

Solvent-free Polymer Electrolyte Membranes

T. Tatrishvili^{a,b}, E. Markarashvili^{a,b}, I. Esartia^{a,b}, M. Barnabishvili^{a,b}, J. Aneli^b, O. Mukbaniani^{a,b}

^aDepartment of Macromolecular Chemistry, Faculty of Exact and Natural Sciences,

Iv. Javakhishvili' Tbilisi State University, Chavchavadze Blvd., 1, Tbilisi 0179, Georgia

^bInstitute of Macromolecular Chemistry and Polymeric Materials, Iv. Javakhishvili' Tbilisi State University, I.

Chavchavadze Blvd., 13, Tbilisi 0179, Georgia

E-mail: omarimu@yahoo.com

Interest in polysiloxane-based polymer electrolytes arose early in the 1980s. Poly(ethylene oxide) (PEO) - substituted polysiloxanes as ionically conductive polymer hosts have been previously investigated. Their relatively high ionic conductivity was ascribed to the highly flexible inorganic backbone, which produced a totally amorphous polymer host. In recent years, improved battery performance has been observed for systems containing polymer electrolytes, with a Li^+ transference number close to unity. Efforts have also been made to design and synthesize siloxane-based single-ion conductors.

Polysiloxanes are promising components for comb polyelectrolytes because they possess a flexible backbone that enhances the transports of ions. Their amorphous and highly flexible $[\text{Si-O}]_n$ backbone produces glass transition temperatures as low as -100°C and yields little or no crystallinity at room temperature. In addition, each monomer unit has two sites for cross-links or functional side chains through bond formation with silicon. Simulations indicate that comb polyelectrolytes should display higher conductivity values than their analogs to local motion of the bound anions in comb systems.

In order to improve ionic conductivity, the various approaches may be employed. The main requirements for high conductivity are ability to solvate ions and low glass transition temperature affording the facile ion transport. The promotion of the anion-cation dissociation is desirable, as it should lead to enhancement of ionic conductivity via an increase in free ion concentration. Consequently, obtaining of solid polyelectrolyte membranes on the basis of new siloxane matrix is actually.

Hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^{H}) with allyl acetoacetate at 1:4.1 molar ratios of initial compounds in the presence of platinum catalysts have been studied and D_4^{R} type compounds has been obtained. Reaction order, rate constants and activation energies for hydrosilylation reactions in the presence of Karstedt's catalyst have been determined.

Ring-opening polymerization reaction of D_4^{R} in the presence of catalytic amount of powder-like potassium hydroxide has been carried out. Linear methylsiloxane oligomer with regular arrangement of propyl acetoacetate groups in the side chain has been obtained. The synthesized methylorganocyclotetrasiloxane and oligomers were studied by FTIR, ^1H , ^{13}C , ^{29}Si NMR spectroscopy. Comb-type oligomers were characterized by gel-permeation chromatography, wide-angle X-ray and differential scanning calorimetric methods.

Via sol-gel processes of doped with lithium trifluoromethylsulfonate (triflate) or lithium bis(trifluoromethylsulfonyl) imide oligomer systems solid polymer electrolyte membranes have been obtained.

The electrical conductivity of these materials at room temperature belongs to the rather wide range of electrical conductivity magnitudes (10^{-10} to 10^{-4} $\text{S}\cdot\text{cm}^{-1}$) and depends on the structures of grafted anion receptors and the polymer backbones. Higher values of specific volumetric electric conductivity of the membranes containing triflate due to relatively high mobility of the anions of this salt cause mainly higher values of conductivity and electrical currents in all working ranges of temperature and voltage.

Acknowledgment. The financial support of the Georgian National Science Foundation Grant #STCU 5055 is gratefully acknowledged.