



# Effect of monomer structure on ionic conductivity in a systematic set of polyester electrolytes



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## ABSTRACT

Polymer electrolytes may enable the next generation of lithium ion batteries with improved energy density and safety. Predicting the performance of new ion-conducting polymers is difficult because ion transport depends on a variety of interconnected factors which are affected by monomer structure: interactions between the polymer chains and the salt, extent of dissociation of the salt, and dynamics in the vicinity of ions. In an attempt to unravel these factors, we have conducted a systematic study of the dependence of monomer structure on ionic conductivity,  $\sigma$ , and glass transition temperature,  $T_g$ , using electrolytes composed of aliphatic polyesters and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt. The properties of these electrolytes were compared to those of poly(ethylene oxide) (PEO), a standard polymer electrolyte for lithium batteries. We define a new measure of salt concentration,  $\rho$ , the number of lithium ions per unit length of the monomer backbone. This measure enables collapse of the dependence of both the  $\sigma$  and  $T_g$  on salt concentration for all polymers (polyesters and PEO). Analysis based on the Vogel–Tammann–Fulcher (VTF) equation reveals the effect of different oxygen atoms on ion transport. The VTF fits were used to factor out the effect of segmental motion in order to clarify the relationship between molecular structure and ionic conductivity. While the conductivity of the newly-developed polyesters was lower than that of PEO, our study provides new insight into the relationship between ion transport and monomer structure in polymer electrolytes.

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## 1. Introduction

Replacing conventional organic liquid electrolytes with a nonflammable alternative is a crucial step toward safer rechargeable lithium batteries. Ion-conducting polymers are of particular interest in electrochemical applications due to their non-volatile nature and easily tunable properties [1,2]. Despite 40 years of persistent research, the ionic conductivity of the most promising solvent-free polymer electrolytes remain insufficient for use in commercial batteries. Our ability to design new and improved ion-conducting polymers is compromised by a lack of knowledge of the relationship between monomer structure and ion transport.

The mechanism that enables ion transport in polymers is inherently different from traditional liquids [3–5]. Solvent-free polymers solvate low lattice-energy salts through the formation of stable ion-polymer complexes; [6–8] hopping from one solvation complex to another is a mechanism that allows ions to travel through polymers [9–11].

Therefore, ion-conducting polymers must contain polar groups which interact with at least one of the ions (typically the cation) to enable salt solvation [12], but the strength of these interactions will impact hopping dynamics. The solvation of salt and the transport of ions are intrinsically coupled, and the type of polar groups present will directly affect the conductive properties of the material. Furthermore, the location and spacing of these groups influence the stiffness of the chains. More flexible chains exhibit rapid segmental motion which facilitates ion transport, and thus are desirable in polymer electrolytes [13,14]. Due to the complexity of these interrelated factors, determining relationship between molecular structure and ion transport remains an outstanding challenge.

A vast majority of the literature on polymer electrolytes is focused on mixtures of poly(ethylene oxide) (PEO) and lithium salts such as lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) which exhibit reasonable ionic conductivities at temperatures above 60 °C, the melting temperature [8,11,14–17]. The ionic conductivity of PEO/LiTFSI in the vicinity of 80 °C is  $1 \times 10^{-3}$  S/cm [15,16], significantly lower than the room temperature conductivity of liquid electrolytes used in current electric vehicles. The desire to obtain

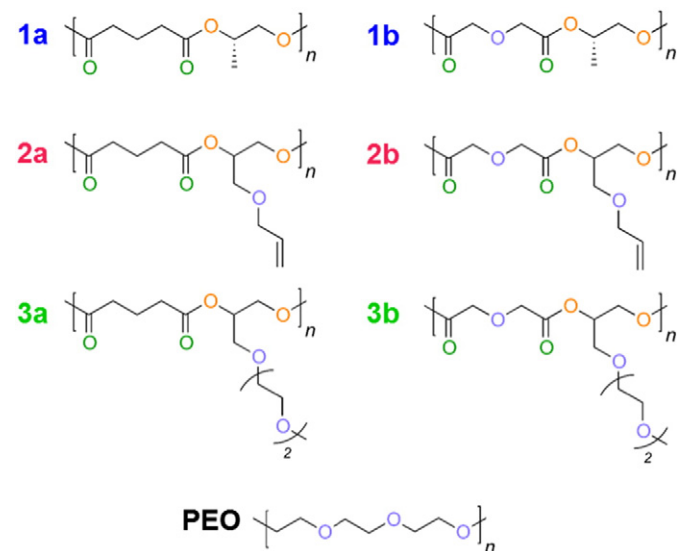
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polymer electrolytes with improved lithium ion transport has motivated studies of conductivity in a variety of polymers such as polyesters [18–22], polycarbonates [23,24], polysiloxanes [25–28], polyphosphazenes [29], and perfluoropolyethers [30]. Changes in the monomer structure affect the glass transition temperature, dielectric constant, ion solvation, salt dissociation, and ion hopping rates in ways that are, at this stage, difficult to predict. It is unclear which of these effects are responsible for the observed differences in conductivity due to the fact that the chemical structure of the monomers listed above are drastically different. Comparison between the results presented in references [18–30] is further complicated by differences in salt used to create the electrolytes, salt concentration, and polymer molecular weight; the conductivity of polymer electrolytes is significantly affected by these parameters. To our knowledge, there is no framework that enables quantification of the factors that underlie ion transport in the chemically distinct polymers chains listed above.

In this paper, we have studied ion transport in a series of polyesters wherein the locations of the cation-solvating oxygen atoms in the monomer are systematically changed. The same salt was used in all the electrolytes and our study covers a wide range of overlapping salt concentrations. We ensured that the molecular weight of the polymers exceeded 4 kg/mol. In this regime the conductivity of PEO/LiTFSI mixtures is independent of chain length [14,16], and the chemical identity of the endgroups [31]. We assume the same holds for the polyester electrolytes. We thus interpret differences in conductivity solely in terms of differences in the chemical structure of the monomers.

The chemical structure of the aliphatic polyesters used in this study is shown in Fig. 1. We use two different backbones, one with an alkane link between the backbone ester groups, labeled *a*, and another with an ether link between the backbone ester groups, labeled *b*. Polymers labeled 1 have a methyl side chain, polymers labeled 2 have a methoxyallyl side chain, and polymers labeled 3 have an ethylene-oxide sidechain with three ether oxygens. For completeness we also studied PEO. Careful consideration went into choosing these structures. We explore two polar groups: ethers and carbonyl-containing esters. Ethers are of particular interest in the polymer electrolyte community, while carbonyl groups are used in current lithium battery electrolytes [5]. In contrast to previous reports on polyesters [18–22], the polymers in Fig. 1 all possess sidechains of varying lengths. We chose to avoid linear polyesters to thwart crystallization; the comb polyesters in this study



**Fig. 1.** Structure and naming convention for polyesters and PEO. The monomer units for all polymers including PEO correspond to 9 atoms along the backbone. Oxygens are distinguished using color: carbonyl oxygens are green, ester oxygens are orange, and ether oxygens are purple.

(Fig. 1) are amorphous over the entire salt concentration and temperature ranges of interest.

The properties of the electrolytes listed in Fig. 1 have been previously studied in the dilute salt concentration limit in reference [33]. The focus of that work was to experimentally determine the dilute-ion transport characteristics of polyester electrolytes and utilize simulations for molecular-level insight describing the coordination environment and hopping mechanisms of a lithium ion. It is, perhaps, worth noting at the outset that the ionic conductivities of the newly-developed polyester electrolytes are less than that of PEO (at fixed temperature and salt concentration). The present study is mainly motivated by our desire to begin building a framework for understanding the relationship between monomer structure and ion transport.

## 2. Experimental section

### 2.1. Polymer synthesis and characterization

The polyesters used in this study were synthesized and characterized using methods described in reference [33]. Table 1 provides the number-averaged molecular weight,  $M_n$ , and polydispersity,  $D$ , for each polymer.

### 2.2. Electrolyte preparation

Electrolytes were prepared by mixing each polymer with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt. Due to the hygroscopic nature of LiTFSI, all sample preparation was carried out in an argon glovebox (MBraun) where  $H_2O$  and  $O_2$  levels were maintained below 0.1 ppm and 1 ppm respectively. The set of six polyesters were dried, along with 5 kg/mol PEO (Polymer Source), at 90 °C under vacuum in the glovebox antechamber for a minimum of 8 h, and then transferred into the glovebox. Dry polymer and LiTFSI salt (Novolyte) were dissolved into anhydrous N-methyl-2-pyrrolidone (NMP) and the solutions were mixed at 90 °C for a minimum of 5 h. Once the solutes were fully dissolved, the caps were removed from the vials allowing NMP to evaporate and leave behind a homogeneous polymer/salt mixture. After drying on the hotplate at 90 °C for 2 days, the electrolytes were transferred to the glovebox antechamber and dried under vacuum for 8 h at 90 °C to remove any excess NMP. Most of the dry electrolytes were very viscous liquids at room temperature with the consistency of molasses. Electrolyte 1b was solid-like at room temperature.

It is convenient to define concentration,  $\rho$ , as the molar ratio of lithium ions to polymer repeat units,  $\rho = [Li^+/\text{monomer}]$ , wherein the monomer is defined in Fig. 1. It is perhaps worth noting that a PEO “monomer” is defined as having 3 repeating  $CH_2-CH_2-O$  units. The lengths of the backbones of all the monomers are thus comparable. Electrolytes with  $\rho = 0, 0.02, 0.04, 0.08, 0.12, 0.16, 0.2, 0.24,$  and  $0.28$  were created for each polyester and PEO. These values were chosen to span the full range of salt concentrations in an attempt identify the maximum conductivity of each polymer.

### 2.3. Differential scanning calorimetry

Samples were prepared by depositing 3–7 mg of each electrolyte into hermetically sealed aluminum pans. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments DSC Q200 instrument with the following temperature scan: heat to 110 °C at 20 °C/min, cool to –75 °C at 5 °C/min, heat to 110 °C at 20 °C/min. The glass transition temperature,  $T_g$ , values of the electrolytes was obtained from the second heating scan.  $T_g$  measurements were found to be repeatable within 1 °C.

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