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POLYMER ELECTROLYTES WITH EXCLUSIVELY CATIONIC CONDUCTIVITY

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ABSTRACT

The synthesis of exclusively cation conducting polymer electrolytes based on a nylon-1 backbone, ethylene-oxide side chains, and attached dibutyl phenolate anions is described. The tendency for ion pair formation appears to be reduced as the conductivity of the sodium-containing compound reaches ~2 X 10^{-6} S-cm^{-1} at 50°C. ^{23}Na nuclear magnetic resonance measurements demonstrate: i) motional narrowing of the mobile Na^+ resonance above the glass transition temperature; ii) mobile Na^+ concentrations of ~75% at 40° C; iii) insensitivity of the linewidth to applied hydrostatic pressure up to 2 kbar. Similaries between these findings, and those in "conventional" polymer-salt electrolytes are discussed.

Introduction

Polymer electrolytes formed by complexing a host polymer such as poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) with a suitable salt have been studied extensively [1-3]. It is often found that cation transference numbers can be less than 0.5 in these materials. Moreover, for complexes with high salt concentrations, ionic aggregation effects can limit the number of available charge carriers [4,5]. These factors have led several groups to investigate various polyelectrolytes, in which the anionic charge is fixed to the backbone or sidegroup, as potential ion conducting polymers [6-8]. However, room temperature ionic conductivities of the polyelectrolytes tend to be quite low ($\leq 10^{-7}$ S-cm^{-1}), especially in cases where strong interactions between the cations and immobilized anions are expected.

We describe the synthesis and study of a cation conductor consisting of a nylon backbone, attached anionic groups and polyether side chains. In order to diminish the interaction between cations and anions, 2,6- dibutyl phenolate ions are employed. Nuclear magnetic resonance (NMR) techniques, particular for the nuclei ^{7}Li and ^{23}Na, have been employed productively in probing cation dynamics in polymer electrolytes [9,10]. The NMR measurement strongly confirm the results of other types of experiments which conclude that significant cation mobility is possible only above the glass transition temperature, T_g. ^{23}Na NMR measurements on the nylon-backbone cation conductor are reported.

Experimental Details

Triethylene glycol monomethyl ether was obtained from Fluka and 4-acetamidophenol and 3,5-di-tert-butyl-4-hydroxybezoic acid were purchased from Aldrich. All chemicals were dried over molecular sieves and purified by either recrystallization or distillation. The synthesis of the oligo ethylene oxide isocyanate monomer has been described elsewhere [11]. The hindered phenol monomer was synthesized according to the following scheme:

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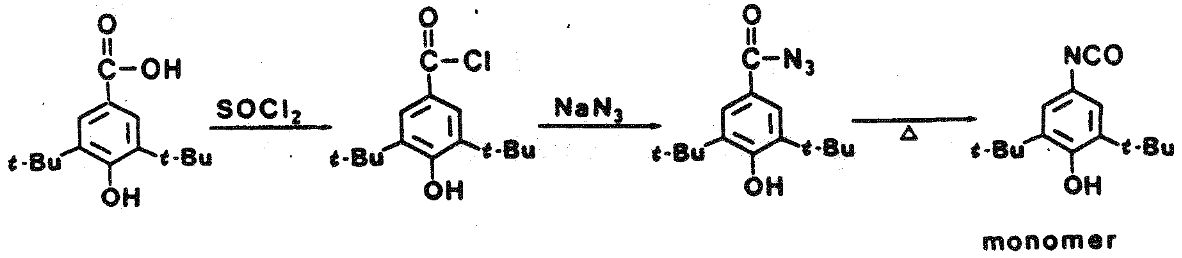
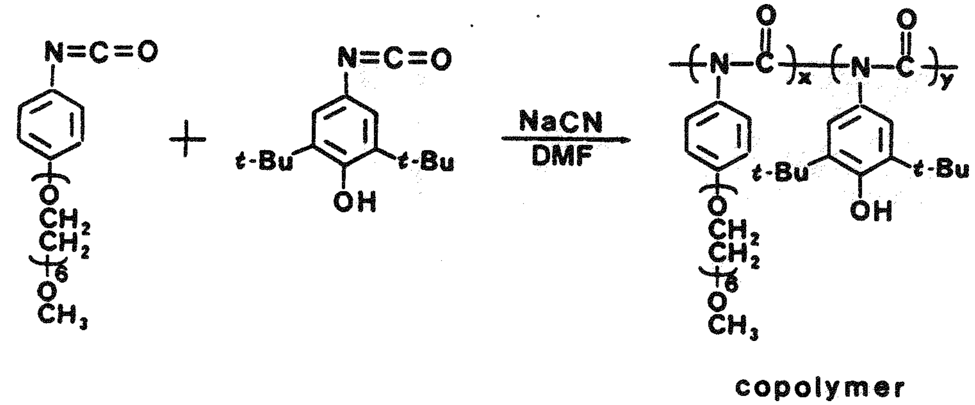


The copolymer was then prepared as shown below.

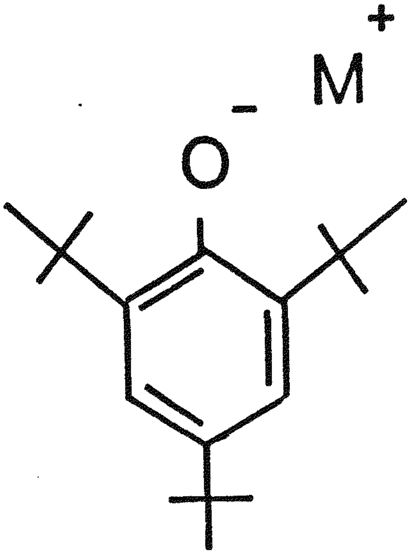


The compounds isolated in each step were identified by their IR and ^{1}H NMR spectra. The copolymerization of the two monomers was carried out by Shashoua's method [12]. The resulting copolymer was then dissolved in chloroform and washed with water to remove the inorganic initiator. The chloroform layer was collected and evaporated, yielding a pale brown, clear, and viscous polymer. The components of the copolymer were determined by ^{1}H NMR as x:y being 2:1. In order to prepare the alkali salts, THF solution of the copolymer was mixed with equal molar quantity of either Li, Na, or K *t*-butyloxide to form the corresponding phenolate. After removing the THF and by-product *t*-butyl alcohol, the samples were dried at 60°C under 0.05 mm Hg for at least 24 hours prior to performing measurements. The Li containing polymer is yellow, while the corresponding Na and K materials are dark green and dark blue, respectively.

The DSC data were obtained by using a DuPont 2100 Thermal Analyzer equipped with a 910 Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. The copolymer without any salt showed a central glass transition temperature (T_g) at around -40°C, while the Na ion containing sample gave a T_g at -19°C. The increase in T_g upon formation of the salt is presumably attributable to interactions between the ether oxygens and the cations. Elevation in T_g of the host polymer is commonly observed in the polymer-salt complexes [2,3].

The conductivity measurements were carried out using a Hewlett-Packard 4192A Impedance Analyzer with a frequency range from 5 Hz to 13 MHz. The dried sample was fixed between two nickel electrodes in a nitrogen dry box before measurement.

The ^{23}Na NMR measurements were performed at 81 MHz utilizing standard pulse techniques. NMR data were also acquired at elevated hydrostatic pressure by placing the rf coil/sample assembly in a stainless steel pressure bomb. The sample was enclosed in a rubber finger-cot and fluorinert (3M) was utilized as the pressure transmitting fluid.



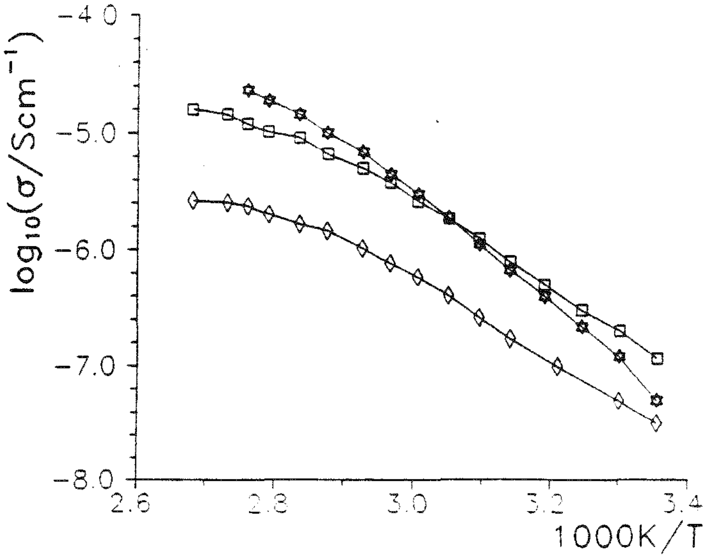


Figure 1- 2,4,6 - tributyl phenolate anion-cation pair (M=Li, Na, K).

Figure 2- Ionic conductivity of polymer complexes: Li - diamond; K - stars; Na - squares.

Results and Discussion

The 2,4,6-tributyl phenolate anion is shown schematically in Fig. 1. The two most important features of this anion are the delocalization of the negative charge over the ring and the steric influence of the large butyl groups adjacent to the oxygen. The combined effect of these two features is expected to limit the tendency to form cation-anion pairs in the material. Preliminary NMR measurements on sodium phenolate and sodium tributyl phenolate show that the ^{23}Na resonance in the latter compound is substantially quadrupole broadened, reflecting the steric influence of the butyl groups. A more complete account of this result will be presented elsewhere.

The ionic conductivity temperature dependence for the copolymers containing Li, Na, and K is shown in Fig. 2. The curvature of the data on the Arrhenius plot is characteristic of amorphous polymer electrolytes. The sodium compound has a conductivity of about 10^{-7} S-cm^{-1} at 26°C and rises to the mid 10^{-6} region at about 50°C. The potassium complex has somewhat higher conductivity than the sodium material at higher temperature. The lithium compound, on the other hand, has a lower conductivity than the previous two materials over the entire temperature range shown in Fig. 2. This result suggests the possibility that the steric influence of the butyl groups is somewhat less for Li^+ than for the larger cations.

As in previous work on polymer-salt complexes, or "conventional" polymer electrolytes, the NMR spectrum consists of two distinct components: a short T_1 (spin-lattice relaxation time) resonance with a strongly temperature dependent linewidth; and a long T_1 resonance with a temperature independent linewidth. The short T_1 resonance is associated with mobile Na^+-ions while the latter component reflects the presence of relatively large (> 10) aggregates of ions. The linewidth of the mobile Na^+ signal is plotted as function of temperature in Fig. 3. The temperature dependence of the linewidth is characterized by motional narrowing just above T_g and subsequent broadening starting about 55 K above T_g. The broadening is attributable to extremely fast ($\leq$ 300 μs) spin-lattice relaxation observed in the high temperature region. This result clearly indicates the importance of segmental motion of the polymer - presumably the ethylene oxide segments - to ion mobility. Similar ^{23}Na behavior has been observed in a wide variety of Na salt-containing polymer electrolytes in which the role of segmental motion is well established [10,13,14].

Mobile Na^+ concentrations are shown in Fig. 4 in which the ratio of the mobile to bound NMR intensities obtained by direct integration of the respective free induction decays is plotted as a function of temperature. There appears to be a steady increase in mobile Na^+ concentration with increasing T until about 40°C, above which the concentration remains constant at approximately 75%. Thus the availability of charge carriers at or near room temperature is certainly adequate for conduction.

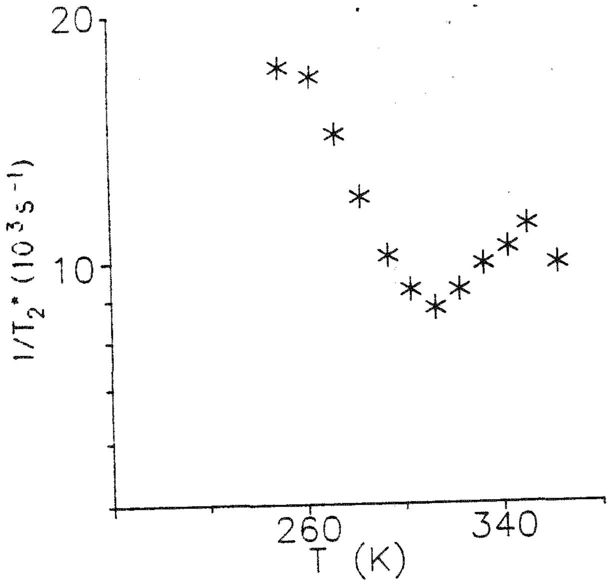


Figure 3- Temperature dependence of reciprocal $^{23}Na^+$ FID time constant for mobile Na^+ in polymer complex.

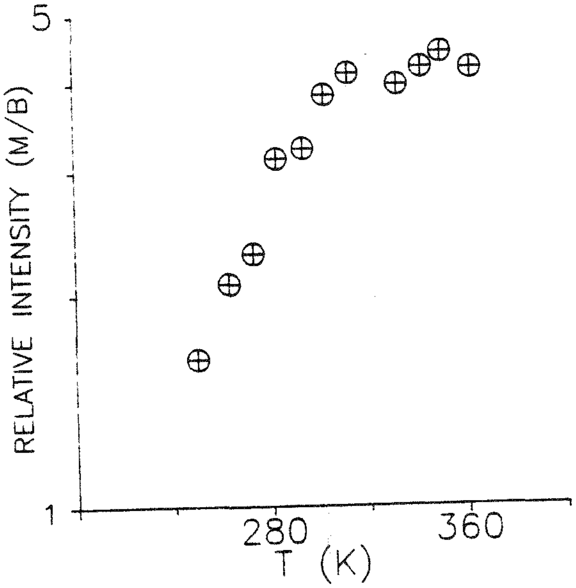


Figure 4- Temperature dependence of Mobile to bound Na^+ ratio in complymer complex.

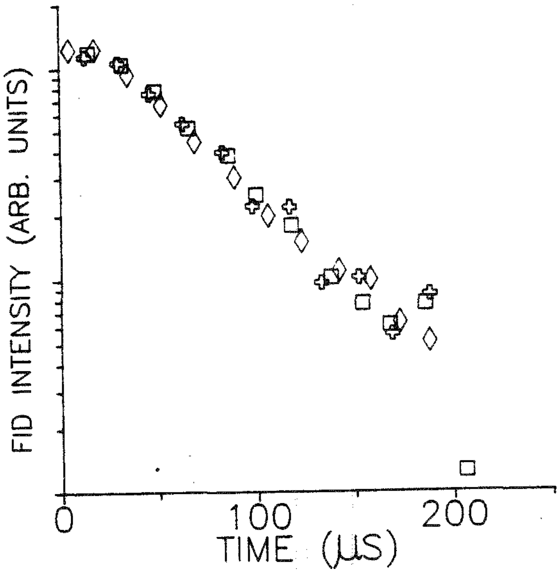


Figure 5- Pressure dependence of ^{23}Na FID in polymer complex, 1 bar (atmospheric)- diamonds 1 kbar- squares; 2 kbar- crosses.

Finally the effects of hydrostatic pressure on the NMR spectrum have been explored. The application of hydrostatic pressure is known to decrease ionic conductivity in PEO, PPO, and siloxane based polymer salt complexes [10,13]. It has also been shown that the partially narrowed ^{23}Na NMR linewidth of PPO_8NaI at 40°C broadens appreciably under pressure [13]. Both phenomena are explainable by simple free volume concepts which predict a pressure induced increase in T_g of approximately 10-15 K/kbar. Figure 5 displays the free induction decay amplitude of the mobile Na^+ signal in the nylon cation conductor under varying degrees of pressure, from 1 bar to 2 kbar. All points clearly follow approximately the same decay trend indicating that the linewidth (in the frequency domain) does not exhibit appreciable pressure dependence. The apparent pressure insensitivity of the linewidth is thus inconsistent with the behavior observed in the PPO-Na salt system, especially in view of the motional narrowing results shown in Fig. 3. Further studies of analogous cation conductors based on flexible siloxane rather than nylon-1 backbones, which are currently in progress, are expected to provide some insight into the anomalous pressure result.

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