

# Linear and network structures of polymer electrolyte based on phosphate and polyether copolymers

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## 1. Introduction

Ion conducting polymers have been extensively investigated because of their potential application as an electrolyte in solid state batteries [1]. Among the polymer electrolytes, solid polymer electrolytes (SPEs) composed of ion conducting polymer and alkali metal salt have many advantages such as high ionic conductivity, high energy density and light weight. This made them suitable replacement for liquid electrolytes. PEO-based electrolytes were widely investigated because the PEO can easily solvate cations by interaction with polar ether groups in the main chain, and it can coordinate effectively with cations and form homogeneous solutions [2]. Although these systems have high ionic conductivity at 100°C, its ionic conductivity is as low as  $10^{-7} \sim 10^{-8}$  S/cm at room temperature. In addition, PEO tends to crystallize or form crystalline complexes resulting in a dramatic decrease of ionic conductivity, which greatly restricts its practical application in lithium rechargeable batteries. Recently, network polymer electrolytes have been investigated because of their excellent mechanical property and good thermal stability comparing to the corresponding linear polymer electrolytes.

In this research, linear and network polymer electrolytes based on phosphate and polyether copolymers were prepared to improve ionic conductivity and chain flexibility. Ionic conductivity and thermal behavior of polymer electrolytes were investigated with various copolymer compositions, salt concentrations and temperatures. The plasticizer which has a low molecular weight and high dielectric constant ( $\epsilon = 89.6$ ) was added to phosphate-polyether network to increase ionic conductivity. Ionic conduction behavior of linear and network polymer electrolytes were investigated.

## 2. Experimental

Poly(ethylene glycol) (PEG, Aldrich Chemical Co.) as an agent involving solvating

unit with different molecular weight of 600 and 1000 was dehydrated *in vacuo* at 60°C for 24h before use. Poly(tetramethylene glycol) (PTMG, Mitubishi Chemical Co.) as a soft segment with molecular weight of 1000 was used without further purification. Methylphosphorodichloridate (MPC, TCI Co.) and phosphorus oxychloride (POC, Fluka Co.) were used as a linking agent. Lithium triflate (LiCF<sub>3</sub>SO<sub>3</sub>, Aldrich Chemical Co.) as a salt was dried *in vacuo* at 80°C for 24h before use. Linear phosphate-polyether copolymers (LPC) were synthesized by polycondensation reaction of MPC and PEG/PTMG copolymer with different composition ratios (100/0, 70/30, 50/50, 30/70). Phosphate-polyether networks (PPN) were prepared by polycondensation reaction of POC and PEG/PTMG (70/30) copolymers.

### 3. Results and discussion

For LPC6 series-LiCF<sub>3</sub>SO<sub>3</sub> complex systems, temperature dependence on the ionic conductivity was not linear, which suggested that ionic conduction followed the Williams Landel Ferry (WLF) mechanism [3]. It indicated that ion transport in polymer electrolytes was correlated with polymer segmental motion [4]. Thus, the results were more effectively represented by the empirical Vogel Tamman Fulcher (VTF) equation, as shown in Figure 1.

$$\sigma = A T^{-\frac{1}{2}} \exp \left[ \frac{-B}{T - T_0} \right] \quad (1)$$

where, A and B are constants, and T<sub>0</sub> is a reference temperature. The VTF equation can be derived from the Adam-Gibbs configurational entropy model [5], and then constant B is a complex accumulation of terms;

$$B = \frac{T_0 S_c^* \Delta \mu}{k_B T \Delta C_P} \quad (2)$$

where, k<sub>B</sub> is the Boltzmann constant, S<sub>c</sub><sup>\*</sup> is the minimum configurational entropy required for a cooperative rearrangement of a polymer chain segment involved in ion transport in the matrix (which can be approximated by k<sub>B</sub>ln2). ΔC<sub>p</sub> is the heat capacity changes at temperature T as the system moves from the glassy to the rubbery state, and Δμ is the potential energy barrier hindering the cooperative

movement of a chain segment whose size is the minimum capable of undergoing a spatial rearrangement independent of its environment. A non-linear least square analysis was applied to evaluate the relevant parameters, and the values are listed in Table 1 for LPC673 and LPC637-LiCF<sub>3</sub>SO<sub>3</sub> complexes. For LPC637-LiCF<sub>3</sub>SO<sub>3</sub> complexes, the values of parameter B and the potential energy barrier ( $\Delta\mu$ ) hindering the cooperative movement of chain segments are relatively lower than those of LPC673-salt systems over the entire range of salt concentrations. This means that the segmental motion of polymer backbone represented by chain flexibility occurs more readily in LPC637-salt systems than LPC673-salt systems.

The ionic conductivity of PPN-LiCF<sub>3</sub>SO<sub>3</sub> complexes with various salt concentration is dependent on the temperature. At higher temperatures, thermal movement of polymer chain segments and dissociation of salts would be improved, which increase ionic conductivity. However, at lower temperatures, the presence of lithium salt leads to salt-polyether or cation-dipole interactions, which increase the cohesive energy of network polymer. As a result, free volume was decreased, and polymer segmental motion and ionic mobility were hindered, thus ionic conductivity decreased. The network structure improved ionic conductivity of PPN-LiCF<sub>3</sub>SO<sub>3</sub> complexes by decreasing the degree of crystallinity. However, the lower ionic conductivity in network polymer electrolytes is due to their reduced polymer segmental motion comparing to the corresponding linear polymer electrolyte. To improve ionic conductivity ethylene carbonate (EC) as a plasticizer was added to PPN-salt complexes. The ionic conductivity of PPN-salt complexes increased with increasing EC content. It could be explained that free volume of EC-rich phase increases due to an increase of the amount of EC comparing to PPN-salt complexes.

## References

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Table 1. VTF parameters and activation energies from non-linear least squares analysis of ionic conductivity data for LPC673-LiCF<sub>3</sub>SO<sub>3</sub> and LPC637-LiCF<sub>3</sub>SO<sub>3</sub> complexes.

Samples	[Li <sup>+</sup> ]/[EO]	B (K)	T <sub>0</sub> (K)	$\Delta C_p$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta \mu$ (kJmol <sup>-1</sup> )
LPC673	0.01	1243.1	161.2	29.1	68.4
	0.02	1186.8	163.9	27.0	60.3
	0.05	1097.3	169.1	24.3	49.8
	0.10	1156.5	170.4	26.8	59.8
	0.15	1376.2	172.3	44.2	113.2
	0.20	1530.4	176.6	56.3	159.5
LPC637	0.02	978.3	159.7	25.2	46.7
	0.10	1051.0	168.3	29.1	57.2
	0.15	1256.5	171.8	37.9	88.7
	0.20	1396.5	175.1	48.7	126.1

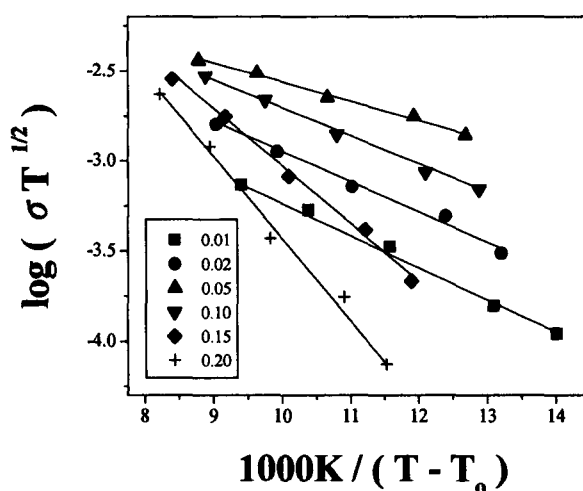


Figure 1. VTF behavior of ionic conduction for LPC673-LiCF<sub>3</sub>SO<sub>3</sub> complexes.