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Electrical Properties of Poly(ethylene oxide)-based Ionomers as Single Ion Conductors RALPH H. COLBY, SHICHEN DOU, SHIHAI ZHANG, ROBERT J. KLEIN, JAMES P. RUNT, KARL T. MUELLER, Materials Research Institute, Pennsylvania State University — Polyethers, such as poly(ethylene oxide) (PEO) are of interest for development of advanced lithium batteries because Li^+ ions have facile transport in this media. We make ionomers based on PEO by reacting poly(ethylene glycol) (PEG) oligomers with the sodium salt of dimethyl 5-sulfoisophthalate. Since the sulfonate group is covalently bonded to the chain, it is essentially immobile and hence these materials are single-ion conductors. The charge spacing on the chain can be directly controlled by the molar mass of the PEG oligomers (we use $M = 400, 600$ and 900) used in the synthesis. Conductivity depends strongly on temperature, with nearly identical conductivities in all of our samples at the same $T - T_g$, suggesting that Li^+ ion transport is controlled by segmental motion of the PEO. Using the onset of electrode polarization (usually considered a nuisance in dielectric spectroscopy) we quantitatively estimate the free ion concentration and mobility, based on work of MacDonald (1952 & 1974) and Coelho (1983 & 1991). The temperature dependence of the free ion concentration is described by a simple pairing energy, which decreases in going from Li^+ to Na^+ to Cs^+ , consistent with larger ions being less strongly bound to the sulfonate groups. The ion mobility shows a Vogel-Fulcher temperature dependence, as anticipated by the polymer's segmental motion controlling ion mobility.

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