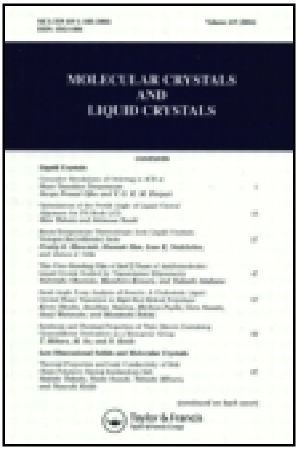

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Single Ionic Conduction Based on Poly(Siloxane-g-Ethylene Oxide) Effect of Sterically Hindered Groups on Ion Dissociation

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Single Ionic Conduction Based on Poly(Siloxane-g-Ethylene Oxide) Effect of Sterically Hindered Groups on Ion Dissociation

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We have synthesized and characterized poly(siloxane-g-ethylene oxide) containing Li, Na and K 2,6-di-t-butyl phenolates, and studied the effect of steric hindrance on the ionic conductivities. These polymers have a flexible siloxane main chain and the anion source bonded on it, such that only the cation can migrate. The ionic conductivity of lithium, sodium and potassium phenolate was found to be 10^{-7} – 10^{-5} s/cm at 30°C. The conductivity of Na and K salts was approximately 10^2 greater than that of the Li salts. This was accounted for by the improved ion pair separation in the Na and K phenolates due to the steric hindrance of the t-butyl groups. The temperature dependence of ionic conductivity suggests that the migration of ions is controlled by segmental motion of the polymer, since linear curves were obtained in VTF plots.

INTRODUCTION

Recently, polymer solid electrolytes have been investigated extensively. A number of publications have appeared describing polyethers,[1] polyimines,[2] polysulfides,[3] poly(ethylene succinate),[4] poly(ethylene oxide-co-propylene oxide),[5] poly(phosphazene-g-ethylene oxide)[6] and poly(siloxane-g-ethylene oxide).[7] These polymers mixed with $LiClO_4$ or $LiSO_3CF_3$ showed an ionic conductivity of 10^{-4} -10^{-9} s/cm at room temperature.

For many applications of these solid electrolytes, such as high energy density batteries, undesirable local concentration gradients occur due to anion mobility which degrades the energy efficiency. A significant decrease in dc ionic conductivity is inevitably observed.[8] Several groups, therefore, have investigated various polyelectrolytes in which the anionic charge such as carboxylate or sulfonate is attached on the polymer backbone. The ionic conductivity of these polymers has generally been found to be very low due to the formation of strong ion pairs.

The importance for single-ion conduction in polymer electrolytes is to find an ion source, in which the ion pair can be well separated. In that context we have investigated sterically hindered phenols as anions which incorporate extensive charge delocalization as well as steric hindrance, both of which are expected to promote charge dissociation.

Sterically hindered phenols such as 2,6-di-t-butyl phenol have been utilized in a variety of applications in organic reaction.[9,10] The noteworthy properties of the compound include a) the stability of the phenol radicals, and b) a failure to exhibit normal phenol properties.[11] Geometrical calculations indicate that bulky t-butyl substituents in 2,6-positions of phenoxide serve in separating alkali metal ions such as K^+ and Na^+ from the phenoxide. The cations are, therefore, expected to be more mobile compared to systems having strong ion pairs. Thus, sterically hindered phenol groups bound covalently to poly(siloxane-g-ethylene oxide) backbones were synthesized. The typical structure is shown in Figure 1. The ionic conductivities of alkali metal salts of these polymers were measured and the relationship between the ionic conductivity and their chemical structure is reported.

EXPERIMENTAL

Materials and Instruments

Polymethylhydrosiloxane (MW = 2270) was purchased from Petrarch Systems, Silanes & Silicones Group; 2,6-di-t-butyl-4-methylphenol was obtained from Polyscience, Inc.; and polyethylene glycol (MW = 350) and other chemicals were purchased from Aldrich Chemical Company. Proton NMR and IR were used to identify the product in each step. The transition temperatures were determined by

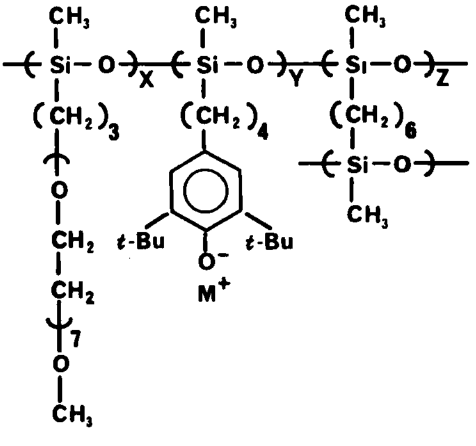
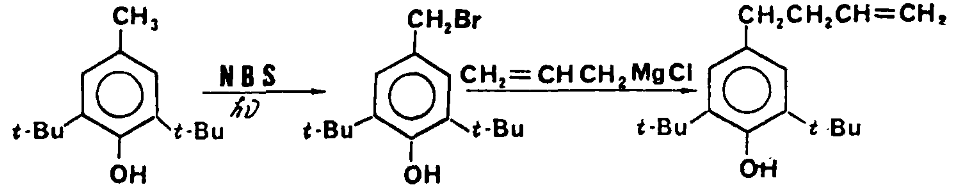


FIGURE 1 General Structure of Siloxane-PEO-di-t-Butylphenolate Copolymer. $M^+ = Li^+, Na^+, K^+$; x = 3, 4, 6, 8, 10, 12, 14, 16; y = 1; z = 0, 0.5, 1.5, 2.0.

a DuPont 2100 Thermal Analyst Equipped with a 910 DSC and the conductivities were measured by a Hewlett-Packard 4192A Impedance Analyzer.

Preparation of 2,6-di-t-butyl-4-butenyl(3')phenol

The butenylphenol was prepared by the following reactions:



95.7 g of 2,6-Di-t-butyl-4-methylphenol was dissolved in hexane and gradually added into 80.9 g N-bromosuccinimide hexane solution and irradiated by a sun lamp. The reaction was kept refluxing under sun light for two hours. After removing the solid product the solution was added dropwise into 600 ml of 2.0 M allylmagnesium chloride THF solution at room temperature. After refluxing for an hour, the solution was washed with water and dried over $MgSO_4$, and the 2,6-di-t-butyl-4-butenyl(3')phenol obtained was distilled at 100–103°C/1.0 mmHg, resulting in 63.9 g with a yield of 56.5%.

Preparation of methoxy (oligo ethylene oxide) allyl ether

The ether was synthesized by the following reactions:

$$CH_3O(CH_2CH_2O)_nH + NaH \longrightarrow CH_3O(CH_2CH_2O)_nNa$$

$$CH_3O(CH_2CH_2O)_nNa + CH_2{=}CHCH_2MgCl \longrightarrow CH_3O(CH_2CH_2O)_nCH_2CH{=}CH_2$$

197.5 g of poly(ethylene glycol methyl ether) (MW 350) was added into 16.4 g sodium hydride suspended in 100 ml THF, and the reaction was carried out at room temperature for an hour. Then 75 ml allyl chloride was added into the reaction mixture, and kept for two hours. After filtering the salt produced, 129.6 g (yield 65.6%) of product was obtained by distillation at 180–240°C under 0.03 mmHg. The average of n = 7, MW 380, was determined by proton NMR.

The hydrosilylation reaction of butenylphenol and allyl ether

The siloxane-PEO-di-t-butylphenol was prepared by reacting 2,6-di-t-butyl-4-butenylphenol (0.85 g, 0.0033 mole) with polymethylhydrosiloxane (MW = 2270, 1.8 g) in the presence of H_2PtCl_6 in THF under nitrogen at 70°C, and then methoxy (oligo ethylene oxide) allyl ether (10.0 g , 0.026 mole) was added into the solution and heated to 80°C to complete the hydrosilylation reaction. The reaction was monitored by measuring the NMR spectrum (disappearance of Si-H (5.2 ppm) and CH=CH (5.3 and 6.0 ppm) respectively). The crosslinked polymer was synthesized using 1,5-hexadiene to react extra Si-H groups. The structure of the resulting polymer was determined by measuring IR and NMR.

Preparation of salts

Lithium phenolates were prepared by using equal amounts of butyllithium to react phenols in THF. Sodium and potassium ethyl alcoholates were used to neutralize the phenol to form sodium and potassium phenolates in ethanol. The salts were dried in vacuum at 70°C over night.

Conductivity measurements

The conductivity measurements were carried out using a Hewlett-Packard 4192A Impedance Analyzer with a frequency range from 5 Hz to 13 MHz. The samples were dried at 60°C under vacuum for at least 24 hours prior to the measurement.

RESULTS AND DISCUSSION

Effect of cation content on conductivity

The dependence of the ionic conductivity on the cation (Li^+, Na^+, K^+) content was evaluated for the siloxane-PEO-di-t-butylphenolate copolymer with different cation species. A typical data set is shown in Figure 2. In the case of K and Na salts, the maximum conductivity was reached with a phenolate/ethylene oxide ratio of 0.014. The maximum conductivity was 5×10^{-5} s/cm for K and 2×10^{-5} s/cm for Na at 30°C. On the other hand, the Li salts were found to have a maximum conductivity of 5×10^{-6} s/cm for a ratio of phenolate/ethylene oxide unit of 0.019. In general, increasing salt concentration increases the ion pairing and the microviscosity of the polymer-salt complex which causes a decrease of the mobility of the carrier ions.[8] The conductivity maxima found are attributed to a competition between these two factors. Increase of cation radius makes the maximum conductivity higher by the facilitating ion dissociation. Similar results have also been reported in other polymer electrolyte systems.[12] The large difference between sodium and lithium ion conductivity is attributed to the steric effect of t-butyl groups of the phenolate promoting ion dissociation for the larger Na ion.

Temperature dependence of single-ion conductivity

The temperature dependence of the cation conductivity of the siloxane-PEO-di-t-butylphenolate copolymer system was measured from 25°C to 100°C, and log σ is plotted against reciprocal absolute temperature in Figure 3. The temperature dependence was found to be nonlinear, indicating that the ionic conduction followed a Williams-Landel-Ferry (WLF) mechanism.[13] This result suggests that carrier ions migrate, assisted by polymer segmental motion with continued ion-dipole interaction. Vogel-Tammann-Fulcher (VTF) plots,[14] which are known to describe trans-

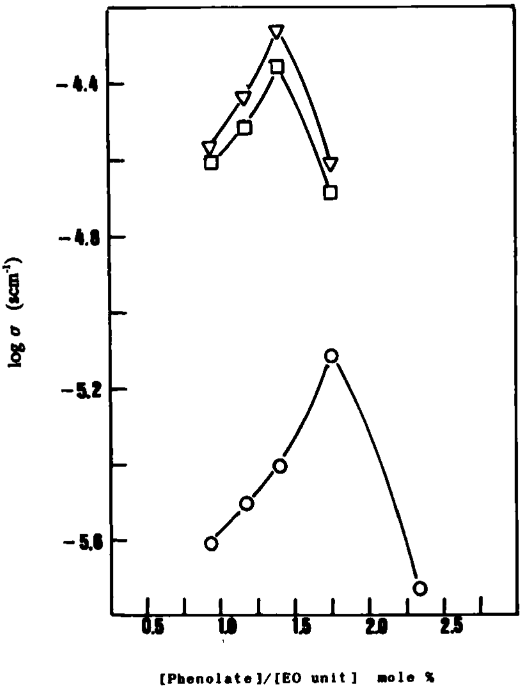


FIGURE 2 Conductivity vs. Composition of Copolymer of Siloxane-PEO-di-t-Butylphenolate System at 30°C (non crosslinked). Li$^+$ (○), Na$^+$ (□) and K$^+$ (▽).

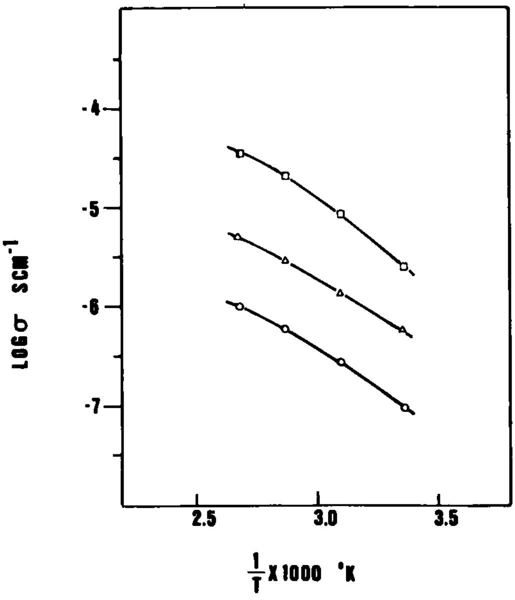


FIGURE 3 Conductivity vs. Temperature on Siloxane-PEO-di-t-Butylphenolate Copolymer (x:y:z = 3:1:0.5). Li$^+$ (○), Na$^+$ (△) and K$^+$ (□).

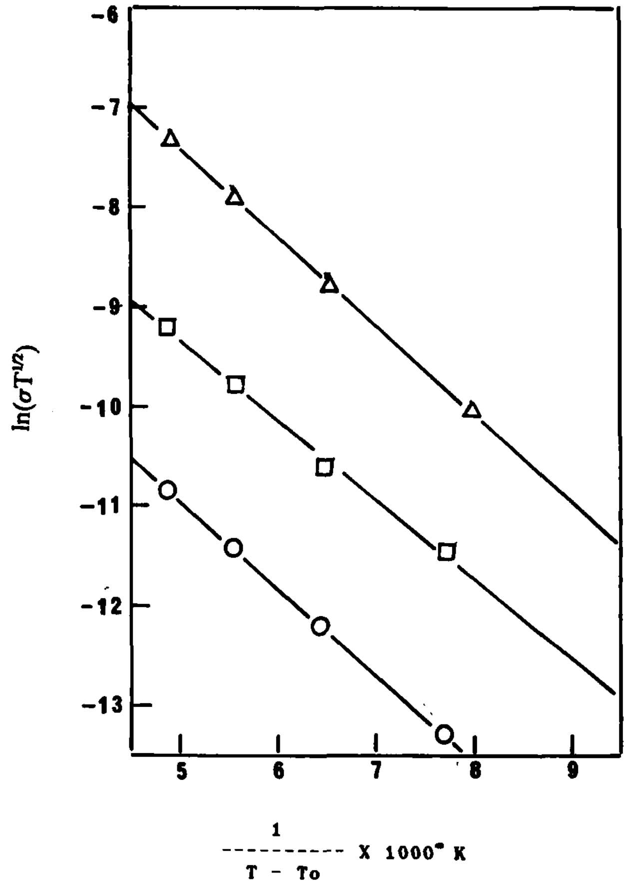


FIGURE 4 Vogel-Tammann-Fulcher Plots for Siloxane-PEO-di-t-Butylphenolate Copolymer (x:y:z = 3:1:0.5). Li^+ (○), Na^+ (□) and K^+ (△).

port properties in a viscous matrix, show linearity when the standard temperature is defined as T_g − 50°C (Figure 4). The glass transition temperatures in the case of K, Na and Li phenolates were −50°C, −53°C and −55°C, respectively. These results suggest that ionic conduction is considerably affected by the polymer segmental motion in siloxane-PEO-di-t-butylphenolate copolymer.

CONCLUSION

Siloxane-PEO-di-t-butylphenolate copolymers with exclusive cation conductive characteristics were prepared. The cation conductivities of Li, Na and K metal ions were in the 10^{-7} to 10^{-5} s/cm range at room temperature. The effect of sterically hindered 2,6-di-t-butyl groups was found to effectively separate Na and K ions and phenolate.

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