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Solvent-Free Cation-Conducting Polysiloxane Electrolytes with Pendant Oligo(oxyethylene) and Sulfonate Groups

Guang-bin Zhou, Ishrat M. Khan, and Johannes Smid*

Polymer Research Institute, Faculty of Chemistry, College of Environmental Science and Forestry, State University of New York, Syracuse, New York 13210-2786

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ABSTRACT: Solvent-free polymeric alkali-metal ion conductors consisting of a comblike polysiloxane with oligo(oxyethylene) side chains and pendant sulfonate groups were synthesized by the hydrosilylation of an allylmethoxypoly(ethylene glycol) and allyl glycidyl ether, followed by sulfonation of the oxirane ring. Due to the tightness of the alkali-metal sulfonate ion pair, conductivities (σ) reach values of only 10^{-6} S cm^{-1} at 25 °C and 10^{-5} S cm^{-1} at 70 °C. They increase in the order Li < Na < K < Cs and exhibit a maximum at a ratio of ethylene oxide (EO) units to cation ≈13. The temperature dependence of σ obeys the Vogel–Tammann–Fulcher relationship $\sigma T^{0.5} = A \exp[-B/(T - T_0)]$, implying a free-volume cation transport mechanism. Additives such as linear and macrocyclic polyethers strongly enhance σ by stretching the interionic $SO_3^-M^+$ ion pair bond and by lowering the glass transition temperature. Particularly effective is tetra(ethylene glycol) (TEG) which at TEG/Na = 1 raises σ to 2×10^{-5} S cm^{-1} at 25 °C and to 10^{-4} S cm^{-1} at 70 °C.

Introduction

Following the early work by Wright et al.[1-3] on the transport of ions in solid-state complexes of alkali-metal salts and poly(ethylene oxide), a large number of studies have been published on the synthesis and properties of ion-conducting solvent-free polymer electrolytes. Reviewed in several recent papers,[4-7] the results have provided new insights into the transport of ionic species in a solid polymer matrix and have led to the design and development of electrochemical devices with thin film polymer electrolytes as the conducting phase.[4-8] In general, ion transport is facilitated by using electrolytes of low lattice energy (e.g., triflates, perchlorates) and polymers with low glass transition temperatures (e.g., polysiloxanes, polyphosphazenes) and containing polar or cation-chelating groups capable of solubilizing the electrolyte. Crystalline regions, while improving mechanical properties, usually impede ion transport. The microviscosity of the material can be lowered and the dissociation of the electrolyte enhanced by means of ion-chelating or polar additives.[9-11] Conductivities exceeding 10^{-3} S/cm at room temperature and 10^{-2} S/cm at 80 °C can be achieved.

In most polymer electrolytes both anion and cation are mobile, but measurements of transference numbers have shown that the anion frequently carries the bulk of the current due to complexation of the cation with chelating polymer substituents. For this reason, and because of enhanced electrode degradation by the mobile anions,[4] several studies have reported the synthesis and properties of polymeric single-ion conductors with the anion bound covalently to the polymer matrix. Examples of such cation-conducting polymers include plasticized poly(styrenesulfonate)[12] and polyelectrolytes with carboxylate[13-15] sulfonate,[15-20] phosphate,[21,22] and phenolate[23] moieties. Although cation transference numbers were found to be equal or close to unity, tight ion pairing and ionic interactions in these systems resulted in relatively low conductivities. However, conductivity enhancements were achieved by means of ion chelating or polar additives.

In preliminary publications[18,19] we reported the synthesis and properties of comblike polysiloxanes with oligo(oxyethylene) side chains and pendant sulfonate moieties (Scheme I). This paper presents a more detailed account of these cation conductors. The effects of cation, temperature, ion content, T_g, and additives on the conductivity of the materials are discussed.

Experimental Section

Materials. Poly(hydrogen methylsiloxane) (PHMS, MW 2260 and 6500) and the hydrosilylation catalyst platinum divinyltetramethyldisiloxane (3% in xylene) were products from Hülls (Petrarch). Allyl chloride, glycidyl isopropyl ether (GIE), allyl glycidyl ether (AGE), methoxypoly(ethylene glycol) (MPEG, MW 350), and other polyglycol derivatives (all Aldrich products) were distilled over CaH_2 under vacuum. The alkali-metal salts in this study were used without further purification.

Synthesis. The synthesis of allylpoly(ethylene glycol) methyl ether from MPEG 350 (abbreviated as AG8) has been described elsewhere.[24] The hydrosilylation of AG8 and AGE with PHMS was carried out under nitrogen in THF at 40 °C. The ratio n/m (see Scheme I) was varied by adjusting the amount of AG8, the molar concentration of which was always less than that of the available SiH groups. In a typical reaction, 0.1 mL of the platinum catalyst was added to a mixture of 6 g (92.7 mmol of SiH) of PHMS (MW 2260) and 18.6 g (47.7 mmol) of AG8 in 90 mL of THF. The solution was kept at 40 °C until the ^{1}H NMR spectrum showed no residual AG8 vinyl protons. To the mixture was then added 7.4 g (64.9 mmol) of AGE, and the reaction continued at 40 °C until no residual SiH bonds could be detected by either IR (2150 cm^{-1}) or ^{1}H NMR (4.61 ppm). The total reaction time varied from 4 to 8 h. The resulting polymer (abbreviated as PA8GE, see Scheme I) was then precipitated three times in a 20/1 (v/v) hexane–THF mixture to remove excess AGE and catalyst. The clear and highly viscous polymer was dried on a high-vacuum line, and its structure was confirmed by IR and by ^{1}H and ^{13}C NMR (Figure 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.06 (m, $SiCH_3$, including end groups), 0.5 (m, $SiCH_2$), 1.61 (m, $SiCH_2CH_2$), 3.25 (s, OCH_3), 2.58 and 2.77 (d, epoxy-CH_2), 3.12 (m, epoxy-CH), 3.32–3.7 (OCH_2). ^{13}C NMR: δ −0.15, −0.56 ($SiCH_3$); 13.27 (s, $SiCH_2$); 22.98 ($SiCH_2CH_2$); 43.85 (epoxy-CH_2); 50.32 (epoxy-CH); 58.65 (s, OCH_3); 69.65–73.64 (OCH_2).

Sulfonation Reactions. Sodium 2-Hydroxy-3-(1-methylethoxy)propanesulfonate. To 10 g (86 mmol) of GIE in a 100-mL water–methanol mixture was added 8.95 g (86 mmol) of $NaHSO_3$. The mixture was reacted at about 60 °C for a few days,[25] the solvent was then evaporated, and the white powdery residue was dried over vacuum at 100 °C. Conversion was quantitative according to IR, ^{1}H NMR, and ^{13}C NMR. The product decomposes above 274 °C and is water soluble.

Poly{[ω-methoxyhepta(oxyethylene)propyl]-methylsiloxane-*co*-[(2-hydroxy-3-(sodiosulfonyl)propyl)oxy-3-propyl]methylsiloxane}, abbreviated as $PSGSO_3Na$ (Scheme I) was obtained by adding a 4-fold excess of $NaHSO_3$ to a 20 wt % PA8GE solution in water–methanol and allowing the mixture to react for several days at about 60 °C. The progress of the reaction was monitored by checking for epoxy protons in the NMR. The sulfonation product was purified by repeated ultrafiltration through a 3000

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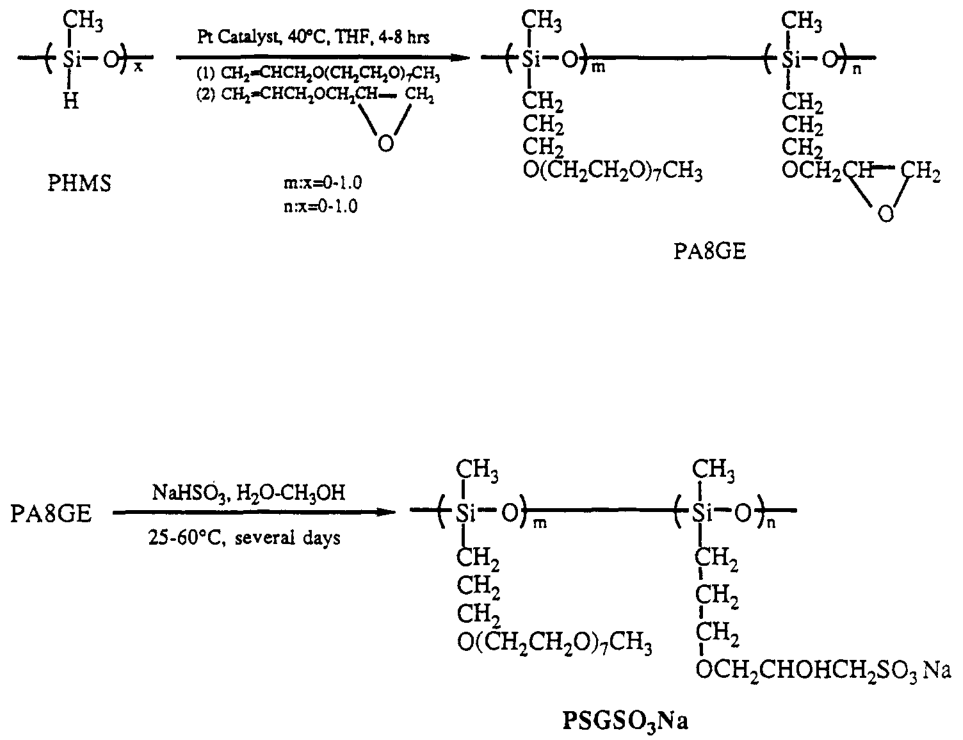
Scheme I



MW cutoff membrane to remove excess $NaHSO_3$. Most of the water was then removed by evaporation, and residual moisture azeotropically with benzene. ^1H NMR (D_2O): δ 0.01 ($SiCH_3$), 0.44 (m, $SiCH_2$), 1.52 (m, $SiCH_2CH_2$), 3.22 (s, OCH_3), 3.25–3.4 (m, $CH_2SO_3^-$, M^+), 3.3–3.7 (m, OCH_2), 3.6–4.0 (CHOH).

$PSGSO_3M$ polymers with other counterions were synthesized by using either $MHSO_3$ (the potassium salt is available) or by cation exchange. In the latter case, a large excess of LiCl, KCl, or CsCl was added to $PSGSO_3Na$ in water and the solution ultrafiltrated through a 3000 MW cutoff membrane. This procedure was repeated at least three times and then again a number of times with deionized water until, with $AgNO_3$, no chloride ions could be detected in the filtrate. The polyelectrolytes were stored in aqueous solution and dried prior to use. Additives were incorporated in the polymer samples by mixing them with an aqueous $PSGSO_3M$ solution to obtain the required additive to SO_3M ratio. The mixtures were dried as described below. To identify the sulfonate content of the polymers, the fraction $n/(n + m)$ of side chains containing a terminal $-SO_3M$ group is shown in front of the polymer name. For example, $0.5PSGSO_3Na$ denotes a polymer in which half the side chains have a terminal SO_3Na group while the rest are $-(CH_2)_3(OCH_2CH_2)_7OCH_3$ chains.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Varian XL100, Bruker WH360, or GE GN-500 spectrometer with $CDCl_3$ or D_2O as solvent. A Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 20 °C/min was used to determine the T_g of the polymers taken at the middle point of the inflection. Polymer samples for DSC and conductivity studies were dried by repeated azeotropic distillation of the $PSGSO_3M$ samples with benzene, followed by vacuum drying at 50–60 °C for at least 1 week. No traces of water could be detected in the infrared spectrum. For conductivity studies polymer samples were pressed into pellets of known thickness and placed between two copper electrodes. Conductivities (ac) were measured under a stream of dry helium using a General Radio Corp. automatic capacitance bridge operating at 1 kHz. Details are described elsewhere.[26] The same cell configuration was used for dc (3-V) conductivity measurements with a Keithley 228A power supply, a millivolt ammeter, and a Keithley solid-state electrometer.

Results and Discussion

Polymer Synthesis. Scheme I depicts the overall synthesis of the comblike polysiloxanes with bound sulfonate groups. The hydrosilylation of the allyl ether AG8 with PHMS is quantitative. The subsequent reaction with excess allyl glycidyl ether (AGE) converts the remaining SiH groups of PHMS into side chains with terminal epoxy groups. Both hydrosilylations appear to proceed without significant side reactions and are very similar to those reported for the same allyl ethers with tetramethylcyclotetrasiloxane.[26,27] Under our experimental conditions (THF, 50 °C) the addition is chiefly to the β-vinyl carbon. In toluene about 20% α-addition has been reported in the reaction with the cyclotetrasiloxane D4H.[28]

A ^{13}C NMR spectrum for one of the polymers is depicted in Figure 1. It clearly shows the presence of the epoxy ring with its C atoms at 43.85 (CH_2) and at 50.32 (CH). The fraction of glycidyl side chains along the polysiloxane backbone was varied by adjusting the initial molar ratio of SiH to AG8. Properties of these polymers are listed in

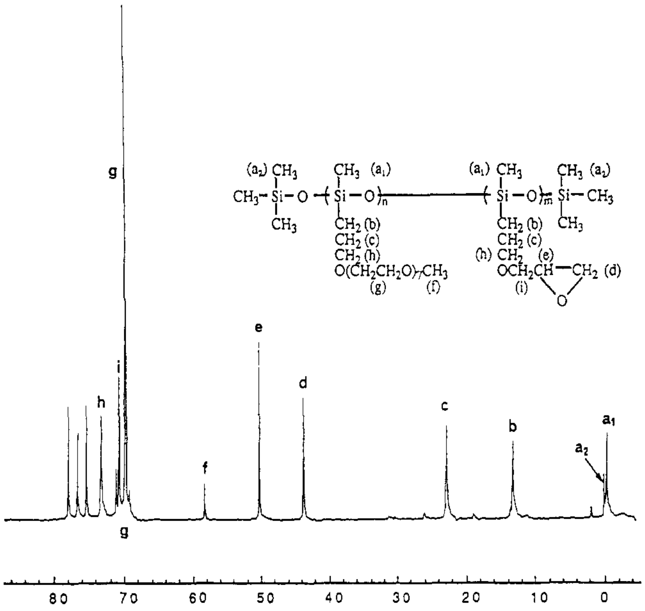


Figure 1. ^{13}C NMR spectrum (25.2 MHz) of PA8GE in $CDCl_3$.

Table I
Properties of Comblike Polysiloxanes with MPEG and AGE Side Chains[a]

n	$n/(n+m)$	MW_n[b]	HLB	solubility H_2O, 25 °C
0	0	15 900	15.36	poor
7.0	0.20	14 000	14.71	good
10.5	0.30	13 000	14.32	good
15.8	0.45	11 600	13.61	good
17.8	0.50	11 100	13.32	cloudy
19.3	0.55	10 600	13.03	poor
24.5	0.70	9 150	11.92	poor
35.0	1.0	6 250	8.18	poor

[a] See Scheme I. MW_n of PHMS = 2260, i.e., DP_n = 35. The average number of propyl glycidyl ether side chains per polymer molecule is denoted by n, and $n + m = DP_n = 35$. [b] MW 2260 + 390m + 114n, 390 being the MW of the allylmethoxypoly(ethylene glycol) used in the synthesis. [c] HLB = 20(349m + 73n)/(2260 + 390m + 114n). The numbers 349 and 73 are the respective molecular weights of the hydrophilic parts of the side chain MPEG and AGE.

Table I. The ratio $n/(n + m)$ (Scheme I) giving the fraction of glycidyl side chains was varied from 0 to 1. Molecular weights were calculated from that of PHMS (MW 2260), assuming all SiH groups reacted with the two allyl ethers.

The neutral polymers are polysoap-type macromolecules with hydrophilic and hydrophobic segments. Their water solubility decreases with an increase in the fraction of glycidyl side chains (Table I). Solutions become translucent when the ratio $n/(n + m)$ approaches the value 0.5 while polymers with $n/(n + m) > 0.7$ are water insoluble. The hydrophile–lipophile balance (HLB) for these polymers was calculated from the expression HLB = $20M_H/(M_H + M_L)$, where M_H and M_L denote the respective formula weights of the hydrophilic and hydrophobic segments of the molecule.[29] The HLB number has been used to correlate chemical structure with properties such as cloud points and critical micelle concentration.[30,31] Values used for M_H and M_L in calculating the HLB number are given in Table I. The results suggest that for HLB > 13.3 the polymer solutions are clear. This is consistent with results reported for nonionic surfactants.[29] The low solubility of the homopolymer $n = 0$, in spite of its high HLB number, results from the tendency of the side chains to crystallize. This was reported and discussed recently[32,33] for similar comb polysiloxanes.

Sulfonation of the epoxy ring[25] yielding the PSGSO$_3$Na polymers is quantitative. Polymers of Table I that were poorly water soluble ($n/(n + m) > 0.5$) were dissolved in methanol–water mixtures. During the sulfonation process the methanol was slowly evaporated to allow complete solubilization of the sodium bisulfite. Although the PSGSO$_3$Na polymers are water soluble, cloudiness develops in concentrated solutions especially for polymers with $n/(n + m) > 0.5$. The aggregation is reversible on dilution, but once the water is removed by azeotropic distillation in benzene, the sulfonated polymers are hard to dissolve. Additives such as crown ethers or polyglycols can be added by swelling the polymers in benzene, followed by drying. Cation exchange in aqueous PSGSO$_3$Na solutions is effective as long as the excess alkali-metal salts are carefully removed by repeated ultrafiltration. Conditions for optimal sulfonation were also checked by reacting glycidyl isopropyl ether with NaHSO$_3$ in water–methanol mixtures. The white sulfonate salt was used to obtain the NMR assignments for the PSGSO$_3$Na polymers. The salt could not be used to make homogeneous polymer electrolytes with the neutral comb poly[siloxane-*g*-oligo(oxyethylene)] due to its poor solubility in organic solvents. A ^{1}H NMR spectrum of PSGSO$_3$Na is shown in Figure 2. The epoxy protons of PA8GE in the 2.7–3.1 region have been replaced by the $CH_2SO_3^-$ protons at 3.25–4 ppm, although there is overlap in this region with the oxyethylene chain protons.

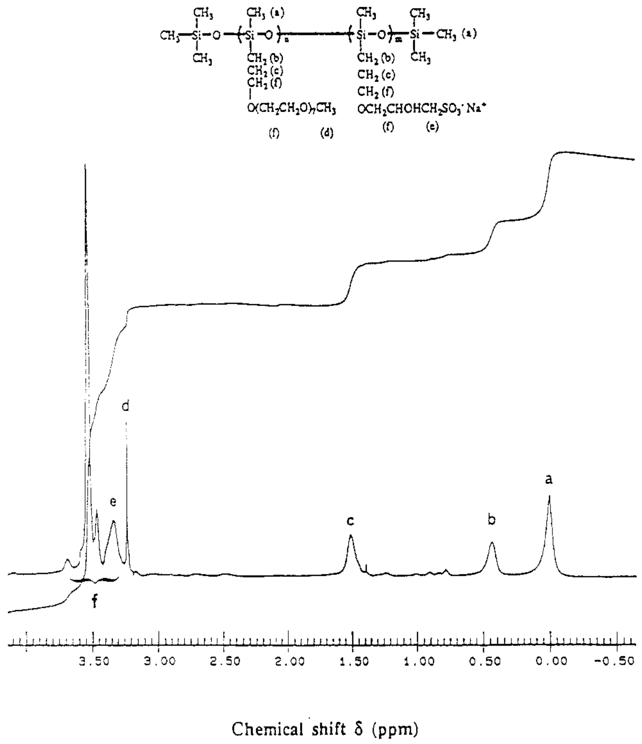


Figure 2. ^{1}H NMR spectrum (300 MHz) of 0.5PSGSO$_3$Na in CDCl$_3$.

Conductivity Measurements. With dc polarization, single-ion conductors generally give stable conductivities. Those for biionic polymer electrolytes rapidly decrease under such conditions due to ion pairing near the anode. Experiments with 0.5PSGSO$_3$Na and 0.5PSGSO$_3$Cs show that the dc conductivities at 25 °C over a 2-h period are quite stable, implying that essentially only the cation is mobile.

The ac conductivities, σ, for a number of PSGSO$_3$M polymers at 25 and 70 °C are given in Table II. They vary from 10^{-8} to 10^{-5} S cm^{-1} depending on the alkali-metal ion, temperature, and sulfonate content. The σ values are much lower than we previously reported for LiClO$_4$ or LiCF$_3$SO$_3$-containing comblike poly[siloxane-*g*-oligo(oxyethylenes)]. For example, at a ratio of ethylene oxide units (EO) to lithium = 15, $\sigma = 7 \times 10^{-5}$ S cm^{-1} at 25 °C for LiClO$_4$-containing polysiloxane with MPEG side chains of eight EO units. At this temperature $\sigma = 1.6 \times 10^{-7}$ S cm^{-1} for 0.5PSGSO$_3$Li (EO/Li = 9).

The conductivities of the PSGSO$_3$M polymers are consistent with those reported for other cation-conducting polysulfonates. These include PEO-blended poly(styrenesulfonates),[12] poly(phosphazenesulfonate),[16] and poly[(2-sulfoethyl)methacrylate lithium).[20] The low conductivities chiefly stem from the tightness of aliphatic alkali-metal sulfonate ion pairs relative to those of alkali-metal perchlorates or triflates. Apparently, chelation of alkali-metal ions with neighboring oligo(oxyethylene) (glyme) chains does not stretch the interionic SO$_3^-$M$^+$ bond into a loose ion pair. Glyme complexation to alkali-metal ions associated with the more delocalized fluorenyl carbanion frequently results in the formation of loose ion pairs and a strong rise in conductivity.[34,35] However, alkali-metal picrates generally form glyme-complexed tight ion pairs in low polarity solvents, even for a glyme with seven or eight EO units.[36]

Temperature Dependence. Figure 3 shows that application of the Vogel–Tammann–Fulcher (VTF) re-

Table II
Conductivity, T_g, and Various Constants for $PSGSO_3M$ Polymers

cation/additive[a]	$n/(n+m)$	T_g, K	$10^{-7}\sigma$(25 °C), S cm^{-1}	$10^{-7}\sigma$(70 °C), S cm^{-1}	C_1	C_2, K	A, K$^{1/2}$ S cm^{-1}	B, K	T_0, K	E_a, eV
Li	0.5	213	1.6	9.3	9.2	43	0.003	916	170	0.35
Li/TEG	0.5		38	190						
Na	0.2	205	0.9	4.2	9.3	50	0.0016	1130	155	0.38
	0.3	206	1.2	7.4	8.7	50	0.004	997	156	0.37
	0.45	209	4.2	28	9.9	50	0.021	1150	159	0.37
	0.50	210	3.2	20	9.1	47	0.010	987	163	0.36
	0.55	213	2.0	12						
	0.70	236	0.45	3	6.3	40	0.0003	584	196	0.45
Na/TEG	0.30		10	69						
	0.50	208	41	290	8.3	65	0.26	1240	143	0.35
	0.70	208	200	1000	8.5	50	0.36	980	158	0.33
	1.0		130	790						
Na/18C6	0.5		25	150						
Na/MPEG	0.5		14	65						
Na/DMTEG	0.5		6.3	35						
K	0.5	213	6.0	38	9.6	45	0.019	990	168	0.37
K/18C6	0.5		41	250						
Cs	0.5	212	11	89	11.9	42	0.103	1150	170	0.42
Cs/TEG	0.5		60	380						

[a] Additives: TEG = tetra(ethylene glycol); 18C6 = 18-crown-6; MPEG = methoxypoly(ethylene glycol), MW = 350. DMTEG = tetra(ethylene glycol) dimethyl ether. Ratio of additive to cation = 1.

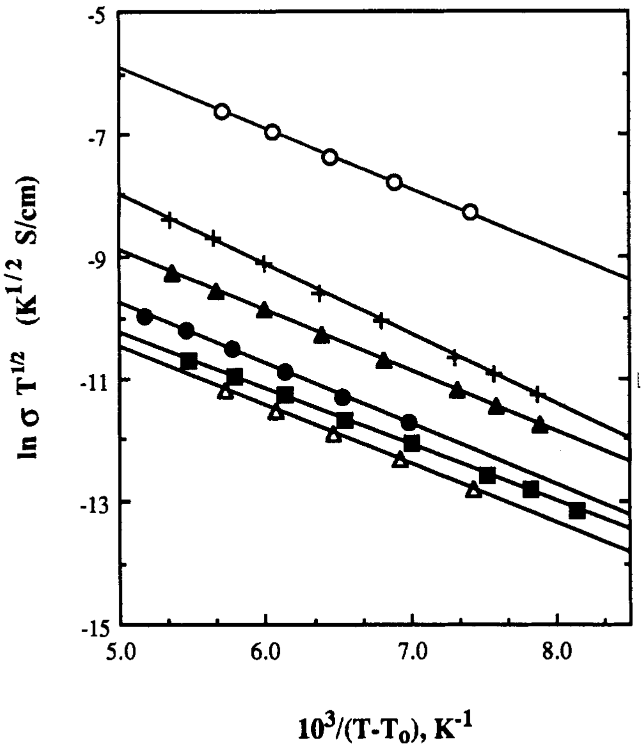


Figure 3. Plots of ln $\sigma T^{0.5}$ vs $10^3/(T-T_0)$ for $PSGSO_3M$ polymers. M and $n/(n+m)$ equal to (△) Na, 0.3; (□) Li, 0.5; (●) Na, 0.5; (▲) K, 0.5; (+) Cs, 0.5; (○) Na, 0.7 with TEG added, TEG/Na = 1.

lationship $\sigma = AT^{-0.5}\exp[-B/(T-T_0)]$ to the conductivity data of a series of $PSGSO_3M$ polymers gives linear plots. It implies a free-volume ion transport mechanism for these single-ion conductors[4,6,21] and also the absence of phase-separated domains. DSC tracings reveal distinct glass transition temperatures (some are listed in Table II) but no indication of crystalline phases in the samples. Crystallinity, often found in solid polymer electrolyte complexes,[1-5] usually lowers the conductivity.

Values of A, B, and T_0 for a number of systems are collected in Table II. A and B are constants related to the number of ion carriers and the activation energy of ion transport, respectively. T_0 is defined as the temperature below which no further entropy loss from conformational changes in the polymer occurs.[4,37] Its value was obtained by applying the best fitting method to ln $\sigma T^{0.5}$ vs $1/(T-T_0)$ plots. The theoretical T_0 value as defined in the WLF equation is 51.6 deg below the T_g.[37] For most reported systems T_0 varies between 40 and 60 deg below the T_g of the polymer electrolyte. Our T_0 values, all of which result in linear plots with correlation factors exceeding 0.999, fall in this range. Table II also lists the activation energies (E_a) derived from the Arrhenius plots ln σ vs $1/T$. The latter are slightly curved, as is usually the case for amorphous polymer elecrolytes.

The VTF equation is mathematically equivalent to the conductivity expression of the WLF equation

$$\log\frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T-T_g)}{C_2+(T-T_g)}$$

where $C_1 = B/2.3(T_g - T_0)$ and $C_2 = T_g - T_0$. The universal constants C_1 and C_2 for amorphous polymers equal 17.4 and 51.6 °C, respectively. Their values obtained for the $PSGSO_3M$ polymers are also listed in Table II. The C_2's are quite close to the C_2 predicted from the WLF equation, but C_1 values are lower. This has been attributed to the fact that the critical volume needed to migrate the ions is less than the volume required to migrate the polymer segments.[38] The deviations may also stem from ionic interactions which are neglected in the WLF equation.

Salt Content. Figure 4 depicts plots of log σ versus the ratio Na/EO for $0.5PSGSO_3Na$ at 25, 50, and 70 °C, as well as a plot of T_g vs Na/EO. The three log σ plots all exhibit a maximum conductivity (σ_{max}) close to a ratio Na/EO = 0.08, or 12 to 13 EO units per Na ion. Maxima of this type are common for both single and biionic polymer electrolytes.[14,16,24,39] Table II shows that the A factor rises with $n/(n+m)$, implying the presence of increased amounts of mobile cations. At the same time the stiffness of the side chains increases due to cation chelation with multiple EO units. Above a ratio $n/(n+m) > 0.45$ (i.e., Na/EO = 0.09) both the number of mobile cations (A factor) and the segmental mobility are lowered considerably as implied by the decrease in A and increase in T_g (Table II). At $n/(n+m) = 0.7$, where 70% of side chains are sulfonated, the T_g has increased from −60 to −37 °C. It is reasonable to assume that at high sulfonate content triple ions, quadruples, and higher ion multiplets are formed. For our single-ion conductors, polymer-bound ionic species such as $-(SO_3)_2^{2-}Na^+$ and $-SO_3^-Na_2^{2+}$ do not contribute to the

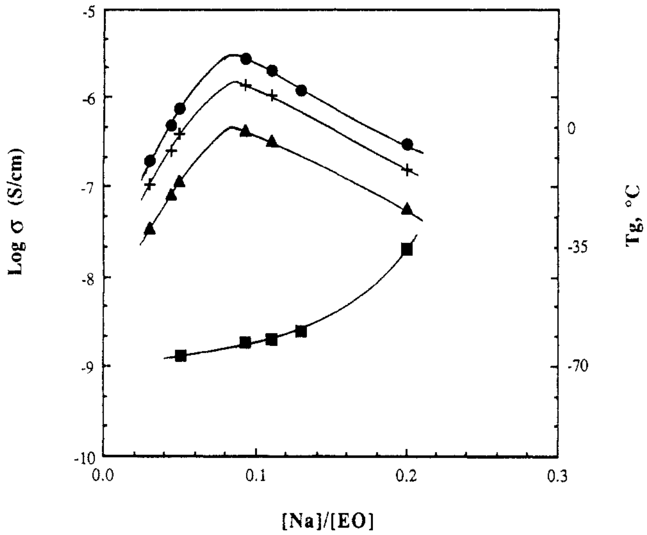


Figure 4. Plots of T_g (■) and of log σ as a function of the ratio Na/EO for PSGSO$_3$Na: (▲) 25 °C; (+) 50 °C; (●) 70 °C.

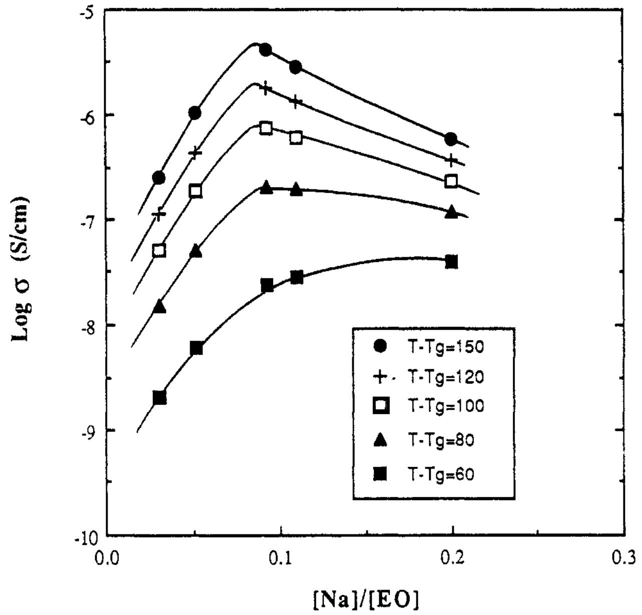


Figure 5. Plots of log σ vs Na/EO for PSGSO$_3$Na at different $T - T_g$ values.

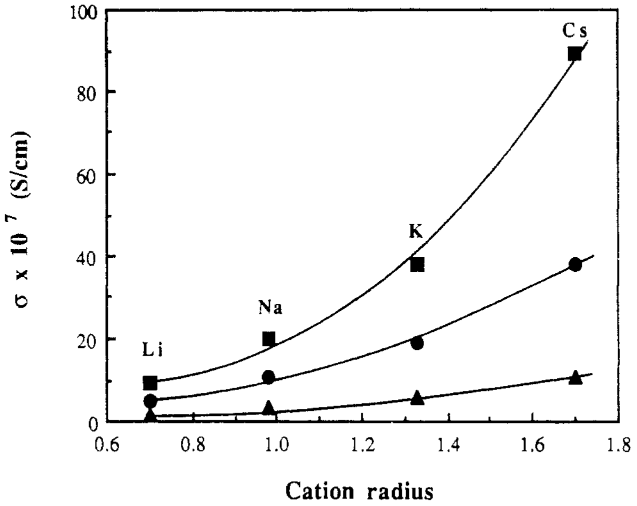


Figure 6. Plots of σ vs the cation radius for 0.5PSGSO$_3$M at (▲) 25 °C, (●) 50 °C, and (■) 70 °C.

cation conduction. They also act as physical cross-links between polymer segments with the Na ions being chelated to EO units, causing the T_g to rise.

To eliminate the T_g effect on σ, log σ is frequently plotted versus the ratio Na/EO at constant $\Delta T = T - T_g$. Figure 5 shows that log σ as a function of Na/EO still has a distinct maximum at high temperatures, but not at low $T - T_g$. A similar behavior was reported for biionic polymer electrolytes and attributed to the formation of ion multiplets.[40] As pointed out, the multiplets are immobilized species. Hence, the σ_{max} at constant $T - T_g$ essentially results from a decrease in the number of mobile cations. That this maximum is more pronounced at high temperature points to an endothermic ion pair dissociation process. For tight ion pairs of charge localized anions the high Coulombic attraction energy is only partially offset by the solvation of free cations formed on dissociation. A reverse behavior may exist for systems with predominantly glyme-separated ion pairs at room temperature. Their conversion to glyme-complexed tight ion pairs is endothermic,[41] implying that an increase in temperature would favor the latter ion pairs, causing a decrease in the number of free ions. Pertinent to the discussion is our recent observation that in solvent-free polymer electrolytes of alkali-metal picrates the interionic ion pair distance is considerably larger than that for the same salt dissolved in a liquid of identical composition.[42,43] Also, the number of EO units available to complete the solvation shell of free alkali-metal ions diminishes at high salt content. This was recently demonstrated in solvent-free solutions of alkali-metal picrates in comb poly(methoxypoly(ethylene glycol) methacrylates).[41] As the lithium picrate concentration was increased from 0.3 to 6.7 M, its optical spectrum clearly shifted to that associated with a tight picrate ion pair. Sufficient free EO units must be available to provide a path for the cations as they migrate through the polymer matrix. Apparently, in our polymers an EO/Na ratio of about 13 is the most favorable salt content for assuring a reasonable conductivity.

Nature of the Alkali-Metal Ion. The dependence of σ on the alkali-metal ion radius for 0.5PSGSO$_3$M polymers at three temperatures is shown in Figure 6. Values for σ and other parameters can be found in Table II. The conductivity increases in the order Li < Na < K < Cs, the difference between Li and Cs being a factor 6.9 at 25 °C and 9.6 at 70 °C. A similar trend in σ was reported for other polymer electrolytes.[4-7]

At $n/(n + m) = 0.5$, the four alkali-metal sulfonate conductors have nearly identical T_g's. A similar observation was reported by Tsuchida et al. for single-ion conductors with pendant carboxylate groups.[14,44] Larger cations can chelate with more EO units. However, diminished accessibility of such sites at the high salt concentrations used in these solid materials may prevent ions such as K and Cs from acquiring the maximum number of EO units. Hence, the number of cation-bound EO units per tight $-SO_3^-M^+$ ion pair may not change much for larger cations. A nearly constant T_g also implies that for $n/(n + m) < 0.5$ physical cross-linking by interionic interactions is minimal. This is not the case for polymers with $n/(n + m) = 0.7$ where T_g has risen to −37 °C (Table II).

With only small changes in E_a and T_g, the significant increase in σ with cation size cannot be rationalized by invoking differences in chain mobilities or in the microviscosities of the respective alkali-metal ion conductors. Tsuchida et al. have argued that the diffusion of the larger K and Cs ions is facilitated by a weaker interaction with EO units.[44] However, such an effect would be offset, in part, by the larger free volume needed by these ions to migrate through the polymer matrix. The authors also rejected their earlier proposition that differences in dissociation constants could explain the trend in conductivities as a function of cation radius. They estimated

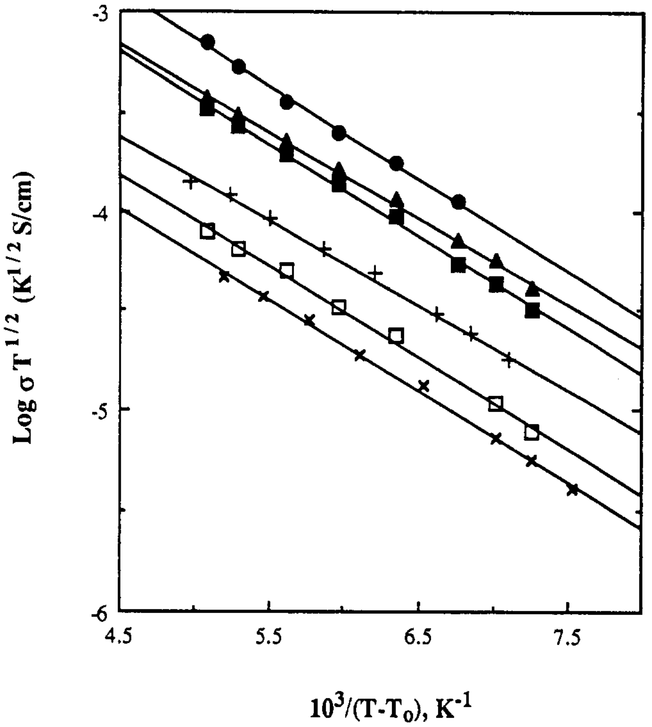


Figure 7. Plots of ln $\sigma T^{0.5}$ vs $10^3/(T - T_0)$ for $0.5PSGSO_3Na$ in the presence of additives: (×) no additive; (□) dimethyl ether of tetra(ethylene glycol); (+) methoxypoly(ethylene glycol)-350; (■) 18-crown-6; (▲) poly(ethylene glycol), MW350; (●) tetra(ethylene glycol).

from ESCA studies a dissociation degree of 0.2 for the sodium carboxylate.[44] It appears to us that for the rather tight COO^-M^+ ion pairs a value of 0.2, is too high, especially considering the relatively low dielectric constant of the polymer matrix. The authors state that variations in σ as a function of cation radius in their system (factors of 51 (Na), 256 (K), and 1160 (Cs) relative to the lithium salt) are too large to originate from differences in dissociation constants. However, such differences are expected to be large for very tight ion pairs. For example, the reactivity of alkali-metal alkoxides in ether-type solvents rapidly increases with cation radius, because of a decrease in aggregation and in the energy required to stretch the ion pair bond. It is our belief that the alkali-metal ion effect on σ for the $PSGSO_3M$ polymers is largely caused by differences in dissociation constants. Determination of such constants in low polarity media would be helpful to support this contention. Of course, in solid ion conductors where salt concentrations are often in the molar range, the dissociation behavior of ion pairs is likely to deviate from that found in more dilute solution.

Tsuchida et al. reported a linear log σ vs log r plot for their polymeric carboxylate salts.[44] The significance of such a relationship is not clear. Our $PSGSO_3M$ polymers also give linear log σ vs log r plots at each of the three temperatures measured, but log σ vs $1/r$ plots are nearly linear as well. The latter relationship would have some physical significance if it is assumed that the ion pair dissociation constants are chiefly determined by the Coulombic attraction energy between the ions of the ion pair.

Additives. The effect of several additives on the conductivity of $PSGSO_3M$ is shown in Figure 7. The temperature dependence of σ again obeys the VTF relationship. For all systems the conductivities are improved, but the extent of the increase depends on the type and amount of additive. Figure 8 shows that on adding tetra(ethylene glycol) (TEG) the σ of $0.5PSGSO_3Na$ at 25 °C increases from 3.2×10^{-7} to 4.1×10^{-6} S cm^{-1} when the ratio TEG/Na reaches unity. At 70 °C the increase is from 2.9×10^{-6} to 3×10^{-5} S cm^{-1}. Above TEG/Na = 1 the further rise in σ is minimal. For the dimethyl ether of TEG (DMTEG) the increase in σ (25 °C) at DMTEG/Na = 1.6 is only a factor of 1.5 at 25 °C and 1.8 at 70 °C. For methoxypoly(ethylene glycol) (MPEG-350) the enhancement is a factor 4.4 at 25 °C and 3.2 at 70 °C, while for 18-crown-6 (18C6/Na = 1) σ rises by factors of 8 and 7.5, respectively. The increase with poly(ethylene glycol) (PEG 350) lies between that of 18C6 and TEG.

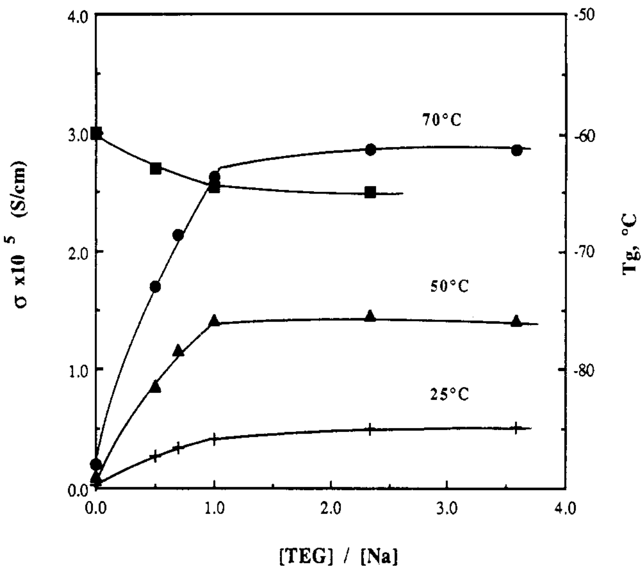


Figure 8. Effect of tetra(ethylene glycol) on the T_g (■) and the conductivity of $0.5PSGSO_3Na$: (+) 25 °C; (▲) 50 °C; (●) 70 °C.

Most additives used in polymer electrolytes are either high dielectric constant compounds, e.g., propylene carbonate, or cation-chelating ligands such as linear or macrocyclic polyethers. The former function by promoting ion pair dissociation through enhancing the permitivity of the polymer matrix, while the latter, used in our work, facilitate free ion formation through effective cation solvation. Both types of additives will also lower the microviscosity of the ion-conducting material. This results in improved segmental mobility of the polymer chains and further enhances the conductivity.

Of the additives shown in Figure 7, TEG is the most effective in raising σ. It exceeds even 18-crown-6, an excellent Na^+- and K^+-chelating ligand. The ineffectiveness of DMTEG, a good cation-solvating agent, suggests that the hydroxyl groups in TEG play a dominant role. Interaction of the OH group with the SO_3^- anion is believed to be the main reason for the effectiveness of TEG.[12] Two observations support this proposition. First, we found that CH_3SO_3Na is not soluble in solvents such as THF, CH_3OH, or DMTEG but the salt dissolves in TEG and in a mixture of DMTEG and CH_3OH. The same was found for the salt $HOCH_2CH_2SO_3Na$. In the solubilization process the OH of TEG interacts with SO_3^- while the EO units solvate the cation. Apparently, both interactions contribute to the stretching of the $SO_3^-M^+$ bond of $PSGSO_3M$ and to the enhancement of σ. Secondly, infrared absorption bands in the 3300–3400-cm^{-1} region of $PSGSO_3Na$–TEG mixtures demonstrate the presence of hydrogen-bonded sulfonate groups. Similar findings were reported earlier by Hardy and Shriver for mixtures of poly(styrenesulfonate) with PEG or MPEG.[12] Also, while their mixtures with PEG were compatible, phase separation occurred with the dimethyl ether derivatives.[12]

The additives also have a plasticizing effect. The decrease in T_g is small for $0.5PSGSO_3Na$ (from −60 to −65

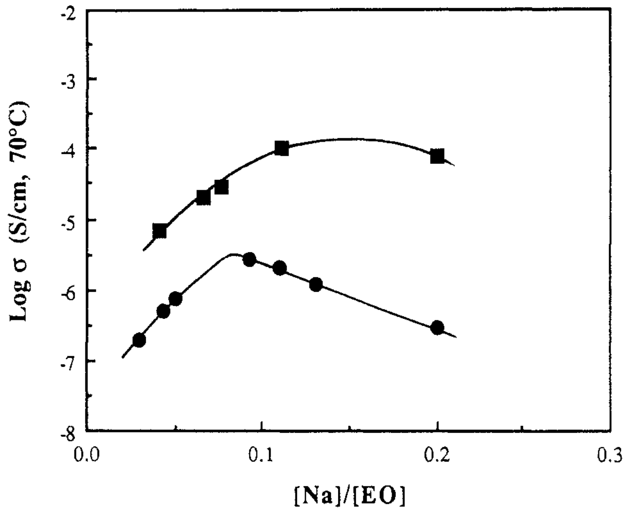


Figure 9. Plots of log σ vs Na/EO for $PSGSO_3Na$ in the absence (●) and presence (■) of tetra(ethylene glycol).

°C), but for 0.7$PSGSO_3Na$ at TEG/Na = 1 the T_g changes from −37 to −65 °C (Table II). The effect is larger at high sulfonate content. For example, at 25 °C σ increases by factors of 8, 13, and 333 for 0.3, 0.5-, and 0.7$PSGSO_3Na$, respectively, while at 70 °C the numbers are 9.3, 14.5, and 333, all at TEG/Na = 1. The fully sulfonated polymer (1.0$PSGSO_3Na$) is a highly crystalline, hard material of very low conductance. Adding TEG renders it completely amorphous, with $\sigma = 1.3 \times 10^{-5}$ S cm^{-1} at 25 °C and 7.9×10^{-5} S cm^{-1} at 70 °C for TEG/Na = 1.

The additive also affects the dependence of σ on the EO/M ratio. Figure 9 shows that the σ_{max} for 0.5$PSGSO_3Na$ at EO/Na = 13 in the absence of TEG shifts to EO/Na = 5 and is also much shallower (the ratio EO/Na includes the EO units of TEG). We reported a similar observation for PEO networks and $LiClO_4$ with added propylene carbonate.[10] In both cases a lower T_g is the chief cause for the shift in σ_{max}. Restrictions in chain motions at high salt content are alleviated by the presence of the additive. A shallow maximum in σ is advantageous when the plastic electrolyte is used in a battery configuration since on discharge the electrolyte resistance will remain more constant.

Finally, the effectiveness of TEG in raising the σ of $PSGSO_3M$ decreases in the order Li > Na > Cs, the same order as for the energy required to dissociate the $SO_3^-M^+$ ion pair. For 0.5$PSGSO_3M$ the σ at 25 °C increases at TEG/M = 1 by a factor 24 for Li, 13 for Na, and 5.5 for Cs, while the respective numbers at 70 °C are 20, 14.5, and 4.3. The σ value for 0.5$PSGSO_3K$ with TEG continuously decreased with time, even after repeating the measurements three times. Slow phase separation may be a possible explanation. The trend in the cation effect on TEG addition can be rationalized by noting that stretching of the very tight $-SO_3^-Li^+$ ion pair will affect the σ of this salt more than when the looser $SO_3^-Cs^+$ is stretched. Also, effective solvation of large cations requires more EO units, and it would be interesting in this respect to check the effect of the length of added PEG molecules on such cation conductors.

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