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Notes

Comb-Branched Polymer Electrolytes Based on Poly[(4,7,10,13-tetraoxatetradecyl)methylsilane] and Lithium Perchlorate

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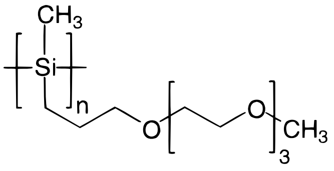
Introduction

The development of solid polymer electrolytes with ionic conductivity values σ of $10^{-5}-10^{-2}$ S/cm at either ambient or moderately elevated temperatures remains a topical issue.[1] Prerequisites to ensure fast ion transport are good solubility of the inorganic salt (Li^+X^-) in the polymer matrix as well as an amorphous structure that permits sufficient segmental motions of the polymer chains at low temperatures; i.e., "low-T_g" materials are preferred.

Recently, functionalized polysilanes $[-(SiR'R'')_n-]^2$ containing oligo(oxyethylene) moieties incorporated in (at least) one of their side chains (R′ and/or R″) have been prepared.[3−5] The polar nonionic poly[(4,7,10,13-tetraoxatetradecyl)methylsilane] (**1**, Chart 1) is a representative example. Both in solution [^{13}C NMR (CD_3CN)[4]] and in the solid state (UV, thin films),[5,6] strong interactions between Li^+ ions and the tri(oxyethylene) groups were subsequently identified after the addition of increasing amounts of $LiClO_4$. Unfortunately, the synthesis of **1** by conventional Wurtz-type coupling (Na in refluxing toluene)[3,4] gave high molecular weight polymer only in poor yield (ca. 1−11%) and, thus, hampered the study of its applicability as a polymer matrix for polysilane-based solid polymer electrolytes. This is of interest since hitherto only solid polymer electrolytes derived from poly[(ethoxyethoxybutyl)-methylsilane] and $LiOSO_2CF_3$ have been investigated.[7] Unfortunately, however, for this polysilane the highest ionic conductivity σ reported at 293 K was found to be only 1.25×10^{-7} S/cm (Li^+/repeating unit ratio of 0.50).

Recently, however, some of us reported that by using another polymerization procedure (C_8K, THF, 273 K) polysilane **1** is accessible in fair yield (30%) and with high purity.[8] Since **1** is an amorphous, low-T_g(DSC, 193 K)[4] comb-branched polymer[1,9,10] containing pendent tri(oxyethylene) units, we were prompted to assess its applicability for ionic conductivity studies.[1] Here we report that solid polymer electrolytes $LiClO_4$/**1** indeed give considerable ionic conductivity σ values over a wide temperature range. The results show that the ionic conductivities of these $LiClO_4$/**1** polymer electrolytes compare favorably with those reported earlier for related comb-branched polymers.[1]

Chart 1



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Experimental Section

Poly[(4,7,10,13-tetraoxatetradecyl)methylsilane], **1**, was prepared according to a literature procedure using C_8K in THF at 0 °C, and all polymer properties were in agreement with those previously reported.[8]

Solid polymer electrolytes $LiClO_4$/**1** were prepared by mixing THF solutions of **1** and $LiClO_4$ in different ratios. The solvent was removed under a N_2 stream and, subsequently, under reduced pressure (0.01 mbar). Samples with $LiClO_4$/repeating unit of **1** ratios of 0.01, 0.05, 0.10, and 0.50 were prepared and studied; they correspond to Li^+/O ratios of 1/400, 1/80, 1/40, and 1/8, respectively.

For the dielectric relaxation spectroscopy (DRS) the $LiClO_4$/**1** polymer electrolytes were spread between two aluminum parallel plate electrodes with a diameter of 20 and 30 mm, which were separated by three spacers of 50 μm (quartz fibers). The measurements were performed with a Solartron 1260 frequency response analyzer in combination with a TNO dielectric interface (frequency 10^{-2} Hz−1 kHz) and a Hewlett-Packard 4284A precision LCR meter (frequency 1 kHz−1 MHz). Ionic conductivity values σ (S/cm) of the bulk of the samples were determined by application of sinusoidal voltages. The values of σ were obtained by fitting up to two Havriliak−Nagami relaxation functions[11] and an ohmic conduction term to the complex permittivity ϵ^* in the frequency range 0.1 Hz−1 MHz and the temperature range 123−373 K.[12,13]

Results

The samples were prepared by mixing THF solutions of **1** and $LiClO_4$ in the ratios presented in Table 1 (see Experimental Section). The temperature dependence of σ in this $LiClO_4$/**1** series was determined with dielectric relaxation spectroscopy (DRS). The glass transition temperature [T_g(DRS)] of the different samples was obtained by an activation energy fine structure analysis[14] of the α-relaxation peak (Table 1). It should be emphasized that for pristine **1** T_g(DRS) is in excellent agreement with T_g(DSC), viz. 191.8 and 193 K, respectively.[4,6] In line with expectation, T_g(DRS) shifts to higher temperatures concomitant with increasing Li^+ loading.

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Table 1. T_g(DRS) as Well as VTF and WLF Parameters Derived from Conductivity Fits for Solid Polymer Electrolytes $Li^+/1$

Li^+/repeating unit **1**	T_g(DRS)^a [K]	VTF parameters			WLF/free volume parameters			
		log σ_0 [S/cm]	E_v [kJ/mol]	T_v [K]	C_2 [K]	C_1	$\alpha_f \times 10^4$ [1/K]	$f(T_g)$
0	191.8	−4.61	9.47	155.1	36.7	13.5	8.78	0.032
0.01	191.8	−3.78	6.31	166.0	25.8	12.8	13.18	0.034
0.05	194.0	−2.52	6.90	166.5	27.5	13.1	12.06	0.033
0.10	197.8	−1.64	8.36	164.1	33.7	12.9	9.96	0.034
0.50	215.2	0.39	12.45	164.2	51.0	12.7	6.68	0.034

[a] See Figure 1.

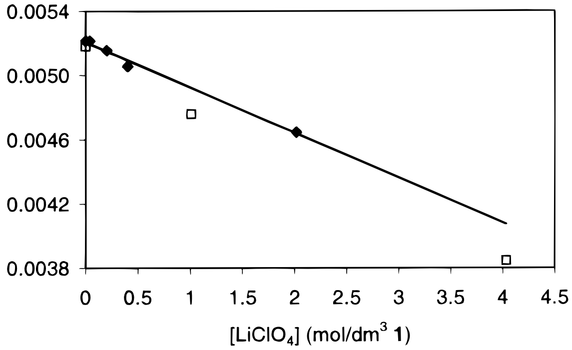

Figure 1. $1/T_g$ vs $LiClO_4$ concentration (in mol/dm^3 **1**)[15] of solid polymer electrolytes Li^+/**1**. Besides T_g(DRS) (◆) values, T_g(DSC) literature values[4,6] (□) are presented. Only the T_g(DRS) data are used in the linear regression.

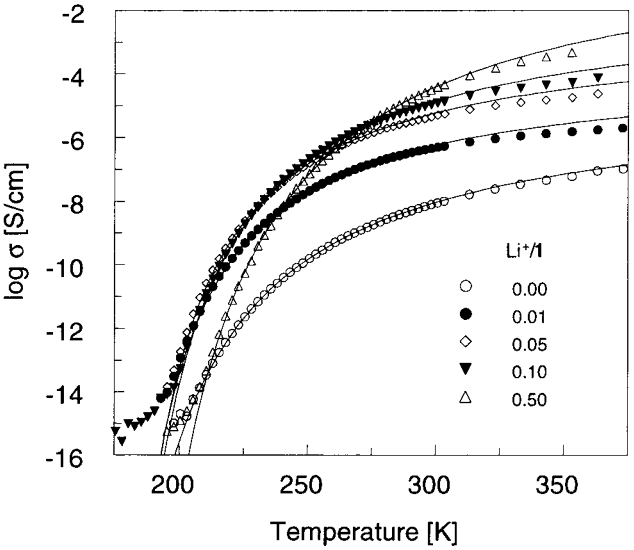

Figure 2. Log σ vs T for solid polymer electrolytes Li^+/**1**.

Within the $LiClO_4$/**1** series $1/T_g$ vs Li^+ concentration gave an excellent linear relationship ($r^2 = 0.99$, Figure 1).[15] The slope (-2.8×10^{-4} dm^3/(mol K)) is identical with that determined for, among others, main-chain polymers containing tri(oxyethylene) sequences (-2.8×10^{-4} dm^3/(mol K)[12,13]) and isocyanate cross-linked poly(ethylene oxide) networks (-2.7×10^{-4} dm^3/(mol K)[16]). This indicates that the shift of T_g is mainly controlled by the extent of Li^+ complexation with the tri(oxyethylene) sequences. This leads to increased stiffening of the side chains and consequently will hamper main-chain segmental motions of the polymer.

Whereas pristine **1** has an ionic conductivity σ of 5.98×10^{-9} S/cm (293 K) and 5.94×10^{-8} S/cm (353 K),[17] for the Li^+/**1** 0.50 sample σ is 2.12×10^{-5} S/cm (293 K) and 4.76×10^{-4} S/cm (353 K, Figure 2). Evidently, upon Li^+ loading, σ increases by almost 4 orders of magnitude. It is noteworthy that considerable σ values are found already for the Li^+/**1** 0.10 sample [8.58×10^{-6} S/cm (293 K) and 5.25×10^{-5} S/cm (353 K)]. In addition, σ at 293 K of the Li^+/**1** 0.50 sample is ca. 100 times higher than that of the related poly[(ethoxyethoxybutyl)-methylsilane]-based electrolyte (vide supra).[7] Apparently, the availability of only two oxygen atoms per side chain in the latter polysilane is insufficient to achieve efficient Li^+ complexation. Hence, polysilane **1** represents an interesting novel matrix for solid polymer electrolytes, which upon $LiClO_4$ loading possesses σ values that compare favorably with those earlier reported for related comb-branched oligo(oxyethylene) functionalized polymer matrices.[1]

Since the temperature dependence of σ for all $LiClO_4$/**1** samples is non-Arrhenius-like, it was analyzed using the Vogel–Tammann–Fulcher (VTF) equation (Table 1).[18–20] The accurate VTF fits in the temperature window $T_g + 25$ K $< T < T_g + 100$ K imply a strong interrelation between σ and chain segment relaxations above T_g (Figure 2).

Interestingly, solution as well as solid-state (thin film) UV spectroscopy revealed that the position of the characteristic λ_{max} (300 nm; $\sigma \rightarrow \sigma^*$ transition) of **1** at 293 K[4] as well as its extinction coefficient ϵ_{max} is not affected by $LiClO_4$ loading.[6] The solid-state λ_{max} values of **1** and the Li^+/**1** samples indicate that the catenated silicon backbone retains its random coil[2] conformation; i.e., addition of $LiClO_4$ does not have a marked influence on the silicon backbone conformations! This supports our conclusion that all $LiClO_4$ has indeed dissolved and that Li^+ complexation presumably leads to the pairing of pendent tri(oxyethylene) moieties. Consequently, segmental motions of the polymer will be hindered, predominantly by stiffening of the side chains (Figure 1).

In line with this interpretation, the VTF analysis shows that the Vogel scaling temperature T_v, i.e., the temperature at which segmental motions are slowed to infinite relaxation times, is nearly independent of the level of Li^+ loading, while the Vogel activation energy parameter E_v increases with increasing Li^+ content in the side chains (Table 1).

Under the likely assumption that decomplexation of the Li^+ ions is triggered by the segmental motions, the ion mobilities μ_i are related to the free volume and therefore obey the Williams–Landel–Ferry (WLF) equation,[21–23] which gives another description of the temperature dependence of σ. Application of the VTF parameters E_v and T_v together with T_g allows the calculation of the "universal constants C_1 [$C_1 = E_v/(2.30RC_2) \sim 16–17$[24]] and C_2 ($C_2 = T_g - T_v \sim 51–52$ K)" of the WLF equation (Table 1). Whereas C_2 increases with increasing Li^+ loading due to the increase of T_g, C_1 is nearly constant (ca. 13). Hence, in the case of Li^+/**1** the changes of C_2 and E_v compensate each other. Consequently, the fractional free volume at T_g, i.e., $f(T_g)$

[$= b/(\ln 10C_1)$ with $b = 1$[21]], is nearly unaffected by $LiClO_4$ addition, and its temperature coefficient $\alpha_f[f(T_g)/C_2]$ changes concomitantly with C_2 (Table 1). The constancy of T_v and C_1 (ca. 13, which deviates moderately from the "universal" value 16−17[24]) supports the view that the occurrence of Li^+ complexation between neighboring side chains represents an additional factor affecting the temperature dependence of σ.[25]

Conclusions

The solid polymer electrolytes $LiClO_4$/**1** have good ionic conductivity properties. Since polysilanes also possess semiconductor-like properties [electronic (hole) conductivity via the catenated silicon backbone],[2] the study of mixed ionic and electronic conductivity can now be initiated using the $LiClO_4$/**1** and related solid polymer electrolytes.[26]

References and Notes

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(15) For **1** a density of 1 g/cm^3 was assumed giving the Li^+ concentration in mol/dm^3 **1**. Note that T_g(DSC) results[4,6] for some Li^+/**1** samples are in line with T_g(DRS) (cf. also Figure 1).

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(17) Pristine **1** most likely contains traces of K^+ from the C_8K mediated polymerization.[8] Already at low levels of Li^+ loading σ increases markedly (Li^+/**1** 0.01 σ of 3.76×10^{-7} S/cm (293 K) and 1.52×10^{-6} S/cm (353 K); see also Figure 2 and Table 1).

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