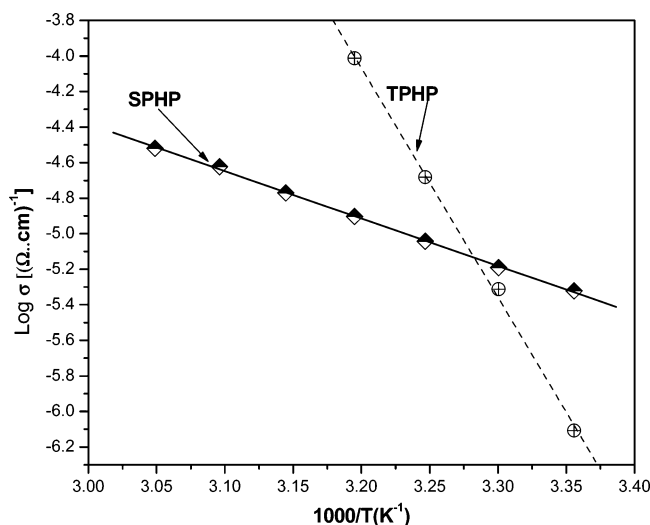
Li<sub>2</sub>CO<sub>3</sub> (10% in mol) was added during the synthesis. A transparent solid polymer was obtained after the solvent was eliminated (under vacuum at 50 °C). The resulting polymer electrolyte was dried at 40 °C for several hours and stored under vacuum for further characterization. The single-phase hybrid polymer named SPHP and the polymer containing excess CA and EG, called TPHP, were then obtained. The thermal properties of these two synthesized polymers were measured by differential scanning calorimetry (DSC) (DSC Netzsch 204 Phoenix) under a dry N<sub>2</sub> flow and at a heating rate of 10 °C/min. The ionic conductivity was measured by the impedance spectroscopy technique (HP 4194A) in a temperature range of 25–60 °C and a frequency range of 100 Hz to 15 MHz. Platinum foils were used as electrodes in these measurements.

Figure 1 shows the DSC curves of the synthesized polymers. Note that the SPHP shows one *T<sub>g</sub>* at −79 °C, confirming the synthesis of a single-phase amorphous polymer. On the other hand, the TPHP polymer presents two *T<sub>g</sub>*, supporting the presence of two amorphous phases. The first *T<sub>g</sub>* (at −67 °C) can be attributed to the hybrid polymer, and the second *T<sub>g</sub>* (at −37 °C) should be related to a polyester formed in response to the reaction of CA and EG, resulting in an organic polymer. It is important to point out the absence of crystallization or melting transition, strongly evidencing that both polymers are amorphous at a temperature ranging from −150 to 60 °C. Room temperature X-ray diffraction analysis indicated the absence of crystallinity in both samples, confirming the DSC analysis.

Ionic conductivity characterization at room temperature showed that the SPHP and TPHP presented a conductivity of  $11.4 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$  and  $7.6 \times 10^{-6} (\Omega \cdot \text{cm})^{-1}$ , respectively. As can be observed, the presence of the second amorphous phase modified the ionic conductivity of the TPHP material, resulting in a material with a lower Li<sup>+</sup> conductivity than that of the SPHP system. The single-phase material (STHP) showed ionic conductivity higher than that usually reported for organic or hybrid polyelectrolytes.<sup>8</sup> These interesting results were in agreement with our expectations. However, the most remarkable result was the Arrhenius behavior displayed by the temperature dependence

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**Figure 2.** Temperature dependence of the conductivity for the SPHP and TPHP.

of the ionic conductivity in the range of temperatures above  $T_g$ . Both polymers showed an Arrhenius behavior, as indicated in Figure 2. Activation energies of 0.21 and 0.61 eV were obtained for the SPHP and TPHP, respectively. It is important to emphasize that the Arrhenius behavior obtained are typical of a segmental motion-decoupled polymer. The low activation energy observed in the STHP material suggests a fast ion transport mechanism and is considerably smaller than that of conventional polymer electrolytes or segmental motion-decoupled polymers. For instance, Imrie et al. reported an activation energy of 0.36 eV for a decoupled liquid crystalline polyelectrolyte.<sup>2</sup>

This remarkable property is far from being fully understood. However, we venture an explanation for it based on the ability of Si atoms to rigidify the polymer chain, which inhibits the formation of the helical conformation, decreasing the coordination of the  $\text{Li}^+$  ion by the carboxyl groups. As

a consequence, an open Si–polyester structure is obtained in which lithium ions are free to move. This explanation is supported by the conformational structure obtained through our theoretical calculation and illustrated in Scheme 1. Therefore, clearly there is considerable scope for more in-depth studies of the ion transport mechanism in this new hybrid polyelectrolytic structure. Undoubtedly, there are many opportunities for new synthetic developments, which could be capable of optimizing ion transport and, when combined, improve the mechanical stability of electrolytes. For instance, it may be possible to synthesize rigid polymer helical free channel sizes and compositions that are more suitable for ion transportation. Furthermore, it is conceivable that this new hybrid organic–inorganic polyelectrolyte will present interesting conduction mechanisms under different conditions of synthesis and salt concentration, an aspect we intend to investigate in future studies.

In summary, we have demonstrated the synthesis, by a sol–gel nonhydrolytic process, of a single-phase hybrid organic–inorganic polyelectrolyte with good Li ion conductivity at room temperature. The STHP material showed an Arrhenius behavior of the ionic conductivity as a function of temperature (in the range of temperatures above  $T_g$ ). The activation energy of the ionic conduction mechanisms was found to be 0.23 eV. These characteristics indicate a fast ion transport mechanism in a segmental motion-decoupled hybrid organic–inorganic polymer. To the best of our knowledge, this is the first time that a segmental motion-decoupled behavior is reported for a hybrid polyelectrolyte. We believe that, by careful engineering of the types of inorganic segment of the hybrid polymer chain, it should be possible to tailor the conductivity mechanism and, hence, to obtain polymer electrolytes with superior performance.

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