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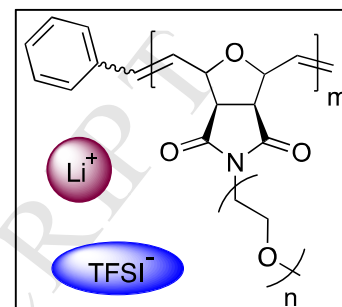
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ABSTRACT

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In order to design more effective solid polymer electrolytes, it is important to decouple ion conductivity from polymer segmental motion. To that end, novel polymers based on oxanorbornene dicarboximide monomers with varying lengths of oligomeric ethylene oxide side chains have been synthesized using ring opening metathesis polymerization. These unique polymers have a fairly rigid and bulky backbone and were used to investigate the decoupling of ion motion from polymer segmental dynamics. Ion conductivity was measured using broadband dielectric spectroscopy for varying levels of added lithium salt. The conductivity data demonstrate six to seven orders of separation in timescale of ion conductivity from polymer segmental motion for polymers with shorter ethylene oxide side chains. However, commensurate changes in the glass transition temperatures T_g reduce the effect of decoupling in ion conductivity and lead to lower conductivity at ambient conditions. These results suggest that both, an increase in decoupling and a reduction in T_g might be required for developing solid polymer electrolytes with high ion conductivity at room temperature.

Improving safety and performance parameters of batteries, fuel cells, and super capacitors continues to be an important focus of current research [1, 2]. In lithium based batteries, metal dendrites can form on electrodes, pushing through the electrolyte and causing shorts, failures and fires [1, 3]. Replacement of traditional liquid electrolytes by solid electrolytes with sufficient mechanical modulus can prevent dendrite growth and improve significantly batteries safety [4-6]. One of the possible solutions could be the use of solid polymer electrolytes [1, 3]. However, active research during the last few decades has yet to result in the development of polymer electrolytes with sufficient ionic conductivity and high mechanical modulus [7]. Despite these efforts, small molecule organic electrolytes such as ethylene carbonate and other carbonates still dominate commercial products due to their high ion conductivity. Low ion conductivity in dry polymer electrolytes at ambient conditions remains a major obstacle for use in batteries and several other applications [7].

Poly(ethylene oxide) (PEO) has long been the main material proposed as a polymer electrolyte, and serves as a benchmark for analysis of any other polymer electrolyte [8, 9]. Continued interest in PEO is also due to its unusually

high Li-salt solubility (50 wt % of salt can be easily dissolved), and the ion conductivity reaches the required 10^{-3} S/cm around 80 °C. However, PEO has low conductivity at room temperature, and suffers from crystallization that also severely reduces ion conductivity at ambient temperature. In addition, the transference number for Li ions in PEO is very low, ~0.2 to 0.3 [10], which likewise decreases electrolyte efficiency. In classical theories, the conductivity of ions in polymer electrolytes is primarily tied to the timescale of structural rearrangement, i.e. segmental relaxation of the polymer [11]. Attempts to improve the ionic conductivity have often focused on reducing the glass transition temperature, T_g , to increase the rate of segmental relaxation at ambient temperature. This approach leads to polymers with a low mechanical modulus, and still insufficient conductivity [12]. There have also been strategies to move the ethylene oxide units to the side chain of a low glass transition polymer [13-17]. This process can frustrate PEO crystallization, but the ion conductivity in these materials still remains low.

Recently a different approach in the development of potential polymer electrolytes has been emphasized [18-23]. This approach builds on the decoupling of ion conductivity

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