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Correlations between Ion Conductivity and Polymer Dynamics in Hyperbranched Poly(ethylene oxide) Electrolytes for Lithium-Ion Batteries

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Supporting Information

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Lithium-ion rechargeable batteries are widely used in portable electronics and are quickly becoming critical power sources for current and future electric vehicles, primarily due to their high energy density, light weight, and high operational voltage.[1] Current lithium-ion batteries utilize liquid, organic electrolytes that come with several shortcomings that limit their widespread usage in large load applications, such as electric vehicles and stationary power. These liabilities are safety related and include electrolyte leakage, decomposition, flammability, and a propensity to develop catastrophic short circuits.[2,3] To circumvent these problems, polymer electrolytes have been extensively studied as an alternative. Poly(ethylene oxide) (PEO) is the most prominent example of a solid polymer electrolyte due to its ability to solvate and transport lithium-ions. However, PEO is semicrystalline with a high degree of crystallization and the Li-ion transport is limited primarily to the minor domains of the mobile amorphous phase. The result is that unmodified PEO has a low Li-ion conductivity (1×10^{-6} S/cm) below its melting temperature ($T_m \approx 65$ °C).[4,5] This is far below the target of 1×10^{-3} S/cm that is required for current battery applications.[3,6]

There are several strategies to suppress crystallization of PEO and improve conductivity. One approach has been to decrease the crystalline fraction through the incorporation of propylene oxide (PO) units into the PEO backbone.[5] While this prevents crystallization, the Li-ion conductivity of these polymers is not substantially improved. It is thought that the nonpolar methyl groups also reduce the solubility of Li-ions in the polyelectrolyte and thus the mobile charge carriers.[3] An analogous approach has been to graft oligo(ethylene oxide) units to other flexible polymers, resulting in comb-branched type architectures that will solvate Li-ions.[3,7] There have also been attempts to swell polyether polymers with small polar molecules, such as propylene carbonate and ethylene carbonate. While effective at improving conductivity, these gel-type systems still exhibit safety issues related to the leakage of liquid additives.[5,8] Cross-linked and branched polymers have also been explored as polymer electrolytes,[9−11] but their Li-ion conductivities remain well below the threshold of 1×10^{-3} S/cm. Hyperbranched polyglycerol was reported to show a Li-ion conductivity of 6.6×10^{-6} S/cm.[11]

It is well-known that hyperbranched polymers are highly effective at frustrating crystallizion. Recently, the first approach for the synthesis of unique hyperbranched poly(ethylene oxide) polymers (*hb*PEO) through a simple, one-step multibranching copolymerization (by ring-opening) of ethylene oxide (EO) and glycidol (G) monomers has been reported.[12] These random copolymers have a hyperbranched structure consisting of linear poly(ethylene oxide) segments interrupted by glycerol branching points (Scheme 1). The resulting materials are highly viscous liquids that have almost no vapor pressure. In comparison to small molecule additive, this reduces the concerns over leakage and flammability.

Here, we present the first study of the Li-ion conductivity and its correlation with polymer segmental dynamics for these hyperbranched PEO (*hb*PEO) with varying branch content. In addition to the hydroxyl-terminated copolymers, a permethylated sample has also been prepared (see the Supporting Information) in order to evaluate the effect of reducing the hydrogen-bonded networks on the Li-ion conductivity. The Li-salt used here is $LiN(CF_3SO_2)_2$ or LiTFSI. Measurements of the conductivity as function of temperature were performed using dielectric spectroscopy for both the neat *hb*PEO and samples loaded with the Li salts (see the Supporting Information). These results are compared with linear PEO of a comparable molar mass. To better understand the variations of Li-ion conductivity with the glycerol contents and permethylation of the hydroxyl termini, the polymer segmental dynamics were quantified by inelastic neutron scattering (INS) measurements. The Li-ion conductivities were then correlated with the fast segmental dynamics through mean-square atomic displacements of the hydrogen-containing groups from INS experiments.

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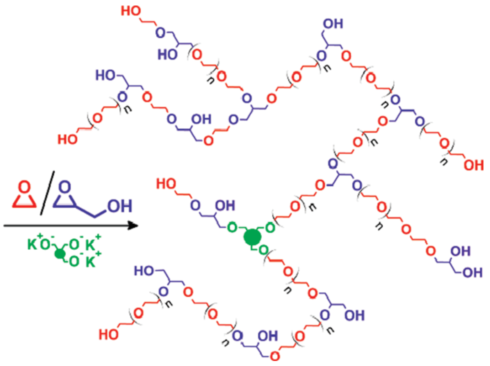
Scheme 1. Schematic Drawing of Hyperbranched PEO Random Copolymers (*hb*PEO) with Glycerol Branching Units[a]



[a] The average linear segment length n depends on the comonomer ratio (EO:G). The hydroxyl groups have also been permethylated for *hb*PEO-G16-OCD$_3$.

Table 1. Characterization Data of the Hyperbranched Poly(ethylene oxide)s (*hb*PEOs)

sample	glycidol fraction	M_n[a] (kg/mol)	M_w/M_n[a]	T_g/T_m[c] (°C)	X_c (%)[d] neat	X_c (%)[d] O:Li[e]
linear	0	50	1.19	−66.6/65.2	85	32
G8	0.08	41.1	1.42	−68.2/1.0	18	0
G16	0.16	60.6	1.22	−61.4/−0.3		
G16-OCD$_3$	0.16	55.7[b]	1.17	−69.4/5.0		
G50	0.50	49.2	1.50	−60.9/−		

[a] Determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) versus the PEO standards. [b] The apparent decrease in M_n is due to changed interactions between polymer and column material upon end group modification. [c] Determined by differential scanning calorimetry (DSC) at 10 °C/min (2nd heating run). [d] Degree of PEO crystallinity calculated from heat of fusion by $X_c = \Delta H/\Delta H^0$, ΔH^0 the equilibrium heat of fusion of PEO. [e] Results for the samples blended with LiTFSI salt at O:Li molar ratio of 25:1.

Varying the glycidol comonomer content permits control of the degree of branching, which decreases the degree of crystallinity without introducing nonpolar moieties. This is important for maintaining Li-ion solubility. Here we investigate hyperbranched PEO copolymers with 8, 16, and 50% glycerol, denoted as *hb*PEO-G8, *hb*PEO-G16, and *hb*PEO-G50, respectively. The total molar masses are in the range of 40 000−60 000 g/mol, and calorimetry confirms that when the glycidol content exceeds 8 mol %, crystallization is effectively suppressed (Table 1). The amorphous material still retains the same low glass transition temperature ($T_g \approx -66$ °C) of the linear PEO, and exhibits the characteristics of thick liquids to soft gel-like materials at room temperature, depending upon the branch content and consequently the number of hydroxyl termini. This is in contrast to linear PEO, which remains solid because of a significant crystalline fraction up to the melting temperature of approximately 65 °C.

The temperature-dependent Li-ion conductivities for the *hb*PEO and linear PEO are shown in Figure 1. The linear PEO shows a large, steplike change near the melting point of the PEO crystallites.[5,14] Discontinuities in the conductivity are not observed in the hyperbranched samples, consistent with the absence of discenable crystallinity in these samples once they are blended with Li salts (Table 1). It is interesting that the Li salt additives generally decreases the crystallinity of PEO, but the extent of relative decrease is much greater for *hb*PEOs (Table 1). The result is an approximately 100-fold increase in the Li-ion conductivity of the *hb*PEO systems over the linear PEO below 50 °C. Li-ion conductivity values of similar magnitude were reported for cross-linked and branched polymers bearing ethylene oxide groups as side chains.[7,9,10]

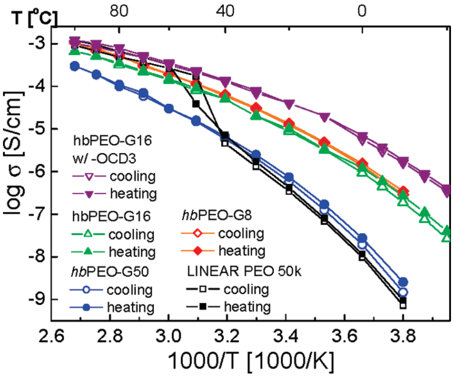


Figure 1. Temperature-dependent Li-ion conductivity for *hb*PEO samples with varying glycerol branching contents and permethylation, as compared with linear PEO, blended with LiTFSI salt in molar ratio O:Li of 25:1.[13]

The Li-ion conductivity exhibits important variations with glycerol branching comonomer content. The *hb*PEO-G8 displays the highest conductivity at room temperature and there is a very small decrease in conductivity when moving from 8 to 16% glycerol content, followed by a more significant drop at 50% glycerol. This decrease in conductivity at higher glycerol fractions probably reflects the increase in the hydroxyl content with the introduction of the glycerol branching moieties. For each glycerol unit of the copolymer, exactly one additional hydroxyl group is introduced, leading to the formation of a hydrogen-bonded network with increased branching. This is consistent with the visual observation that the room temperature viscosity increases from a viscous liquid that readily flows for *hb*PEO-G8 to an elastomer-like gel for the *hb*PEO-G50 sample.

To evaluate the effects of the hydrogen-bonded network, we investigated a permethylated version of the *hb*PEO-G16 with -OCD$_3$ (see below and the Supporting Information) to break up the hydrogen bonds between the polymer termini. As expected, the permethylated sample shows a significant increase in the Li-ion conductivity as shown in Figure 1. The maximum room temperature conductivity of permethylated *hb*PEO, 6×10^{-5} S/cm, is approaching the 1×10^{-3} S/cm mark needed to realize practical Li-ion battery applications.

To better understand the variations of Li-ion conductivity with glycerol content and permethylation, inelastic neutron scattering (INS) measurements were performed for PEO and *hb*PEO samples blended with the Li salt, in molar ratio O:Li in the polymer to salt of 25:1. The INS measurements were fix-window scan (FWS) on the high-flux backscattering spectrometer (HFBS).[15]

In this mode, one measures the change in the elastic scattering intensity, $I_{elastic}(Q)$, as a function of temperature and scattering

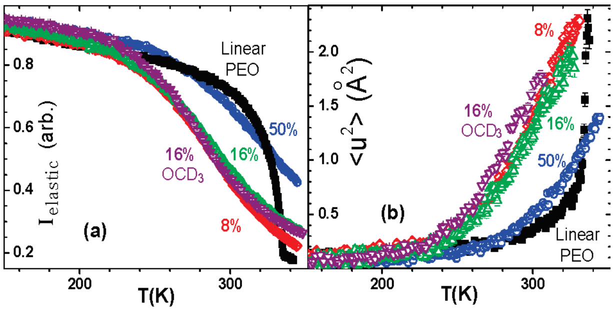


Figure 2. (a) Temperature-dependent incoherent elastic scattering intensity, $I_{elastic}(Q)$, summed over 0.25 Å^{-1} ≤ Q ≤ 1.75 Å^{-1} and (b) The hydrogen mean-square displacement, $\langle u^2 \rangle$, versus temperature for PEO, and *hb*PEO blended with LiTFSI salt in molar ratio O:Li of 25:1. The legend shows the percentage of glycerol branching units and permethylation in *hb*PEO.

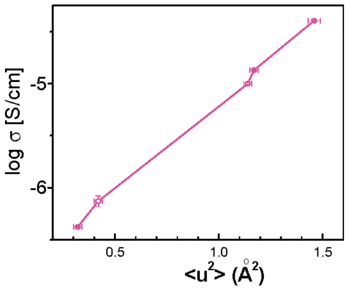


Figure 3. Li-ion conductivity versus the hydrogen atomic mean square displacement $\langle u^2 \rangle$ by INS at room temperature.

vector, *Q*. Local segmental motions (vibrational, translational, and rotational) that cause the hydrogen atoms to move at frequencies faster than 200 MHz (instrumental resolution of 0.8 μeV) affect a decrease in the elastic scattering intensity. The temperature- and *Q*-dependent decrease in $I_{elastic}(Q)$ is treated with a Debye–Waller approximation and modeled as a harmonic oscillator to obtain the mean-square atomic displacements, $<u^2>$, of the hydrogen containing segments in the polymer (see the Supporting Information).[16]

Figure 2a displays the temperature dependence of $I_{elastic}(Q)$, summed over all detectors between 0.25 Å^{-1} ≤ Q ≤ 1.75 Å^{-1}. A decrease in the elastic intensity with temperature reflects the onset of local segmental motions faster than 200 MHz. From the *Q* dependence of these intensities we calculate the magnitude of $\langle u^2 \rangle$ as shown in Figure 2b. The thermal evolution of $\langle u^2 \rangle$ in the low temperature range is approximately linear, consistent with a simple harmonic oscillator model. At approximately 220 K, near the glass transition temperature, the onset of conformational motions in the polymer adds anharmonicity to the segmental motions which is evidenced by the nonlinear and sharp increase in $\langle u^2 \rangle$. It is quite striking that the trends in $\langle u^2 \rangle$ for local dynamics of *hb*PEOs blended with Li salt closely track with the observed Li-ion conductivities (Figure 3). Most importantly, the permethylated *hb*PEO-G16-OD_3 exhibits the largest values of $\langle u^2 \rangle$ and the highest conductivity of 6×10^{-5} S/cm at ambient conditions. Note that a deuterium substituted group is used in the permethylation so that the addition of a methyl rotor does not enhance $\langle u^2 \rangle$.

Of particular significance is the direct correlation between the high-frequency segmental dynamics of *hb*PEOs blended with Li salts probed by the INS measurements and the slower motions of the Li-ions in polymers. It is generally believed that the Li-ions move through PEO by the Grotthus hopping mechanism[17] from one association site to the next, involving a catch-and-release process of Li-ion association/dissociation by the PEO segments. The Grotthus mechanism is then strongly coupled to the segmental reorganization dynamics of the polymer involving the Li-ions. Our findings provide strong evidence that the transport of Li-ions is indeed closely coupled to the local segmental dynamics of polymer chains. The implication is that one should be able to increase the Li-ion conductivity of polymer electrolytes by enabling faster segmental dynamics, as demonstrated here with *hb*PEO-G16-OCD_3.

In conclusion, we have investigated a series of hyperbranched PEO polymers with varying glycerol branching content and different number of hydroxyl end groups as model solid polymer electrolytes for Li-ion batteries. To the best of our knowledge, this is the first work to date that correlates ionic mobility in a hyperbranched material with the degree of branching and the end group functionality. Hyperbranching with the polar glycerol moiety of ca. 8 mol-% effectively prevents crystallization in blends with Li-salts, and leads to approximately a 100-fold increase in the Li-ion conductivity below 50 °C in comparison with linear PEO. However, the Li-ion conductivity decreases in melts due to the development of a hydrogen-bonded network, which lowers the molecular dynamics. However, upon inactivation of the multiple hydroxyl groups by permethylation, the Li-ion conductivity increased significntly to 6×10^{-5} S/cm at ambient conditions for *hb*PEO-G16-OD_3. The variation of Li-ion conductivities with hydroxyl branching contents and permethylation is found to correlate closely with fast segmental dynamics of hydrogen mean-square displacements measured by inelastic neutron scattering experiments.

■ ASSOCIATED CONTENT

S Supporting Information. Details of synthesis and characterization of the materials, dielectric relaxation spectroscopy (DRS), and inelastic neutron scattering (INS) experimental methods and properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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