

SYNTHESIS AND CHARACTERIZATION OF POLYSILOXANE CONTAINING OLIGO(OXYETHYLENE) SULFATE SALT

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Abstract Solvent-free polymeric alkali-metal ion conductors, consisting of a comb-like polysiloxane with oligo(oxyethylene) side chains and pendant sulfate groups were synthesized by the hydrosilylation of allyl oligo(oxyethylene) sulfate salt and allyl methoxy oligo(oxyethylene) with poly(methylhydrosiloxane). The factors influencing the ionic conductivity of the resulting polymer such as the electrolyte content and the nature of the alkali-metal were investigated. The temperature dependence of conductivity was determined, and the ionic conductivity of the polymer follows the Vogel-Tammann-Fulcher (VTF) equation.

Keywords Hydrosilylation, Electrolytes, Ionic conductivity

INTRODUCTION

In recent years, the complexes of polyether with Li-salt have been extensively investigated as polymer electrolyte materials for all-solid state lithium batteries^[1-3]. However, most of the polymer electrolytes ever studied are bi-ionic conductors, in which both the anion and the cation have a chance to move in opposite directions under DC polarization. This anion motion is quite unfavorable for lithium batteries with Li⁺-insertion type cathode because of the intrapolarization in the electrolytes. Some researchers demonstrated that ion transport is often dominated by the anion due partly to the crosslinking of the cation with the immobilized oligo(oxyethylene) ligand^[4, 5].

An effective method to immobilize anions is to anchor them on polymer chains through covalent bonds. Examples of such cation-conductors include polyelectrolytes with carboxylate, sulfonate and phosphate^[5, 6]. However, most single ion conductor research concentrates on poly[methacrylic oligo(oxyethylene)], in which the "hard" polymer backbone is an unfavorable structure for the motion of the lithium^[7]. As is well known, the polysiloxane chain has excellent flexibility, therefore it may be expected that this polymeric system can be used as an ideal material for polymeric electrolytes. In this paper, poly{[ω -methoxy hepta(oxyethylene)propyl methylsiloxane]-co-[sulfate salt oligo(oxyethylene)propyl methylsiloxane]} (abbreviated as PSGSO₄M) was synthesized, and the ionic conductivity of the polymer was investigated.

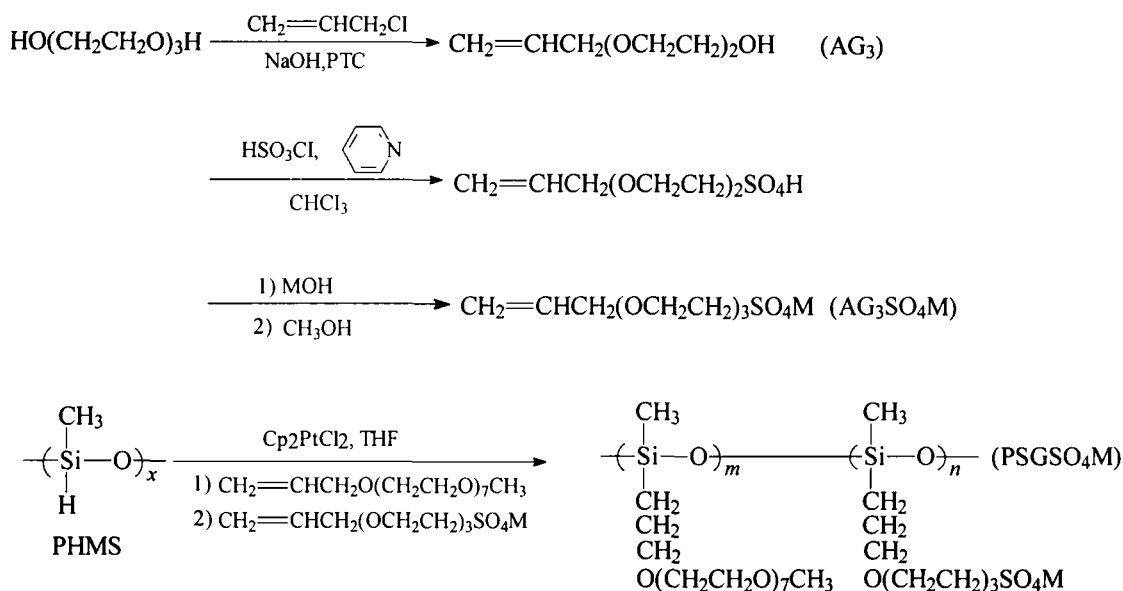
EXPERIMENTAL

Materials

Uarimx oligo(oxyethylene) was obtained from Aldrich and used without further purification. Ploy(methylhydrosiloxane) (PHMS, $M_w = 2250$, Aldrich) was dried under vacuum at 60°C for 48 h. Allyl chloride was distilled

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before use. Pyridine (AR) was distilled over KOH, and chloroform (AR) over CaCl_2 . THF (AR) was distilled over sodium under nitrogen atmosphere. The synthesis of allyl oligo(ethylene glycol) methyl ether from MPEG350 (abbreviated as AG₇E) was described elsewhere^[7]. The synthesis of Cp_2PtCl_2 was performed according to the literature^[8]. Poly{[ω -methoxy hepta(oxyethylene) propyl methylsiloxane]-*co*-[sulfate salt oligo(oxyethylene) propyl methylsiloxane]}, was synthesized according to the following Scheme 1.



Scheme 1

Synthesis of Triethylene Glycol Monoallyl Ether

The compound was prepared by monoetherification of ethylene glycol with allyl chloride using a modified procedure. To a well-stirred mixture containing triethylene glycol (30 g, 0.2 mol), aqueous 50% (*W/W*) sodium hydroxide (40 g, 0.5 mol), allyl chloride (17.5 g, 0.23 mol) was added within 1 h. After the reaction proceeded at room temperature for 24 h, it was allowed to raise the temperature to 60 °C for another 24 h. The mixture was extracted with diethyl ether until the oil phase became colorless. Then the organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The remaining oil was distilled at 116~123 °C/0.80 kPa, and was further purified by column chromatography (silica gel, chloroform as eluent). 18.1 g of liquid monoallyl ether (AG₃) was obtained, yield: 53%. ¹H-NMR (CDCl_3 , TMS), δ : 5.93 (*m*, 1H, $-\text{CH}_2=\text{CH}$); 5.22 (*m*, $-\text{CH}_2=\text{CH}$), 4.04 (*d*, 2H, $=\text{CHCH}_2\text{O}-$); 3.5~3.8 (*m*, 12H, $\text{CH}_2\text{CH}_2\text{O}-$) and 2.8 (*s*, 1H, $-\text{OH}$).

The Sulfating of Triethylene Glycol Monoallyl Ether

A 20% excess of chlorosulfonic acid (28 g, 0.24 mol) was added dropwise to a stirred solution of pyridine (15.8 g, 0.2 mol) and 38 g (0.2 mol) oligo(oxyethylene) monoallyl ether in 100 mL chloroform cooled in an ice bath. When the addition was complete, the reaction mixture was warmed to room temperature, and stirring was continued for half an hour. After chilling again to 0 °C, 30 mL absolute ethanol was added, and the solution was neutralized with a saturated solution of lithium hydroxide (taking lithium salt as example). When the solvent and water had evaporated, the residue was dissolved in hot acetone. Toluene was used to extract the residual ether alcohol. 39 g of viscous allyl oligo(oxyethylene) sulfate lithium (abbreviated as AG₃SO₄Li) was obtained, yield: 70.5%.

¹H-NMR (CDCl_3 , TMS), δ : 5.93 (*m*, 1H, $-\text{CH}_2=\text{CH}$); 5.22 (*m*, $-\text{CH}_2=\text{CH}$); 4.04 (*d*, 2H, $=\text{CHCH}_2\text{O}-$) and 3.5~3.8 (*m*, 12H, $\text{CH}_2\text{CH}_2\text{O}-$). Elemental analysis (%): S = 11.3 (found), and 11.5 (calc.).

Synthesis of Poly{[ω -methoxy hepta(oxyethylene)propyl methylsiloxane]-co-[lithium sulfate oligo(oxyethylene)propyl methylsiloxane]}

The hydrosilylation of allyl oligo(ethylene glycol) methyl ether (AG₇E) and AG₃SO₄Li with PHMS was carried out under nitrogen in THF at 50°C. The ratio of n/m (see Scheme 1) was varied by adjusting the amount of AG₇E, the molar concentration of which was always less than that of the available SiH groups. In a typical reaction, 5 mg platinum catalyst was added to a well-stirred mixture solution of poly(methylsiloxane) (3.0 g, 50 mmol), AG₇E (8.3 g, 30 mmol) and THF (150 mL). The solution was kept at 60°C until the ¹H-NMR spectrum showed no residual vinyl bonds. To the mixture was then added (11.4 g, 30 mmol) of AG₃SO₄Li, and the reaction was continued until no residual vinyl bonds could be detected by both IR and ¹H-NMR. The resulting polymer was precipitated three times in a 20/1 (V/V) hexane-THF mixture to remove the catalyst and the starting material. The polymer was washed many times with mixed solvent and then dried in vacuum, 13 g of solid was obtained. Its structure was confirmed by IR and ¹H NMR.

¹H-NMR (CDCl₃, δ): 3.6~3.7 (*m*, 22H, $\text{CH}_2\text{CH}_2\text{O}-$), 3.4(*s*, 3H, $-\text{OCH}_3$), 0.2 (*s*, 3H, CH_3-Si); 0.6 (2H, *m*, $\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}$) and 1.8 (2H, $\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}$).

Characterization of the Formed Polymer

The thermal properties of the polymer were studied on a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate of 20 K/min. ¹H-NMR spectra were obtained on a Bruker DMX-300 spectrometer. The conductivities were measured using a Hioki LCR 3520 Hi TESTER. The experimental procedure was as follows: after the electrolyte had been dried under vacuum at 80°C for 48 h, the cylindrical disk samples were sandwiched between two platinum electrodes and sealed in a testing tube which was filled with dry nitrogen for conductivity determination.

RESULTS AND DISCUSSION

Polymer Synthesis

The synthesis of AG₃ was suggested by Ref. [8], the reaction was modified and the yield was increased to 53% instead of 37%. The ratio of allyl chloride to oxyethylene was changed from 25% to 115%, thus almost all of the oligo(oxyethylene) can be used up. The reaction temperature was also changed by maintaining it at room temperature for 24 h and at 60°C for another 24 h instead of 100°C for 24 h. One reason for making such alterations is that the oligo(oxyethylene) can be polymerized under these conditions at high temperature; another reason is that the boiling point of allyl chloride is 44°C, but the binary “gas-liquid” system greatly reduces the yield of the product. In the synthesis of AG₃SO₄M, an absolute absence of water is essential, otherwise chlorosulfonic acid is hydrolyzed and the impurity produced cannot be easily removed from the resultant monomer. A mild condition is also important for obtaining light colored product. The hydrosilylation of the AG₇E with PHMS is quantitative, the subsequent reaction with excess AG₃SO₄M converts the remaining SiH group of PHMS into side chains. When the C=C/SiH ratio is about 1.25, the yield of the polymer is the highest.

Ionic Conductivity of New Type of Electrolytes

It is well known that the ionic conductivity (σ) is determined by ionic mobility (μ), carrier number (n) and charge (e) as Eq. (1) shows:

$$\sigma = \sum ne\mu \quad (1)$$

For the PSGSO₄Li system, e is constant while the ionic mobility and carrier number vary with the composition, as shown in Fig. 1.

It can be seen clearly that at the low salt region, the ionic conductivity of the system is rather low. For example, at a ratio of lithium to ethylene oxide units (EO) of 0.05, $\sigma = 10^{-7.3} \text{ S cm}^{-1}$ at 25°C. As the concentration of the salt increases, the conductivity reaches a maximum at a $[\text{Li}^+]/[\text{EO}]$ ratio of about 0.15. The conductivity of the PSGSO₄Li polymers is consistent with those reported for other cation-conducting polymer salts^[9, 10]. In the low sulfate region, the carrier number increases rapidly with increasing salt concentration. At the same time, the stiffness of the side chains increases due to cation chelation with multiple EO units, which is reflected by the

increasing of T_g from -44°C ($m/m + n = 0.5$) to 20°C ($m/m + n = 0$).

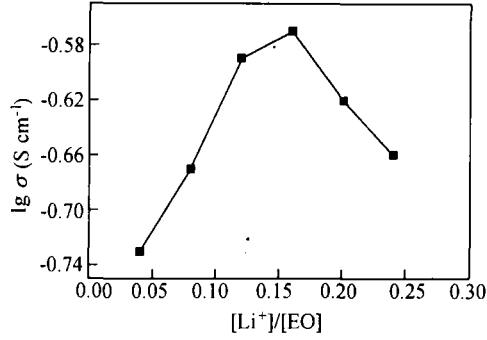


Fig. 1 Isothermal conductivity as a function of the composition of the PSGSO₄Li system at 25°C

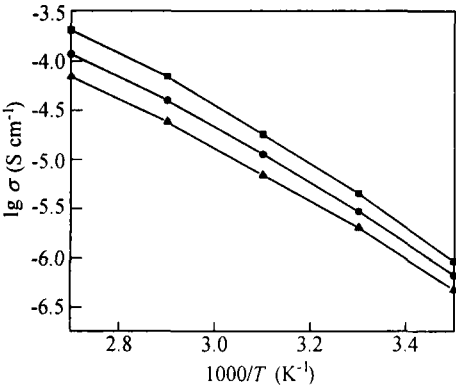


Fig. 2 Arrhenius plot of the conductivity of the PSGSO₄M system ($[M^+]/[EO] = 0.12$)

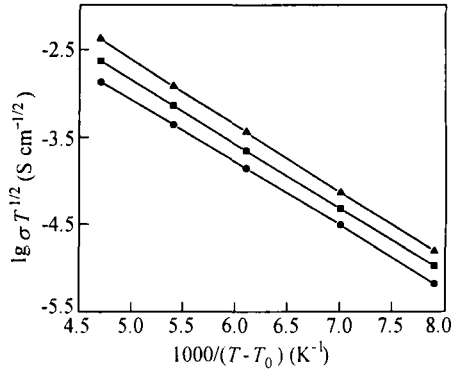


Fig. 3 Vogel-Tammann/Hesse-Fulcher plots for the PSGSO₄M system ($[M^+]/[EO] = 0.12$)

Figure 2 shows the temperature dependence of conductivity for the PSGSO₄M systems ($[M^+]/[EO] = 0.12$). It can be seen that the plot of $\lg \sigma$ versus $1/T$ is a curved line rather than a straight one^[11]. In this viscous matrix transference, the properties are described by the VTF equation^[12]

$$\sigma = AT^{1/2} \exp[-B/(T - T_0)] \tag{2}$$

where A, B are constants, T is the absolute temperature and T_0 is a temperature related to the T_g . According to the Gibbs configurational entropy model the T_0 is regarded as 50 degrees below the measured T_g ^[13]. It can be inferred from Eq. (2) that $\lg \sigma T^{1/2}$ should vary linearly with $(T - T_0)^{-1}$, which is proved by the good linear relationship of VTF plots in Fig. 3, when the data of Fig. 2 are applied. That is to say, the ionic conductivity is considerably affected by the segmental motion of polymer chains in the amorphous region of the electrolyte^[14].

From the result of Figs. 2 and 3, it can also be seen that the nature of terminal ion has an obvious effect on the conductivity of the polymer. PSGSO₄K exhibits relatively higher conductivity than other sulfated single ion conductors at the same salt content and temperature. For example, at 25°C the conductivity of the PSGSO₄K system is $10^{-5.4}$ S cm⁻¹, comparing with $10^{-5.6}$ S cm⁻¹ for the PSGSO₄Na and $10^{-5.8}$ S cm⁻¹ for the PSGSO₄Li system. This result suggests that the conductivity of the PSGSO₄M increases with the ionic radius of the cation, presumably indicating that the dissociation energy of the polymer electrolyte increases in the order of $K < Na < Li$, as is well known for other polymer electrolytes^[10].

CONCLUSIONS

In this paper, a new type of comb-like poly{[ω-methoxy hepta(oxyethylene) propyl methylsiloxane]-co-[sulfate

group oligo(oxyethylene) propyl methylsiloxane}} with oligo(oxyethylene) side chains and pendant sulfate groups was synthesized. Due to its high polarity and good flexibility, an ionic conductivity of the polymer as high as $10^{-5.7}$ S cm⁻¹ can be obtained at room temperature. The temperature dependence of the ionic conductivity suggests that the conduction follows the VTF equation. Thus the single-ion conductivity of these polymeric electrolytes is strongly affected by segmental motion in the polymer matrix.

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