Cryptand Addition to Polyelectrolytes: A Means of Conductivity Enhancement and a Probe of Ionic Interactions

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Abstract: As a means of probing ionic interactions in and enhancing the conductivity of single-ion conducting polymer electrolytes, the effect of the cryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt[2.2.2]) on the conductivity of the sodium salt of poly{poly{{[ω-methoxypoly(oxyethylene)]propyl}methylsiloxane}-*block*-[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butyl]methylsiloxane} (**1**) was studied. Both samples with and without cryptand display the characteristic VTF temperature dependence of their conductivities ($\sigma = AT^{-1/2}\exp[-B/(T - T_0)]$). The addition of crypt[2.2.2] results in a 15-fold increase in conductivity, independent of temperature and concentration. The glass transitions of the materials are unchanged upon cryptand addition, even at high ion concentrations where the glass transition is dependent on ion content. Both the materials with and without crypt[2.2.2] exhibit a conductivity maximum with concentration at [Na]/[ethylene oxide] = 2% (1.4×10^{-6} S/cm neat and 1.7×10^{-5} S/cm with crypt[2.2.2] at room temperature). A model based on equilibrium expressions for free-carrier formation is shown to be more appropriate than one based on an activated process because the former more closely describes the temperature-independent effect of crypt[2.2.2] on the conductivity.

Introduction

The discovery that solutions of salts dissolved in polar polymers exhibit relatively high ionic conductivities has led to a great deal of interest in polymeric materials as potential electrolytes in batteries and other device technologies.[1−8] A principal drawback of these so-called polymer−salt complexes stems from the high transport number of the anionic species.[9−14] In most battery applications, the electrode reactions only involve the cation. As a result, anionic mobility may hamper the performance of a cell through polarization effects.[15] This has led many workers to study solid polyelectrolytes, where the anion is attached to the polymer backbone and, therefore, the transference number for the cation, t_+, is unity.[16−23] In this paper, the use of ion-sequestering agents to reduce ion-pairing effects and perhaps overcome the conductivity limitations caused by ion−polymer cross-links in polyelectrolytes is investigated.

Polyelectrolytes typically have conductivities 1−2 orders of magnitude lower than those of polymer−salt complexes. One origin of this difference is that the anion is usually the predominant charge carrier in polymer−salt complexes; the transport number of the anion is typically greater than 0.5 since the motion of the cation is hindered by solvation from the polymer host.[9−14] Fixing the anion in an otherwise similar material then results in a significant decrease in conductivity. How this particular factor will influence performance of the electrolyte in batteries is unclear since the anion is typically not involved in the electrode reactions. Indeed, simulations have shown that polyelectrolytes with conductivities 1 order of magnitude less than those of polymer−salt complexes can perform as well as in certain battery applications.[15]

Another factor that reduces the conductivity of polyelectrolytes relative to salt complexes is the strong localization of the cation about immobile anionic sites. The extreme of this localization corresponds to the tight ion pair which significantly reduces the number of available conduction ions. As discussed in more detail elsewhere,[24] the localization may be considered in terms of a more general correlation effect resulting from Coulombic attraction between the cation and the fixed anion. Because of these localization effects, ion pairing becomes a central issue in single-ion conducting polymer electrolytes.

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Ion pairing can be reduced through the use of weakly basic and/or sterically hindered anionic centers. Another method is through the use of additives. Two general approaches have been taken. The first involves the addition of high dielectric constant small molecule solvents, such as propylene carbonate,[25−28] which increase conductivity through plasticizing effects and an increase in the dielectric constant. Another approach is to add molecules that specifically target cation solvation, such as cryptands or crown ethers.[29−32]

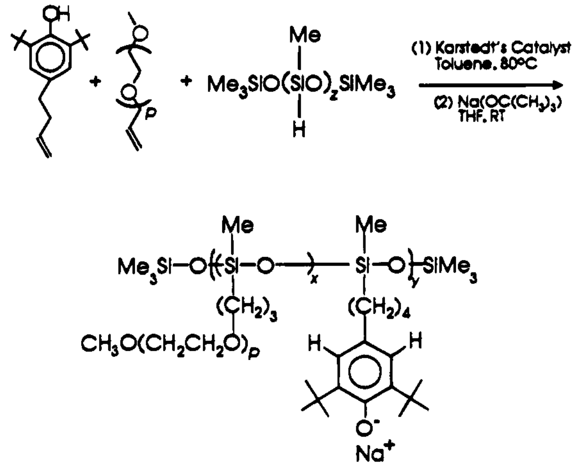
Although cryptands have been shown to improve significantly the conductivity of polyelectrolytes,[30,31] they have not been extensively exploited and questions remain with regard to their action. For example, the effect of cryptand addition as a function of ion concentration has not been studied. To date, the conductivity improvements brought about by cryptands have generally been attributed to weakening cation−anion interactions. An intriguing possibility that has not been thoroughly investigated is the potential of cryptands to prevent ion−polymer cross-linking. As the ion content of a polymer electrolyte increases, the glass transition temperature also increases due to the formation of ion−dipole cross-links.[33−35] These cross-links result in the conductivity eventually decreasing with increasing salt concentration, thereby significantly limiting the maximum conductivity obtainable. The introduction of cation-sequestering agents may prevent these ion−polymer cross-links and thus minimize the effects of increasing salt content on the segmental mobility of the polymer host. To date, there have been few studies of this effect. Zhou *et al.* investigated the action of tetrakis(ethylene glycol) (TEG) as a function of ion content in a siloxane-based polyelectrolyte.[32] Indeed, the conductivity maximum shifted to higher concentrations upon addition of TEG with the largest improvements in conductivity being observed for the samples with the highest ion concentrations. Due to their higher formation constants for the complexation of alkali metal ions, cryptands might more effectively reduce ion-dipole cross-links, thereby pushing the conductivity maximum to higher ion concentrations. Cryptands have been shown to be superior to crown ethers in improving the conductivity of polyelectrolytes,[30] but their effect on ion−polymer cross-links has not been investigated.

In this paper, the effects of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt[2.2.2]) on a siloxane-based polyelectrolyte first synthesized by Yeh *et al.* (**1** in Scheme 1)[21-23] are investigated. This material is an ideal candidate for these studies since it exhibits among the highest conductivity of any cation-conducting polyelectrolyte. The fixed anionic center in this material is a sterically hindered phenolate, and therefore it should not form tight ion pairs with the cryptand-encapsulated cation.

Results and Discussion

The sodium salt of poly{poly{{[ω-methoxypoly(oxyethylene)]-propyl}methylsiloxane}-*block*-[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butyl]methylsiloxane} (**1**) was synthesized according to the procedure developed by Yeh *et al.*[21,22] as summarized in Scheme 1. The hydrosilylation reaction of poly(hydrogen methylsiloxane) (PHMS), poly(ethylene glycol) allyl methyl ether, and 2,6-di-*tert*-butyl-4-(3-butenyl)phenol in the presence of Karstedt's catalyst proceeded in excess of 95% yield in 12 h at 80 °C. Nonetheless, residual SiH groups were evident from IR spectroscopy ($\nu = 2160\ \text{cm}^{-1}$) and estimated at less than 5% by NMR spectroscopy ($\delta = 4.7$ ppm). These residual groups persisted even with the addition of fresh catalyst and additional poly(ethylene glycol) allyl methyl ether, and reaction times in excess of 96 h at 80 °C. The product of the above hydrosilylation reaction was then allowed to react with sodium *tert*-butoxide to yield **1.** The reaction with sodium *tert*-butoxide resulted in the disappearance of the SiH IR resonance. This may be due to the reaction of the liberated *tert*-butyl alcohol with residual SiH groups. Indeed, control experiments show that *tert*-butyl alcohol readily reacts with PHMS under the experimental conditions.

Scheme 1. Synthesis of the Sodium Salt of Poly{poly{{[ω-methoxypoly(oxyethylene)]propyl]}methylsiloxane}-*block*-[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butyl]methylsiloxane} (1)



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The presence of unreacted SiH groups made complete control of the stoichiometry difficult. As a result, some loss of excess poly(ethylene glycol) allyl methyl ether was observed when the product was heated at 80 °C and 5×10^{-4} Torr to remove the solvent. Evacuation at elevated temperatures was continued until the evolution of allyl ether ceased (minimum of 4 days). 2,6-Di-*tert*-butyl-4-(3-butenyl)phenol was allowed to react completely with PHMS before addition of the poly(ethylene glycol) allyl methyl ether, and the phenol-containing polymer was reacted with sodium *tert*-butoxide in the original reaction pot.

In all cases, the resulting polymers were characterized by ^{1}H NMR spectroscopy. To aid in assigning the resonances, the ^{1}H NMR homonuclear correlation spectrum for one concentration was collected (Figure 1). The resulting assignments and the integrated intensities provide the stoichiometry data for polymers a-f, listed in Table 1. With the exception of the two most concentrated samples, for which only a glass transition was observed, the polymers exhibited both glass and melt transitions, T_g and T_m (Table 1). The materials are dark brown and range from a soft tar-like consistency at high phenolate concentration to viscous liquids at low phenolate concentrations. Addition of cryptand (in all cases, the Na:crypt[2.2.2] ratio was 1:1) resulted in little change in the bulk physical properties of the samples. The density of all of the materials with and without crypt[2.2.2] fell in the range 1.08 ± 0.02 g/cm^3.

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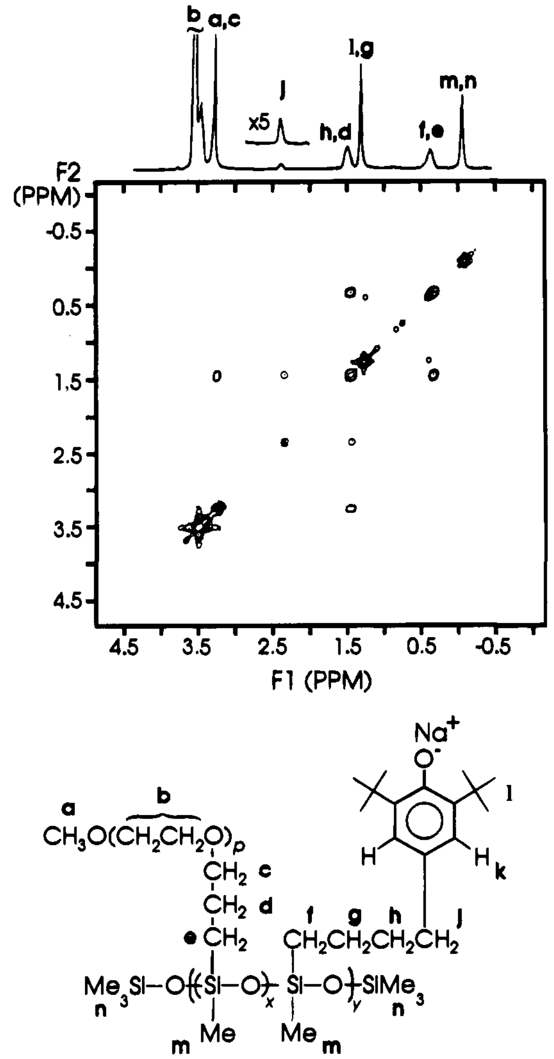

Figure 1. Two-dimensional ${}^1H$ NMR homonuclear correlation spectrum for **1** in $CDCl_3$. The phenyl resonance, k, occurs downfield at δ 6.9 ppm.

Table 1. Stoichiometries and Thermal Analysis data for **1** with and without crypt[2.2.2]

			without crypt[2.2.2]		with crypt[2.2.2]	
	100/*xp*	p	T_g (K)	T_m (K)	T_g (K)	T_m (K)
a	0.97	6.9	196	262	196	261
b	1.6	6.3	196	253	194	253
c	1.9	6.0	193	257	194	253
d	2.2	6.8	198	253	197	253
e	4.4	6.0	203		202	
f	8.4	6.5	208		207	

[a] *x* and *p* are as defined in Figure 1.

The temperature-dependent conductivities of **1** with and without added crypt[2.2.2] are shown in Figures 2 and 3 over a range of concentrations. These data were collected on heating, and the discrepancies with the corresponding cooling curves were generally less than 5–10%. The solid lines represent fits to the VTF equation:

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

where σ is the conductivity and A, B, and T_0 are fitting parameters. The fitting parameters given in Table 2 were determined with T_0 fixed 20 K below T_g. These data demonstrate that the mechanism of diffusion for Na^+ and $[2.2.2]{\cdot}Na^+$ in **1** are similar, with both mobile species strongly coupled to the motions of the host polymer.[2,36,37]

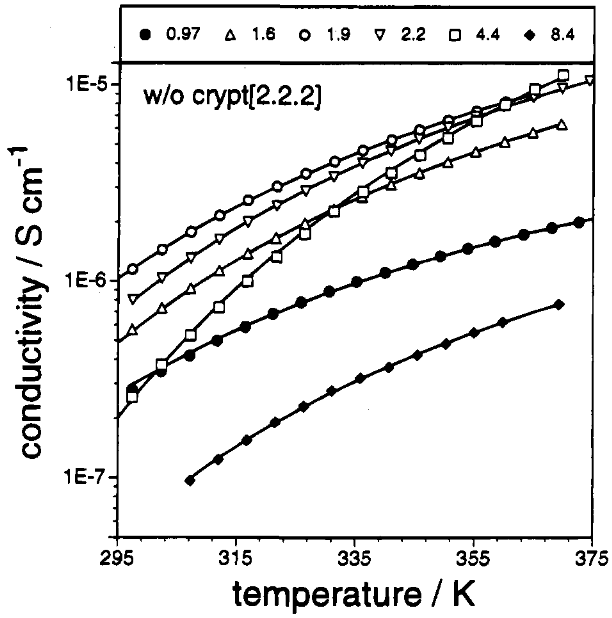

Figure 2. Temperature-dependent conductivity of **1** as a function of overall ion percent concentration. The legend values are 100/*xp* = ([phenolate]/[ethylene oxide]) (%), where *x* and *p* are as defined in Scheme 1. The solid lines represent fits to the VTF equation using the parameters given in Table 2.

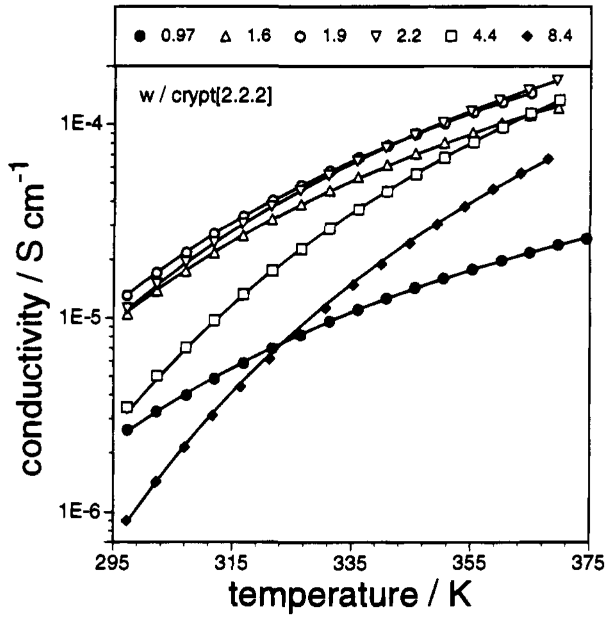

Figure 3. Temperature-dependent conductivity of **1** with crypt[2.2.2] as a function of concentration. The legend values are 100/*xp* = ([phenolate]/[ethylene oxide]) (%), where *x* and *p* are as defined in Scheme 1. The solid lines represent fits to the VTF equation using the parameters given in Table 2.

The concentration-dependent room-temperature conductivity of **1** is shown in Figure 4, where the concentration is expressed as the ratio of phenolate groups to ethylene oxide units ([phenolate]/[EO]). The data pass through a maximum, indicating that the effects of increasing carrier density are overcome by the accompanying decrease in segmental mobility. This decrease in segmental mobility arises from virtual cross-linking and has an obvious signature in the increased glass transition temperatures of the two most concentrated samples (e and f in

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Table 2. Conductivity Data for **1** with and without crypt[2.2.2][a]

	without crypt[2.2.2]				with crypt[2.2.2]			
	A	B	σ(29 °C)	σ(73 °C)	A	B	σ(29 °C)	σ(73 °C)
a	0.001	643	3.5×10^{-7}	1.2×10^{-6}	0.0227	757	3.3×10^{-6}	1.4×10^{-5}
b	0.0088	827	7.3×10^{-7}	3.6×10^{-6}	0.19	843	1.4×10^{-5}	7.1×10^{-5}
c	0.009	759	1.4×10^{-6}	5.9×10^{-6}	0.263	870	1.7×10^{-5}	8.9×10^{-5}
d	0.0135	823	1.0×10^{-6}	5.3×10^{-6}	0.3756	914	1.5×10^{-5}	8.8×10^{-5}
e	0.0996	1150	3.7×10^{-7}	4.4×10^{-6}	1.14	1146	5.0×10^{-6}	5.5×10^{-5}
f	0.00087	740	7.0×10^{-8}	4.2×10^{-7}	1.26	1248	1.4×10^{-6}	2.4×10^{-5}

[a] *A* in units S cm^{-1} K$^{1/2}$, *B* in units of K, and σ in units of S cm^{-1}.

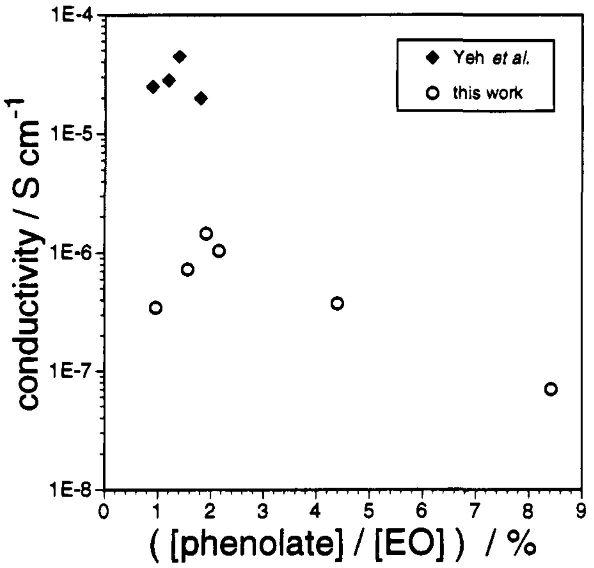

Figure 4. Room-temperature conductivity of **1** as a function of overall ion percent concentration. The data of this work (○) are compared with those reported in the following: Yeh, T. F.; Okamoto, Y.; Skotheim, T. A. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 205 (◆). The conductivity maximum reported by Yeh *et al.* is approximately 30-fold higher than that observed here.

Table 1). The maximum room-temperature conductivity is 1.4×10^{-6} S/cm. By contrast, Zhou *et al.*[32] report a maximum room-temperature conductivity of 4.2×10^{-7} S/cm for the closely related poly{{[ω-methoxypoly(oxyethylene)]propyl}-methylsiloxane-*co*-{{[(2-hydroxy-3-sodiosulpho)propyl]oxy}-3-propyl}methylsiloxane} (PSGSO$_3$Na). Ganapathiappan *et al.*[17] report a maximum of 7×10^{-7} S/cm at room temperature for poly{bis{{[ω-methoxypoly(oxyethylene)]propyl}oxy}phosphazene-*co*-{[ω-methoxypoly(oxyethylene)]propyl}{[(3-sodiosulpho)propyl]oxy}phosphazene}. Although the conductivities determined in the present study are good relative to those of other polyelectrolytes, they are still significantly lower than those reported by Yeh *et al.* for the same polymer.[22] The values reported by Yeh *et al.* are also plotted in Figure 4. The conductivity maximum observed in the present research occurs at higher concentrations, and the maximum conductivity is 30-fold lower than that observed by Yeh *et al.*

A possible explanation for this disparity is unintentional cross-linking in our material, say from the hydrolysis and condensation of SiH moieties or *tert*-butoxy groups introduced during the conversion to the sodium salt. Indeed, the work of Yeh *et al.* demonstrates that intentional cross-linking of their polymer with 1,5-hexadiene reduces its conductivity by approximately 60-fold at room temperature.[23] This decrease was observed for partial cross-linking (22% of the SiH groups used as cross-link sites) of a sample with [phenolate]/[EO] ≈ 1.4%.[38] The cross-linked sample was reported to be a solid. All of the samples reported here are liquid at concentrations [phenolate]/[EO] ≈ 1.4%, indicating that extensive cross-linking has not occurred. The materials reported in this work also exhibit glass transition temperatures similar to those reported by Yeh *et al.* (compare T_g of samples a-c in Table 1 with 193 K reported by Yeh *et al.* for similar concentrations). As discussed below, however, T_g is not very sensitive to cross-link density in these polymers.

For comparison, a cross-linked sample of **1** was prepared (1,5-hexadiene used as the cross-linking agent) with [phenolate]/[EO] = 1.3% and 20% of the SiH groups used as cross-linking sites. The resulting polymer was a rubbery solid with a room-temperature conductivity too low to be measured with our cell geometry and instrumentation. At 346 K, the conductivity of this sample is 9.9×10^{-8} S/cm as compared to 3.6×10^{-6} S/cm for sample b ([phenolate]/[EO] = 1.6%) at 346 K. This 35-fold decrease upon 20% cross-linking is reasonably consistent with the observations of Yeh *et al.*, again supporting the conclusion that significant unintentional cross-linking has not occurred in our materials. Interestingly, cross-linking resulted in only a 5 K increase in T_g. Apparently, cross-linking between backbone chains does not significantly affect the glass transition of the polyether side chains. The small change in T_g suggests that the conductivity decrease observed upon cross-linking arises in part from the nonpolar character of the cross-linking agent.

Yeh *et al.* used poly(oxyethylene allyl) methyl ether of slightly lower average molecular weight (M_N = 346 g/mol) than ours (M_N = 380 g/mol) and employed Speier's catalyst instead of Karstedt's catalyst as used in the present work. It is unlikely that the small difference in polyether chain length could be responsible for a 30-fold change in conductivity. For the polymer PSGSO$_3$Na discussed above, the room-temperature conductivity changes by less than a factor of 3 when the polyether chain length is increased from approximately 7 to 11 ethylene oxide units per side chain (while maintaining the same [ethylene oxide]/[Na] ratio).[39] Although this is a significant variation, it does not approach the factor of 30 observed here for a much smaller chain length difference. We employed Karstedt's catalyst because it is slightly more active and generally results in fewer side reactions than Speier's catalyst.[40] There are no obvious reasons to expect the choice of catalyst to result in significant differences, since colloidal platinum is believed to be the active species for both of these catalysts.[41] Limited structural characterization in the previous report makes further comparisons difficult.

In turning to the effects of crypt[2.2.2] on the conductivity of these polyelectrolytes, it is helpful to discuss the temperature-dependent conductivity in terms of an appropriate theoretical framework. The temperature-dependent conductivity of polymer electrolytes can be described in terms of the free volume model[42]

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(38) This stoichiometry was not directly reported. As a result, it was inferred from the conductivity of the un-cross-linked sample reported in the same figure.

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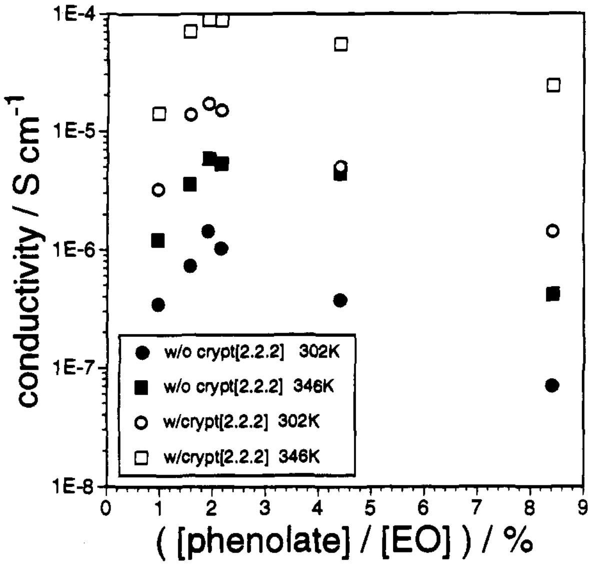

Figure 5. Comparison between the conductivities of **1** with and without crypt[2.2.2]. The increase in conductivity observed upon addition of crypt[2.2.2] is relatively independent of concentration and temperature.

to yield

$$\sigma = \frac{nq^2D_o}{k_BT^{1/2}}\exp\left[-\frac{\gamma v^*}{v_o\alpha(T-T_o)}\right] \qquad (2)$$

where k_B is Boltzmann's constant, D_o and γ are constants, v^* is the critical free volume required for displacement, α is the expansivity, v_o is the van der Waals volume, and n and q are the carrier density and charge. To simplify the discussion, we collect terms that depend exclusively on the polymer host into two constants, A' and B', yielding

$$\sigma = A'nq^2T^{-1/2}\exp\left[\frac{-B'v^*}{(T-T_o)}\right] \qquad (3)$$

Hence, cryptand addition can affect the conductivity by altering T_o, v^*, or n.

Figure 5 compares the conductivity of **1** with and without crypt[2.2.2] at 302 and 346 K. Addition of cryptand results in a significant increase, on average a factor of 15, over the entire concentration range (see also Table 2). Furthermore, the increase is nearly the same at both 302 and 346 K. Table 1 shows that T_g, and hence T_o, is barely altered upon the addition of crypt[2.2.2], indicating that cryptand solvation has little affect on virtual cross-linking. As a result, the maximum in the concentration-dependent conductivity still persists and is not shifted to higher concentrations. If indeed crypt[2.2.2] is sequestering sodium ions, it is surprising that T_g is unchanged, especially at high ion concentrations where T_g depends on ion concentration. On the basis of the difference between formation constants for sodium ion complexation by crypt[2.2.2] and open chain ethers, the majority of the sodium ions are expected to be complexed by crypt[2.2.2]. The B parameters extracted from the VTF fits increase upon crypt[2.2.2] addition, consistent with cryptand–cation complexation. The increase in $B = B'v^*$ may result from the larger critical volume required for crypt-[2.2.2]•Na$^+$ mobility than for polymer segment rearrangement. The small change in T_g upon cryptand addition suggests that virtual cross-linking is a general Coulombic effect which is more complicated than the simple complex formation between the polymer host and the cations.

The small change in T_o and the slight increase in the critical volume, v^*, do not explain the improvement in conductivity observed upon addition of crypt[2.2.2]. In fact, the increase in v^* suggests a decrease in conductivity. The increase must then result from effects to the carrier density, n. In the case of noninteracting sodium ions, the carrier density is simply the stoichiometric sodium ion density, n_o. If, however, a certain number of ions are "unavailable" for conduction, say tied up in strong ion pairs, then n in eq 3 reflects only the number of "free" carriers. The notion of free carriers has long been used in the discussion of solid state ionics. In the study of polymer–salt complexes, the following modification to the VTF equation was proposed to describe the creation of free carriers from ion pairs:[7,36]

$$\sigma = n_o\exp\left[-\frac{E_a}{k_BT}\right]A'q^2T^{-1/2}\exp\left[-\frac{B'v^*}{T-T_o}\right] \qquad (4)$$

Here, E_a is the activation energy for the creation of single ions from pairs. Within this model, addition of cryptand is expected to lower the activation energy for free-carrier generation. Phenomenologically, this would result in a decrease in the B parameter extracted from VTF fits (an increase is observed) as illustrated by rewriting eq 4

$$\sigma = n_oA'q^2T^{-1/2}\exp\left[-\frac{1}{T-T_o}\left[B'v^*+\frac{E_a}{k_B}\left(1-\frac{T_o}{T}\right)\right]\right] \qquad (5)$$

To explain a 15-fold increase in conductivity at these temperatures, the change in E_a would have to be significant. The Bk_B values from the VTF fits are on the order of 8 kJ/mol, whereas the ΔE_a required to explain the 15-fold increase at 300 K would be approximately 7 kJ/mol. This would result in a change in the VTF Bk_B parameter, $\Delta Bk_B = \Delta E_a(1 - T_o/T)$, of 3 kJ/mol at 300 K with $T_o = 175$ K. Such a large perturbation should be apparent. Furthermore, the prefactor A extracted from the VTF fit would be largely unchanged within this model because A depends on the stoichiometric density of sodium ions, which is the same with or without cryptand. Contrary to this expectation, the data in Table 2 show that the largest effect of crypt[2.2.2] addition is to increase the prefactor A rather than to change B. The failure of this model to appropriately describe n is not unexpected. As has been discussed by several workers, the process of salt dissolution in polymers is an entropically unfavored process.[43,44] As a result, increased temperature will decrease the number of free ions, rather than increase them as predict by eq 4. Essentially, eq 4 fails since it is based on an enthalpic argument.

Another approach, toward modeling the concentration-dependent conductivity in polymer–salt complexes,[45–47] is based on equilibrium carrier formation. For polyelectrolytes, one can model the number of free carriers in terms of the following equilibrium:

$$\mathrm{ac} + \mathrm{p} \overset{K_1}{\rightleftharpoons} \mathrm{a} + \mathrm{cp} \qquad (6)$$

where a is the fixed anion, c the cation, and p the solvating unit of the polymer host. The solvated cation, cp, represents

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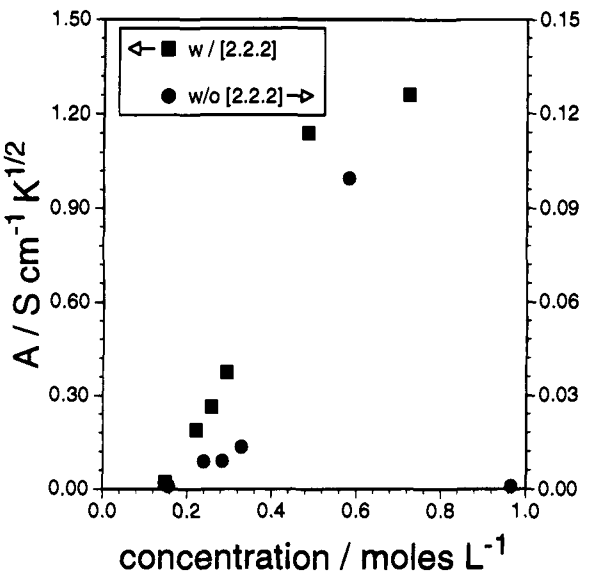

Figure 6. *A* parameter extracted from the VTF fits to the conductivity data in Figures 2 and 3. For the sample with crypt[2.2.2], ■ refer to the scale on the left ordinate, while for the neat polyelectrolyte, ● refer to the right ordinate scale.

the charge carrier. Hence *n* is now related to the stoichiometric sodium ion density, n_o, through the equilibrium constant K_1. The addition of cryptand results in another relevant equilibrium that can contribute free carriers, namely

$$\text{ac} + \text{crypt[2.2.2]} \overset{K_2}{\rightleftharpoons} \text{a} + \text{crypt[2.2.2]}\cdot\text{c} \qquad (7)$$

Here, crypt[2.2.2]·*c* is the cryptand−cation complex. From comparison of the formation constants for ion complexation by cryptand and open chain ethers, K_2 should be much larger than K_1. As a result, the number of carriers is expected to increase upon cryptand addition. Of course, the magnitude of the increase will depend on the equilibrium constants. If K_1 is large, nearly all of the available cations are free carriers and cryptand addition will have little effect. Phenomenologically, any increase in *n* will be largely reflected by an increase in the *A* parameter extracted from VTF fits. Indeed, this is what is observed.

Figure 6 compares the *A* parameter as a function of concentration for **1** with and without cryptand (note the different ordinate scales). Previously, concentration was loosely used to mean the [phenolate]/[EO] ratio. In turning to a discussion of carrier density, we now use concentration in its conventional sense. As a result, the dilution effect of adding cryptand is accounted for. For the samples with a small [phenolate]/[EO] ratio, this represents only a small change, whereas for sample f, crypt[2.2.2] addition results in a decrease of sodium ion molarity from 0.97 to 0.72 M. The *A* parameter for the most concentrated sample of f without cryptand is anomalous, and it will be discussed shortly. With the exception of this sample, the prefactor increases with increasing phenolate concentration for samples with and without cryptand.

The increase in *A* with phenolate concentration is qualitatively expected. The exact functional form of *n*(c) depends on the precise values of the relevant equilibrium constants, however (note that *n* is now the sum of cp and crypt[2.2.2]·c concentrations). For a very large constant, indicating nearly complete dissociation, $n \approx n_o$ and *A* will vary linearly with phenolate concentration. Assuming similar mobilities for Na^+ and Na·crypt and that K_2 is large and hence $n \approx n_o$, the 15-fold increase in *A* upon crypt[2.2.2] addition implies that K_1 must be roughly $5 \times 10^{-4}\, n_o$ since $n \approx 0.07 n_o$.

The *A* factor for the most concentrated sample drops sharply relative to the lower concentrations, implying very tight ion pairing and a pronounced decrease in K_1 with increasing concentration. In the work of Zhou *et al.* on $PSGSO_3Na$, the same decrease is observed and *A* begins to drop after a conductivity maximum at [Na]/[EO] = 7%. For concentrations lower than this, the *A* parameter increases with sodium concentration as observed here.

If the model based on equilibrium constants is appropriate, it must predict that the effect of cryptand is relatively temperature independent. For a large ion pair dissociation equilibrium constant, temperature independence is expected since $n = n_o$, independent of temperature. For the neat polyelectrolyte, however, K_1 is expected to be small and *n* will have some temperature dependence. In order to describe the situation correctly, this temperature dependence must be relatively weak. In the limit $K_1 \ll n_o$, the carrier density is given by

$$n = (K_1 n_o)^{1/2} \qquad (8)$$

The temperature dependence of K_1 is related to the standard enthalpy for the dissociation reaction 6, $\Delta H°_1$, by the Gibbs−Helmholtz equation. Under the usual assumption of the enthalpy being temperature independent, the variance of *n* with temperature is given by

$$\frac{n_{T_2}}{n_{T_1}} = \left\{ \exp\left[-\frac{|\Delta H°_1|}{k_B} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \right] \right\}^{1/2} \qquad (9)$$

Here, $\Delta H°_1 < 0$, indicating that the pair dissociation reaction is exothermic and that the carrier density decreases with increasing temperature. Thus, the model predicts a variation in *n* with temperature, but this variation is smaller than the activated picture of eq 4. It is difficult to quantitatively estimate the temperature variation of *n* without knowledge of $\Delta H°_1$. Such data are very limited. Schantz[48] has analyzed Raman data on pair dissociation for $NaCF_3SO_3$ and $LiClO_4$ dissolved in poly(propylene oxide). Although these systems are very different than the polyelectrolyte studied here, they at least provide some estimate as to the magnitude of $\Delta H°_1$. The thermodynamic analysis of Schantz yielded −4 ± 8 and −13 ± 8 kJ/mol for $NaCF_3SO_3$ and $LiClO_4$, respectively. With $\Delta H°_1$ taken as −8 kJ/mol, eq 9 predicts a 20% change in the carrier density from 300 to 350 K. For the activated picture, the same E_a would correspond to a 50% change. More importantly, a treatment based on equilibrium expressions allows a significant difference between the samples with and without crypt[2.2.2] at the same temperature without necessarily implying a significant deviation from VTF behavior because a large $\Delta H°_1$ is not necessarily required to explain this difference. In contrast, the activated description leading to eq 4 requires a large E_a to explain the 15-fold increase upon crypt[2.2.2] addition, and thus, it implies a significant deviation from VTF behavior.

In the discussion above, the free carriers were assumed to be either the polymer-solvated or cryptand-encapsulated cation and the equilibria treated were those for dissociation of ion pairs to form these carriers. In reality, other equilibria may be involved and the actual carriers may be somewhat different. Even in this more complicated situation, the essential predictions of the above discussion will still hold as long as the number of free carriers is still modeled by the equilibria for their formation. A general discussion of free carriers within the context of the dynamically disordered hopping model[49] has been presented elsewhere.[50]

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There is one additional mechanism that may be important in explaining the difference between samples with and without cryptand. Throughout the above discussion, the carriers have been assumed to diffuse independently. As discussed in more detail elsewhere,[24] the Coulomb interactions between mobile carriers and the fixed ionic centers are likely to introduce correlation effects. The presence of these interactions will cause carriers, although perhaps not strongly ion paired, to be localized about the fixed anionic centers. As a carrier starts to move away from a fixed ionic center, the long-range Coulomb force will tend to oppose its motion. This will introduce a correlation factor into the diffusion equations above. The role of cryptand in weakening these interactions is somewhat uncertain. At short range, it should be effective owing to steric effects. At longer ranges, the cryptand can act by screening the Coulomb interactions. It is not clear, however, how much more effective than the polymer host crypt[2.2.2] would be at screening these interactions. Furthermore, the degree of correlation will be temperature dependent. Thus, if this mechanism were dominant, cryptand addition should result in less conductivity improvement as the temperature is raised. This is counter to our observations, but the temperature range of the measurements is relatively narrow.

Summary

Addition of crypt[2.2.2] to poly{poly{{[ω-methoxypoly(oxyethylene)]propyl}methylsiloxane}-*block*-[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butyl]methylsiloxane} (**1**) results in approximately a 15-fold increase in conductivity. For the most part, this increase is independent of temperature and concentration. The addition of crypt[2.2.2] has almost no effect on the glass transition temperature of the polymers, even in the high concentration regime where T_g is significantly affected by salt content. The invariance of T_g upon crypt[2.2.2] addition indicates that the mechanism for the elevation of T_g by ionic centers is more complicated than simple cation−polymer cross-links or that the sodium ion is not completely encapsulated by the crypt[2.2.2] molecule.

Consistent with the larger critical volume required for crypt[2.2.2] motion relative to that for polymer segment motion, the *B* parameter extracted from VTF fits to the conductivity data increases slightly upon cryptand addition. Modifications to the VTF equation that model the number of "free" carriers in terms of an activation energy for their formation fail to describe the constant increase in conductivity upon cryptand addition as a function of temperature. The largely concentration- and temperature-independent increase is most accurately described by modeling the number of "free" carriers by appropriate equilibrium expressions. The 15-fold increase in conductivity for the samples with crypt[2.2.2] results from the favorable free energy for the formation of the crypt[2.2.2]·Na^+ complex.

Experimental Section

Measurements. The two-dimensional ^1H NMR homonuclear correlation spectrum was collected on a Varian Unity+ 400. Other NMR spectra were collected on a Varian VXR 300. All NMR measurements were performed in $CDCl_3$. IR spectra were collected on the neat materials using a Bomem MB-100 FTIR. Complex impedance was performed with an HP 4192A impedance analyzer. The conductivity cell (geometric factor = 0.101 cm^{-1}) was air tight and loaded in a nitrogen drybox. Temperature control was achieved with a Sun Systems environmental chamber. The extrapolated dc conductivities were extracted in the standard manner from measurements over the frequency range 5 Hz to 5 MHz.[51] DSC thermograms were collected with a Perkin-Elmer DSC-7 using hermetically sealed pans loaded in a drybox under N_2. The reported transition temperatures are onset temperatures for thermograms collected at 10 K/min. Density measurements were performed by filling and weighing a container of known volume and mass.

Materials. *N*-Bromosuccinimide, 2,6-di-*tert*-butyl-4-methylphenol, NaH, poly(ethylene glycol) monomethyl ether, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, hexane, allyl chloride, allyl magnesium chloride (2 M solution in tetrahydrofuran), sodium *tert*-butoxide, and anhydrous toluene were used as received from Aldrich Chemical Co., and Karstedt's catalyst (3% w/w solution in xylenes) and poly(hydrogen methylsiloxane) (PHMS) were used as received from Huls America. Tetrahydrofuran (THF, Aldrich Chemical Co.) was distilled from sodium benzophenone ketyl.

Synthesis of 2,6-Di-*tert*-butyl-4-(3-butenyl)phenol. A 20 g (0.11 mol) of *N*-bromosuccinimide was suspended in 50 mL of hexane. To this suspension was added dropwise 23 g (0.10 mol) of 2,6-di-*tert*-butyl-4-methylphenol in 50 mL of hexane while irradiating with a mercury discharge lamp. The resulting mixture was irradiated for a total of 9 h and then filtered. The yellow supernatant was added dropwise to 100 mL of a 2 M solution of allyl magnesium chloride in THF. The mixture was refluxed for 4 h and then carefully washed with water. The organic layer was fractionally distilled from $MgSO_4$ to yield the product that was kept under dry N_2 (bp 105 °C at0.5 Torr; yield 12 g (42%); ^1H NMR (δ 1.4 (s, 18H), 2.3 (m, 2H), 2.6 (m, 2H), 4.9−5.1 (m, 2H), 5.0 (s, 2H), 5.9 (m, 1H), 7.0 (s, 2H)).

Synthesis of Poly(ethylene glycol) Allyl Methyl Ether. To 7 g (0.29 mol) of NaH suspended in THF and under an atmosphere of dry nitrogen was added dropwise 48 g (0.14 mol) of poly(ethylene glycol) methyl ether (average MW = 350), and the mixture was stirred for 12 h at room temperature. To this, was added 35 mL of allyl chloride (0.30 mol), and the mixture was stirred for 48 h at room temperature. The solution was filtered and the supernatant distilled to yield the product that was kept under dry N_2 (bp 120−260 °C @ 0.5 Torr; yield 32 g (60%); $M_N = 346$ by ^1H NMR).

Synthesis of the Sodium Salt of Poly{poly{{[ω-methoxypoly(oxyethylene)]propyl}methylsiloxane}-*block*-[4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]methylsiloxane} (1). All manipulations were carried out under an atmosphere of dry nitrogen. A typical synthesis proceeded as follows. A 10.83 g (12.8 mmol of SiH) aliquot of PHMS was dissolved in 15 mL of anhydrous toluene, and then 15 μL of a 3% w/w solution Karstedt's catalyst in xylenes was added. The reaction mixture was heated to 60 °C and allowed to stir until the solution was golden. The temperature was raised to 80 °C, 0.32 g (1.3 mmol) of 2,6-di-*tert*-butyl-(3-butenyl)phenol was added, and the mixture was allowed to react until no change in the intensity of the SiH IR resonance was observed relative to that of the OH resonance (a minimum of 90 min). A 4.00 g (11.5 mmol) sample of poly(ethylene glycol) allyl methyl ether ($M_N = 346$) was then added and allowed to react for 12 h. The toluene was removed under vacuum, the resulting polymer was redissolved in anhydrous THF, and a solution of 0.12 g (1.25 mmol) of sodium *tert*-butoxide in anhydrous THF was added. The solution was stirred at room temperature for 12 h, the THF removed under rough vacuum, and the polymer dried at 80 °C and 5×10^{-4} Torr for a minimum of 4 days. The ^1H NMR is shown in Figure 1.

Synthesis of 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt[2.2.2]) Complexes of 1. All manipulations were carried out under an atmosphere of dry nitrogen. The Na:crypt[2.2.2] mole ratio was 1:1. For the less viscous samples, a stoichiometric amount of crypt[2.2.2] was first ground in a mortar and pestle and then dissolved directly in the polymer with thorough stirring. For the more viscous samples, **1** and crypt[2.2.2] were codissolved in THF and stirred for several hours, the THF was then removed under rough vacuum, and the resulting polymer was dried at 80 °C and 5×10^{-4} Torr for 24 h.

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