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Synthesis and ionic conductivity of comb-like polysiloxanes with pendant oligo(oxyethylene) side chains and quaternary ammonium groups

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Summary

A series of novel comb-like polysiloxanes with oligo(oxyethylene) side chains and quaternary ammonium groups, has been synthesized by hydrosilylation of poly(methylhydrosiloxane) with poly(ethylene glycol) allyl methyl ether and *N,N*-dimethylallylamine, followed by quaternization with methyl iodide. The glass transition temperature of these solvent-free electrolytes was measured and found to be dependent on the content of quaternary ammonium side groups anchored to the polysiloxane backbone. The influence of quaternary ammonium group content and temperature on the ionic conductivity has been investigated. A maximum conductivity of 1.57×10^{-5} S cm^{-1} at 25 °C was achieved for a polysiloxane containing 30 % quaternary ammonium side groups. The temperature dependence of the ionic conductivity shows the "Vogel-Tammann-Fulcher" (VTF) behavior. The values of the VTF parameters were calculated.

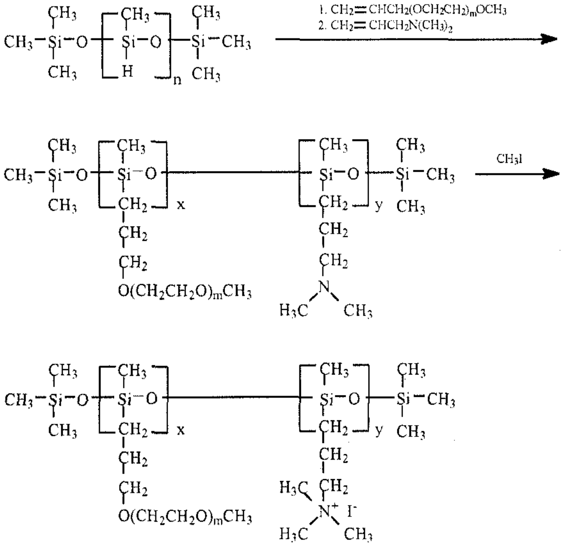
Introduction

In recent years, polymer electrolytes have received considerable attention for their potential application in modern electronics. Being solvent free, complexes of poly(ethylene oxide) (PEO) and alkali metal salts have been studied as polymer electrolytes [1]. However, some problems such as low ionic conductivity at room temperature and inadequate cationic conductivities still remain to be solved for their practical use.

Most polymer electrolytes ever studied are bi-ionic conductors, in which both cations and anions are mobile in opposite directions under the influence of the electrical field. The motion of anti-ions is quite unfavorable because of the formation of a polarization potential across the electrolyte, which will offset the imposed voltage and consequently impede the ion transport. There is migration not only of free cations and anions, but also of triplets and ion clusters in bi-ion conducting systems. In spite of relatively high ion concentration, the ionic conductivity is little improved in these systems. In the case of single-ion conducting systems, only the positively or the negatively charged ions are mobile, while migration of the anti-ions is negligible.

However, the bulk ionic conductivities of these systems at room temperature are lower than that of bi-ion conducting systems, due to the limited number of mobile ions. An effective method to immobilize anions is to anchor them on the polymer backbone or the side chains covalently. There are a number of different approaches to the design of cation conducting polymers [2-7]. Unfortunately, few studies on anionic conductors, in which only anions contribute to ionic conduction, have been reported [8]. Single-ionic conductors containing "hard" backbones suffer drawbacks from low flexibility and high T_g, which inhibit ion transport. It may be expected that polysiloxanes can be used as an ideal material to solve the above problem.

In this paper, novel solvent-free anionic conductors, comb-like polysiloxanes with oligo(oxylethylene) side chains and quaternary ammonium groups, were designed and synthesized, as outlined in Scheme 1. The glass transition temperature and the effect of quaternary ammonium group content on the ionic conductivity as well as temperature dependence of the ionic conductivity were studied.



Scheme 1. Synthesis of polysiloxanes with oligo(oxyethylene) side chains and quaternary ammonium groups

Experimental Part

Materials

Poly(methylhydrosiloxane) (PMHS) and poly(ethylene glycol) methyl ether (PEGME) with average molecular weight 350 were obtained from Aldrich and dried under vacuum at 60 °C for 48 h. Allyl bromide and methyl iodide were A. R. grade and used after freshly distilled. *N*,*N*-dimethylallylamine (DMAA) was synthesized according to the literature [9] and distilled over sodium before use. The hydrosilylation catalyst dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) was prepared as previously reported [10]. Toluene used in the hydrosilylation reactions was first refluxed over sodium and then distilled under nitrogen. All other reagents were A. R. grade and purified by using standard methods.

Synthesis of poly(ethylene glycol) allyl methyl ether (APEGME)

APEGME were prepared by a modified method similar to that described by Lestel et al [11]. Into a round-bottom flask, 0.1 mol PEGME, 0.2 mol NaOH and a large excess of allyl bromide was added. The reaction mixture was refluxed for 24 h under nitrogen. After filtration and evaporation of excess allyl bromide, the crude product was taken up in chloroform. The solution was washed with water and dried over $MgSO_4$. Then the chloroform was removed under vacuum. The allyl group content was determined by ^{1}H-NMR and found to be better than 0.99 per macromolecule.
^{1}H-NMR ($CDCl_3$): δ =5.90 ($-CH=CH_2$), 5.18 ($-CH=CH_2$), 3.97 ($=CHCH_2O-$), 3.49-3.60 (CH_2CH_2O-) and 3.32 ($-OCH_3$).

Synthesis of functionalized polysiloxanes containing oligo(oxyethylene) side chains and dimethylamino groups by hydrosilylation

The functionalized polysiloxanes containing oligo(oxyethylene) side chains and dimethylamino groups were prepared according to the following general procedure, which is described for the specific case of the polysiloxane containing 50 % dimethylamino groups. To a solution of 1.95g APEGME (5 mmol vinyl) in 25 ml toluene, 0.6g PMHS (10 mmol SiH) was added. The mixture was heated at 60 °C under nitrogen for 30 min, and 0.5 ml Cp_2PtCl_2 was then injected through a syringe as a solution in methyl chloride (1 mg / mL). After the mixture was agitated at 90 °C for 24 h, 0.64 g DMAA (7.5 mmol, 50 mol % excess to the residual SiH groups) and 4.8 ml Cp_2PtCl_2 solution was added. The mixture was stirred at 90 °C for another 24h. After the reaction was completed, volatile compounds were evaporated in vacuum.
^{1}H NMR ($CDCl_3$): δ = 3.51-3.61 (CH_2CH_2O-), 3.34 ($-OCH_3$), 2.31-2.59 ($-CH_2N(CH_3)_2$), 1.57 ($SiCH_2CH_2$), 0.51 ($SiCH_2$), 0.08 ($SiCH_3$).

Quaternization of the functionalized polysiloxanes

The quaternization of the above functionalized polysiloxanes was carried out in ethanol. In a typical reaction, the polysiloxane containing 5 mmol dimthylamino groups was dissolved in 25 ml ethanol. Methyl iodide (10-fold excess versus dimthylamino groups) was added dropwise at room temperature. Then the reaction mixture was stirred at 40 °C for 24 h. After completion of the reaction, the solvent and excess methyl iodide were removed under reduced pressure.
^{1}H NMR ($CDCl_3$): δ = 3.39–3.72 ($-OCH_3$, CH_2CH_2O-, $-CH_2N^+(CH_3)_2$), 1.62 ($SiCH_2CH_2$), 0.55 ($SiCH_2$), 0.13 ($SiCH_3$).

Measurements

^{1}H-NMR spectra were obtained on a Bruker DMX-300 spectrometer. Thermal properties were recorded by using a TA 5000 differential scanning calorimeter at a heating rate of 20 K min^{-1}. The ionic conductivity was measured using HIOKI LCR 3520 Hi TESTER at 1 kHz. After drying in vacuum at 60 °C for 24 h, the sample was placed in a poly(tetrafluoroethylene) (PTFE) spacer ring compressed between two stainless steel blocking electrodes and sealed in a testing cell for conductivity measurement. The ionic conductivity (σ) was calculated from the electrolyte resistance value (R) according to the following equation:

$$\sigma = l / RA \qquad \textbf{(1)}$$

where l is the thickness and A is the surface area of the spacer ring.

Results and discussion

Synthesis

Comb-like polysiloxanes with oligo(oxyethylene) side chains and tertiary amino groups were synthesized by hydrosilylation reactions of PMHS with the terminal double bonds of APEGME and DMAA. The content of quaternary ammonium groups in the polysiloxanes or the salt content could by controlled by adjusting the initial molar ratio of APEGME to SiH. Cp_2PtCl_2 was chosen as catalyst because it is soluble in toluene and its catalytic activity keeps high during the period of the reaction [12]. However, the catalytic activity of platinum derivatives can be suppressed in the presence of tertiary amino groups [13]. Under our experimental condition, the reaction of hydrosilylation needs relatively high platinum concentration. The molar ratio of [Cp_2PtCl_2] to [SiH] was maintained to be about 1:1000 when DMAA was added. After the reaction was completed, no peak was found near 4.6 ppm, confirming the complete conversion of SiH. In hexane about 30 % α-addition has been reported in the reaction of poly(dimethylsiloxane-*co*-methylhydrosiloxane) with DMAA [14]. Under these conditions, the proportion of the α-isomers was about 30 %. Initially, the crude products were purified with charcoal to remove any traces of residual catalyst, but it was later found that conductivity results were no different if this procedure was omitted. Subsequently this step was discontinued. Conversion of tertiary amino groups to quaternary ammonium groups was quantitative as indicated by the absence of the signal around 2.45 ppm corresponding to tertiary amino protons in the ^{1}H-NMR spectra of the quaternized polysiloxanes.

Thermal analysis

Typical DSC scans of the comb-like polysiloxanes containing 30 % and 70 % quaternary ammonium side groups are shown in Figure 1. All comb-like polysiloxanes show a single glass transition located at near –70 °C in the studied temperature range, suggesting that the synthesized polymers behaved as homogeneous compatible systems. The glass transition values of the comb-like polymers are displaced toward higher temperature as the number of quaternary ammonium side groups increases, as expected if we consider that the short spacer chains terminated by quaternary ammonium groups is significantly less flexible than that of oligo(oxyethylene) side chains. Results show that T_g increases from –74 °C for the polysiloxane with 30 % ammonium groups to –70 °C for the polysiloxane with 70 % ammonium groups.

According to the DSC measurements, an endothermic peak is observed at about 2.5 °C in all of the present comb-like polysiloxanes, which corresponds to the melt of oligo(oxyethylene) side chains. Thus, all samples have an amorphous character at room temperature. It is also seen that the decrease in the number of oligo(oxyethylene) side chains leads to a melting transition with a broader peak and lower enthalpy value.

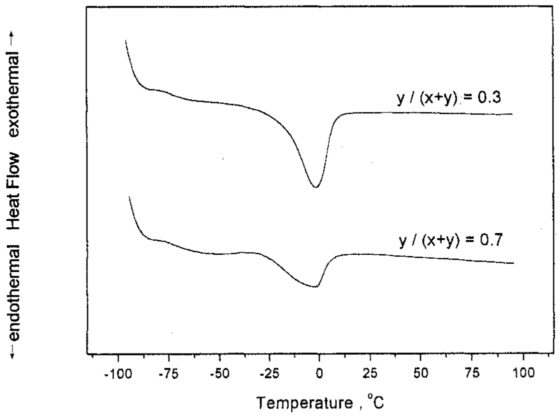


Figure 1. DSC curves for the polysiloxanes containing 30 % and 70 % quaternary ammonium side groups

Ionic conductivity

The majority of polymer electrolytes are bi-ionic conductors in which conduction is a result of both cation and anion motion. The comb-like polysiloxane proposed in this work is a quaternary ammonium salt consisting of a high molecular weight polycation and anions, and migration of the polycation can be negligible. Thus, the present polymer electrolytes can be expected to be anionic conductors. Dependence of ionic conductivities measured at 25 °C, 40 °C, 60 °C and 80 °C on the content of quaternary ammonium groups is illustrated in Figure 2. As the figure shows, all the plots have the same general character. The ionic conductivity initially increases and attains a maximum. After the maximum conductivity is reached, the conductivity gradually decreases with the increase of quaternary ammonium group content. A maximum ionic conductivity is observed at y / (x + y) = 0.3, where 30 % of side chains are quaternized.

Conductivity (σ) is determined by ionic mobility (μ), carrier number (n), and charge (q) as eq. (2) shows:

$$\sigma = \Sigma \mu n q \qquad \textbf{(2)}$$

For the present anion conductors, charge is constant while ionic mobility and carrier number vary with the ratio of oligo(oxyethylene) side chains to quaternary ammonium groups.

At the lower salt region, the increase of quaternary ammonium groups in the polysiloxanes gradually raises the number of charge carriers, resulting in an increase in ionic conductivity. It has been proved that ionic mobility is intimately connected with the segmental motion of the polymer chains. As more of the side chains are quaternized, the progressive increase in T_g leads to a drop in chain flexibility. The ionic conductivity decreases because the mobility of charge carriers is restricted in the more rigid system. The cationic sites in the polysiloxanes are linked together by short spacer chain. Thus, the charge density along the polycation chain is quite high, causing strong Coulombic interaction between I^- and the polycation, which might also result in the decrease in ionic mobility. As a result, there exists a maximum conductivity at a certain salt content. Figure 2 shows that the drop in ionic conductivity under high salt concentration range was considerably reduced with increasing temperature. As the temperature increases, the polymer can expand easily and the free volume increases [15]. The anions can move into the free volume, leading to an increase in ionic mobility. Therefore, the decrease in ionic mobility and ultimately the drop in ionic conductivity at high salt concentration can be reduced.

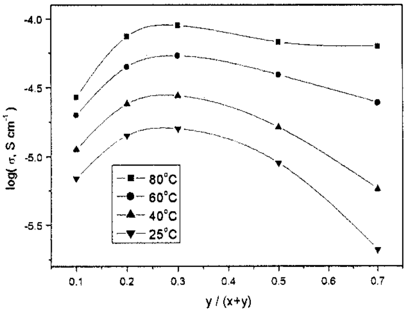


Figure 2. Dependence of the ionic conductivity on the content of quaternary ammonium groups at different temperatures

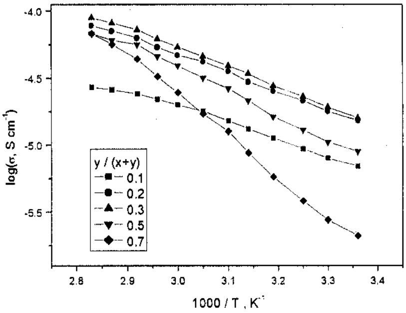


Figure 3. Temperature dependence of the ionic conductivity for the polysiloxanes with different content of quaternary ammonium groups

As shown in Figure 3, the ionic conductivity increases with increasing temperature, which could be rationalized by recognizing the free volume model [16]. At higher temperatures, polymer segmental movement and ionic mobility of the anions dissociated from quaternary ammonium groups would be improved, leading to an increase in ionic conductivity. The highest ionic conductivity was shown for the polysiloxane containing 30 % quaternary ammonium groups in the overall range of temperature investigated. At 25 °C and 80 °C, its ionic conductivities are 1.57×10^{-5} and 8.94×10^{-5} S cm^{-1}, respectively. These values were higher than those for the cationic conductor based on lithium-*N*(4-sulfophenyl) maleimide by almost three orders of magnitude [17]. The reason that may be invoked to account for the high ionic conductivities of the present electrolytes is attributed to the flexibility of polysiloxane backbone and a larger extent of the dissociation of quaternary ammonium salt. In lithium ion conducting systems, oxygen atoms can coordinate to lithium ions, resulting in the formation of ionic cross-links between coordination sites. In the case of present system, the anion is free from the strong binding of ether oxygen in the oligo(oxyethylene) side chains, which will favor ion transport.

It can be noticed from Figure 3 that the ionic conductivities at elevated temperature are almost the same when $y / (x + y) \geq 0.2$. The relatively low conductivity of the polysiloxane containing 10 % quaternary ammonium side groups seem to be caused by the fewer carriers dissociated from the polycation at high temperature.

All comb-like polysiloxanes proposed in this work are entirely amorphous at room temperature, as indicated by the DSC analysis. Figure 3 shows that the conductivity plots are slightly curved rather than linear, which agree well with the general temperature dependence observed for amorphous polymer electrolytes.

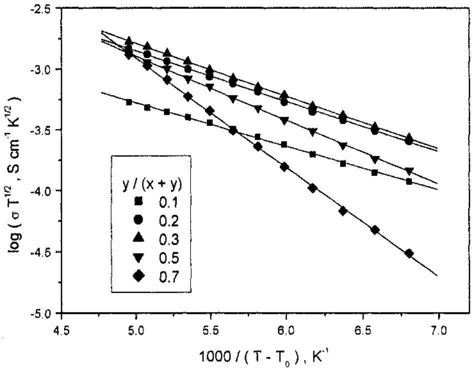


Figure 4. VTF plots of the ionic conductivity for the polysiloxanes with different content of quaternary ammonium groups

Table 1. Ambient ionic conductivities and VTF parameters for the synthesized polysiloxanes

y / (x + y)	σ (25 °C) (S cm^{-1})	A (S cm^{-1} K$^{1/2}$)	E$_a$ (KJ mol^{-1})
0.1	6.84×10^{-6}	0.03	6.83
0.2	1.50×10^{-5}	0.17	7.94
0.3	1.57×10^{-5}	0.25	8.35
0.5	8.87×10^{-6}	0.53	10.06
0.7	2.07×10^{-6}	29.57	16.84

For amorphous polymer electrolytes, the temperature dependence of the ionic conductivity can often be described by the Vogel-Tammann-Fulcher (VTF) equation [18]:

$$\sigma = AT^{-1/2} \exp\{-E_a / R\,(T-T_0)\} \qquad (3)$$

where pre-exponential factor A is related to the number of charge carriers in the

electrolyte system, and pseudo-activation energy E_a is associated with the configurational entropy of the polymer chain. T_0 is related to the equilibrium state glass transition temperature. The Adam-Gibbs configurational entropy model predicts T_0 to be about 50 K lower than T_g of the electrolyte [19].
In our case, T_0 is selected to be T_g –50 K, where T_g is the midpoint of the glass transition. The results of the fitting are shown in Figure 4. From plots $\log(\sigma T^{1/2})$ against $1/(T-T_0)$, good straight line fit was observed. This indicated that the process of ion conduction was closely related to the polymer segmental motion. The fitted parameters A and E_a are calculated and shown in Table 1. Table 1 shows that pre-exponential factor A rises when the ratio y / (x + y) increases, indicating that the number of mobile anions increases with the increase of quaternary ammonium group content.

Conclusions

A series of comb-like polysiloxanes containing oligo(oxyethylene) side chains and quaternary ammonium groups were synthesized. The glass transition temperature increase as the number of quaternary ammonium side groups present in the polysiloxane rises. The influence of the quaternary ammonium group content on the ionic conductivity has been investigated. The optimized comb-like polysiloxane attained peak ionic conductivities of 1.57×10^{-5} S cm^{-1} and 8.94×10^{-5} S cm^{-1} at 25 °C and 80 °C, respectively. Our studies indicate that the temperature dependence of the ionic conductivity follows the VTF equation, implying a free volume ion transport mechanism.

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