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POLYELECTROLYTES WITH STERICALLY HINDERED ANIONIC CHARGES

T.F. Yeh*, H. Liu*, Y. Okamoto*, H.S. Lee and T.A. Skotheim
Brookhaven National Laboratory
Upton, New York 11973
* Polytechnic University
333 Jay Street
Brooklyn, New York 11201

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ABSTRACT

The central problem in the development of single phase polymer electrolytes with exclusive cation conduction has been inadequate ion mobility due to extensive ion pairing between the mobile cation and the covalently attached anion. We have developed a new class of single ion conducting polymers, or polyelectrolytes, based on highly flexible polysiloxane backbones and attached sterically hindered phenolate anions. The combination of a highly delocalized and sterically enclosed anionic charge facilitates charge separation and consequently enhanced cation mobility.

INTRODUCTION

For many applications of polymer solid electrolytes, such as to lithium batteries, undesirable local concentration gradients occur due to anion mobility, with consequently deleterious effects on the power output of the device. This problem has opened up an area of research in developing single-ion conductors, or polyelectrolytes, where the ionic charges of one polarity are chemically bonded to the polymer backbone. In principle, therefore, the polyelectrolytes will have unity transference number for the un-bonded ion species. The same requirements for chain flexibility to assist the ion motion hold for polyelectrolytes as for dual-ion conductors. The choice of ion pair is also critical to achieve adequate dissociation of the salt.

Several attempts to synthesize single-ion conductors have appeared, with most accounts describing specific cation conductors[1-5]. In general, only low conductivities have been achieved,

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usually in the 10^{-9} - 10^{-7} S/cm range, at room temperature. Higher conductivities have been achieved by using poly(ethylene glycol) as plasticizer[1]. For long term stability, however, single-phase materials are required.

In the absence of solvents, tight ion pairing is always likely to occur in such systems as the screening of the counterionic charge is reduced by the bonding constraints. This significantly reduces the mobility of the charge carriers, leading to systems with room temperature conductivities which are too low for practical applications. Nevertheless, these systems represent important advances in a direction which will lead to new generations of highly conducting specialized polymer electrolytes.

We have taken a new approach to the design of single-ion conducting polymers. The design approach has two essential aspects: (1) A highly flexible polymer backbone is necessary for local segmental motion to aid in the transport of the ions. This requirement is identical to that for dual-ion conductors. (2) The anionic charge, which is covalently attached to the polymer backbone, incorporates both steric hindrance and delocalization to prevent ion pairing.

With polyelectrolytes based on polysiloxane backbones and sterically hindered phenol compounds, the room temperature conductivities are generally in the 10^{-5} S/cm range, depending on the cation. The highest conductivities were achieved with K^+ ions and the lowest with Li^+ ions, clearly demonstrating that the dissociation is a function of the size of the cation.

POLYMER SYNTHESIS

Previous attempts to develop exclusive cation conducting polymers have been based on covalent attachment of carboxylate and sulfonate groups to the polymer backbone or side groups[1-5]. With a relatively localized bonded anionic charge, the electrostatic screening required for efficient charge separation becomes inadequate. The conductivity, consequently, is lower than that of dual ion conductors with equivalent ion pairs.

Sterically hindered phenols, such as 2,6-di-t-butyl phenol, have been used in a variety of applications in organic synthesis[6,7]. Among the noteworthy properties of the compound are the stability of the phenol radical and the absence of normal phenol properties[8]. Geometrical calculations indicate that bulky t-butyl substituents in 2,6-di-t-butyl phenoxide effectively separate alkali metal cations such as K^+ and Na^+ from the phenoxide oxygen. The resulting charge separation would be expected to result in more mobile ions as well as a higher charge carrier density compared with more closely associated ion pairs.

Since the movement of ions is closely coordinated with the local segmental motion of the polymer, the anionic groups should be attached to a flexible polymer backbone with low glass transition temperature (T_g) in order to achieve high mobility at ambient temperatures. Polysiloxanes have long been known for their unique combination of stability and flexibility, with an exceptionally low energy barrier to rotation of the polymer backbone[9]. This is reflected in the low glass transition temperatures, generally in the -120 to -130°C temperature range for linear polymers.

Scheme 1 shows the procedure for the synthesis of a comb polysiloxane with oligo-oxyethylene side chains and attached 2,6-di-t-butyl phenol moiety. Poly(hydro methyl siloxane) (PHMS) (Petrarch) was partially hydro-silylated with the phenol compound (I) and the allyl ether (II) using H_2PtCl_6 as catalyst at 90 °C under nitrogen atmosphere until the SiH and allyl compounds were reacted. The typical ratio of x:y was 8:1. For the preparation of the alkali salts, the polymer was neutralized with n-butyl Li and Na and K t-butyloxide. The cast films were dried at 60°C under vacuum for at least 24 hours prior to the conductivity measurements. The T_g of the copolymer without salt was about -100°C, while the Li, Na and K salts had T_g's about -80°C.

[Scheme 1]

IONIC CONDUCTIVITY

Figure 1 shows the ac conductivity measurements using stainless steel blocking electrodes of Li, Na and K salts of the polymer shown in Scheme 1. As expected, the effect of steric hindrance is most pronounced for the larger K^+ ion. The Na^+ falls somewhere in between the K^+ and the Li^+ ions. The conductivities are remarkably high compared with previous results with exclusively cationic conductors. The room temperature conductivity is a factor of 100-1000 times that previously reported[1-5]. The activation energy is low, indicating efficient charge separation at all temperatures.

[Figure 1]

Previous studies using ^{23}Na NMR of sterically hindered phenolate anions attached to nylon-1 backbones have shown that the charge separation is efficient[10]. The ratio of bound to mobile Na ions reached 75% at 40°C and remained constant above that temperature. This implies that the availability of charge carriers at or near room temperature is adequate for high conductivity.

Figure 2 shows the effect of increasing the steric hindrance at the 2,6 positions of the phenolate anion. The conductivity of the Li complex is practically unchanged and the conductivity of the K complex is marginally increased. The largest effect of the additional steric hindrance is in the substantially increased conductivity of the Na complex. This is expected from geometrical calculations which shows that the enhanced screening effect of the added ethyl groups primarily effects Na^+ ions. The di-t-butyl groups are adequate for screening K^+ ions.

[Figure 2]

Adding steric hindrance beyond the additional ethyl groups does not appear to afford appreciable increase in the conductivity of the Li complex. This is believed to be due to a decrease in the effective dielectric constant in the increasingly more hydrocarbon-like environment. There thus appears to be an optimum size of the steric groups for maximum conductivity. In terms of approaching specific Li^+ ion conductivities of the order of 10^{-4} S/cm at room temperature, the present approach may be inadequate. However, for devices based on Na^+ ion mobility, e.g. insertion batteries, the present approach provides adequate bulk conductivities. Studies are presently underway to optimize the conductivity and determine the electrochemical stability of this class of electrolytes.

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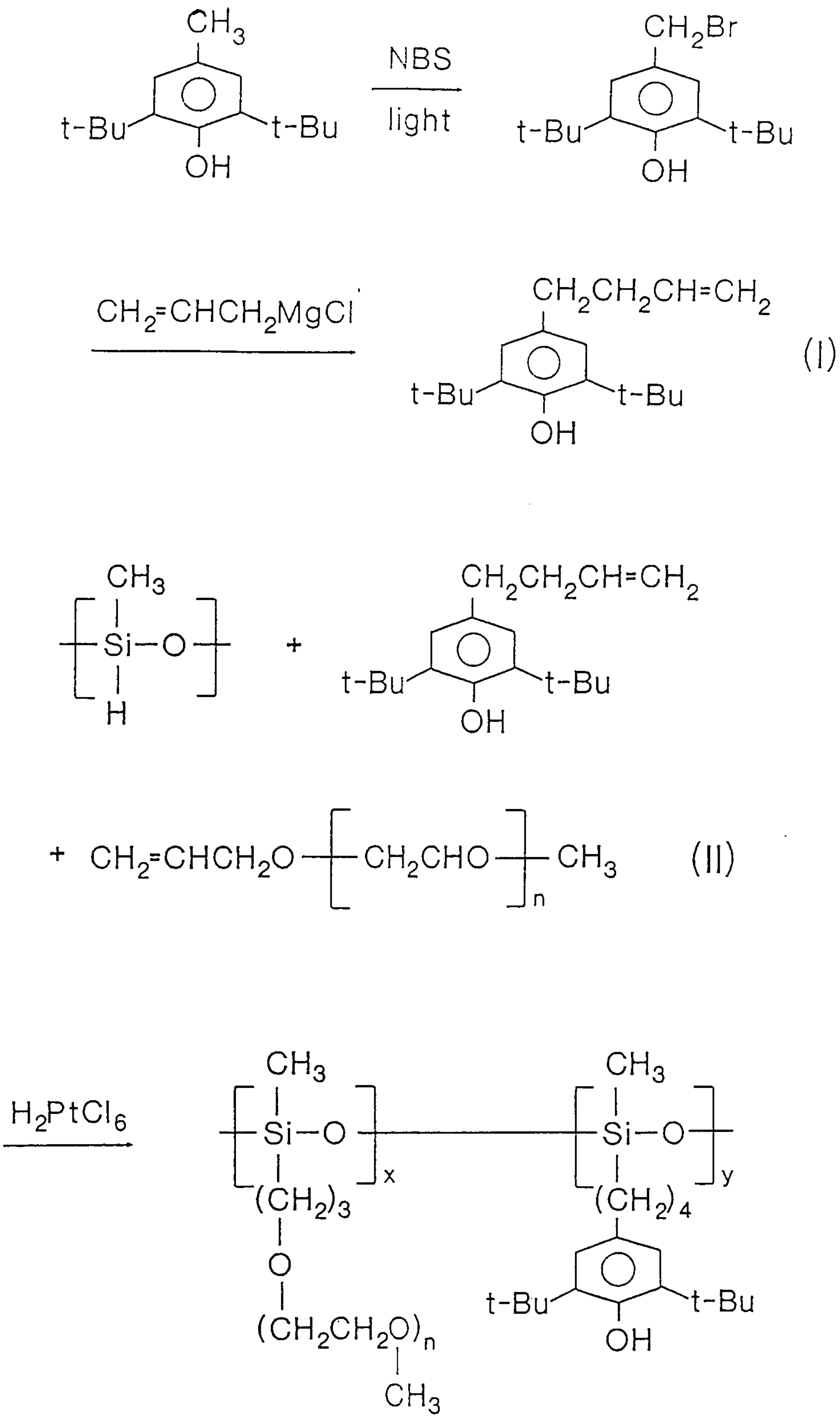
FIGURE CAPTIONS

Scheme 1. The synthesis of polysiloxane based polyelectrolytes with exclusive cation conductivity.

Figure 1. Temperature dependence of the ac conductivity of exclusive cation conducting polymers with 2,6-di-t-butyl phenol groups covalently bound to a the polysiloxane backbone as in Scheme 1.

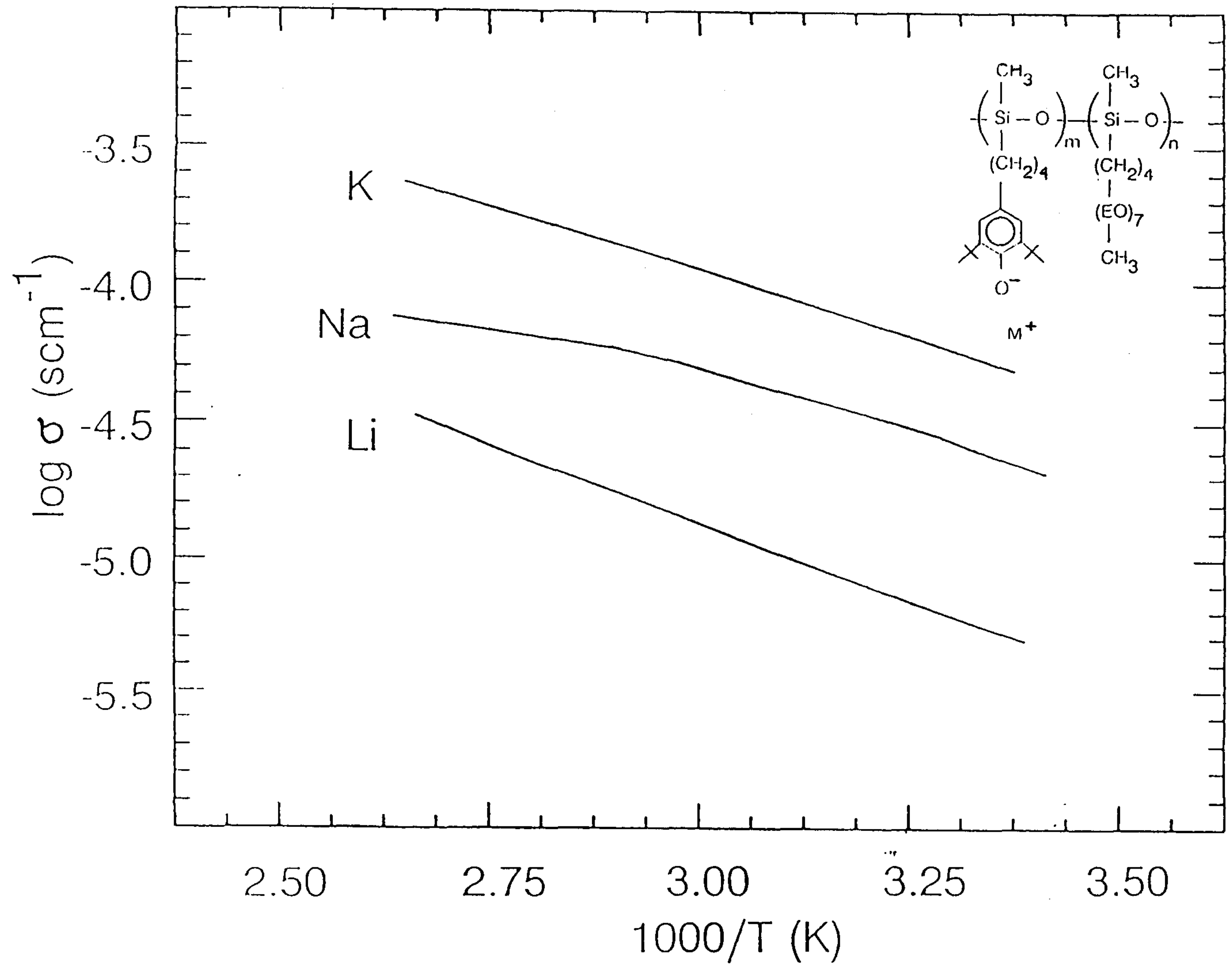
Figure 2. Effect on the temperature dependence of the ac conductivity of additional steric hindrance at the 2,6 position of the phenolate anion.



x:y = 8:1 n = 7

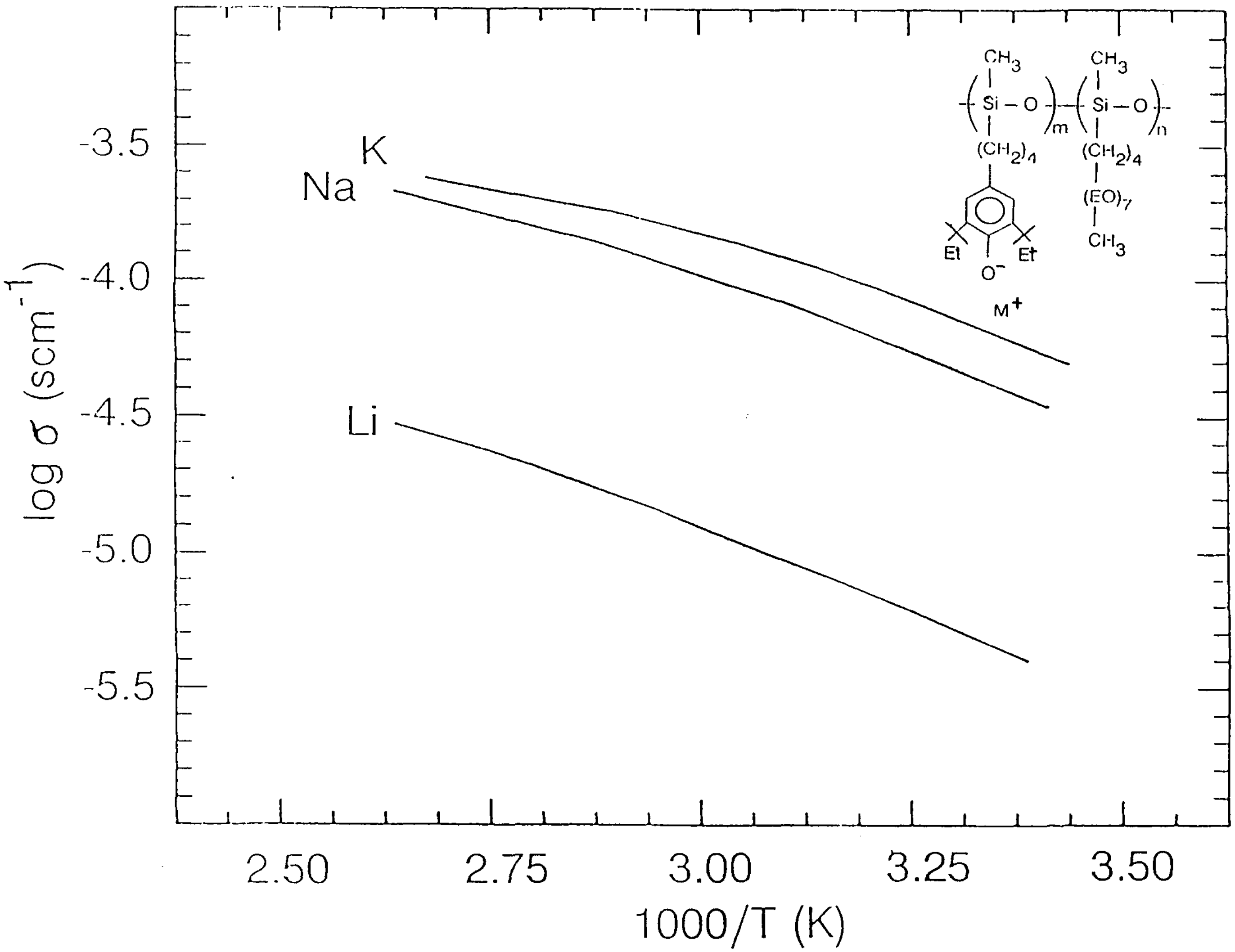
Scheme 1

Fig. 1



log σ (scm^{-1})
-3.5
-4.0
-4.5
-5.0
-5.5
K
Na
Li
2.50
2.75
3.00
3.25
3.50
1000/T (K)
CH$_3$
Si
O
m
(CH$_2$)$_4$
O$^-$
M$^+$
CH$_3$
Si
O
n
(CH$_2$)$_4$
(EO)$_7$
CH$_3$

Fig 2



log σ (scm^{-1})
-3.5
-4.0
-4.5
-5.0
-5.5
K
Na
Li
2.50
2.75
3.00
3.25
3.50
1000/T (K)
CH$_3$
Si – O
m
(CH$_2$)$_4$
Et
Et
O$^-$
M$^+$
CH$_3$
Si – O
n
(CH$_2$)$_4$
(EO)$_7$
CH$_3$