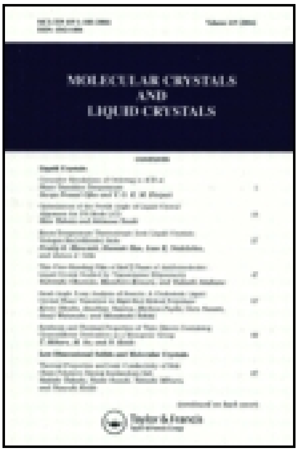

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A New Ionic Conducting Polymer Based on Oligo(Ethylene Oxide) Substituted Nylon-1

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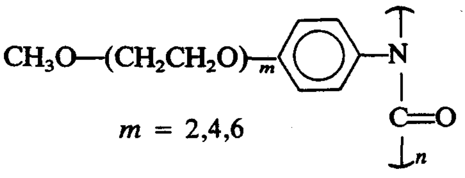
INTRODUCTION

The potential application of solvent-free polymer-alkali salt complexes as electrolytes in high energy density batteries[1] and solid state thermoelectrochromic display[2] has stimulated considerable investigations on synthesis and characterization of poly(ethylene oxide) and poly(propylene oxide)—alkali salt complexes. These linear polymers are highly crystalline at ambient temperature and the crystalline domains are known to impede ion conduction. Thus, more recent work has focused on polymers having flexible chain structure and lower glass transition temperature (*Tg*). This can be accomplished for polymers with pendant oligo(ethylene oxide) chains on flexible polymer backbones such as poly-(methacrylate),[3] poly(phospazene)[4] and poly(methylsiloxane).[5,6]

The structure of poly(alkyl isocyanate) is generally considered as a rod-like molecular posture.[7] On the other hand, poly(aryl isocyanate) has been reported to be rather flexible.[8] However, Gargallo and Morawetz[9] have investigated the fluorescent properties of poly(phenyl isocyanate). They concluded that the conformational restraints in poly(phenyl isocyanate) is much less severe than in the alkyl-substituted polyisocyanate, they are still sufficiently stiff to inhibit to a large extent internal quenching of the excited phenyl groups.

In searching for new electrolyte systems, we have synthesized oligo(ethylene oxide) substituted poly(phenyl isocyanate) (Nylon-1).[1]



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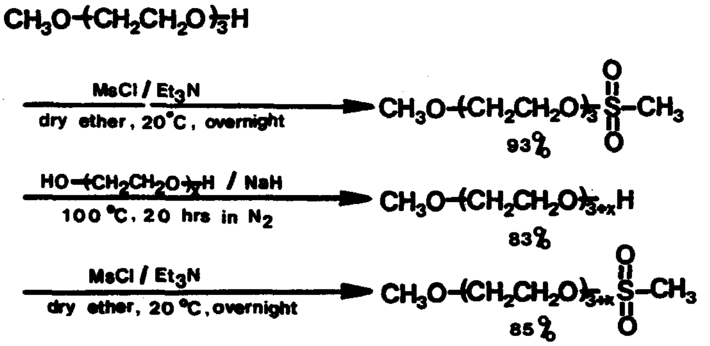
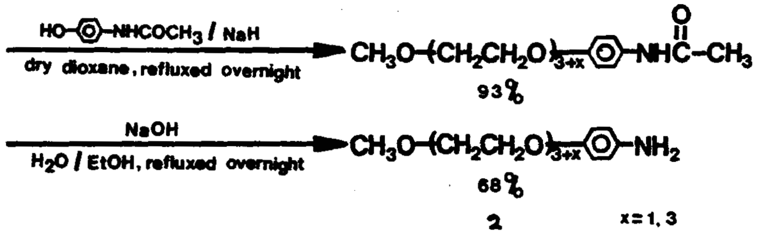
Complexes of the polymer CF_3SO_3Li were prepared and the ionic conductivities as a function of ethylene oxide unit length were measured. In this paper, we report the preliminary results with these systems.

EXPERIMENTAL

Synthesis

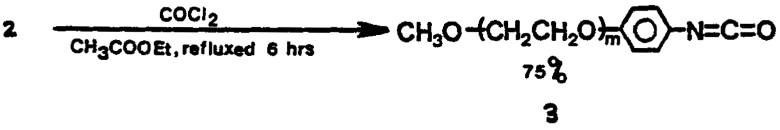
4-(ω-Methoxy oligo (ethylene oxide)) anilines 2 were prepared according to Scheme 1. Triethylene glycol monomethyl ether was obtained from Fluka and triethylene glycol, ethylene glycol, 4-acetamidephenol and 4-(2-methoxyethoxyl)ethoxyl aniline were purchased from Aldrich Chemicals and dried over molecular sieves and distilled.

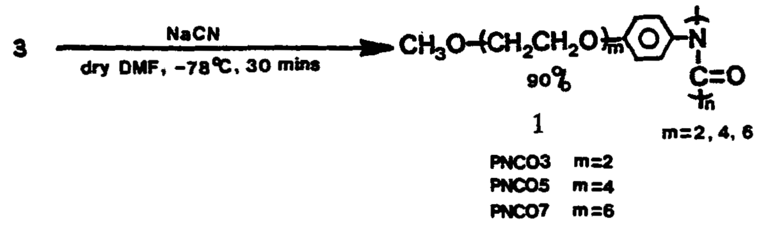




SCHEME 1 The synthetic route for 4(ω-methoxy oligo(ethylene oxide)) aniline.

The aniline compounds were reacted with phosgene in ethylacetate to form the corresponding isocyanates 3. The isocyanates were polymerized using NaCN as the catalyst to form poly(isocyanates) *1*.[10] The compounds isolated in each step were identified by measuring I.R. and NMR spectra.





Viscosity measurements and molecular weight determination

Dilute solution viscosities of the polymers synthesized were determined in chloroform at 25°C using a Cannon-Ubbejohde glass viscometer. The average molecular weight was estimated from the intrinsic viscosity (η) measured according to the Mark-Houwik relation using the *k* and *a* values obtained for poly(4-methoxyphenyl isocyanate).[11]

Differential scanning calorimetry (DSC) measurements

The DSC data of the uncomplexed and Li-salt complexed polymers were obtained using DuPont 1090 Thermal Analyzer equipped with a 910 Differential Scanning Calorimeter at a heating rate of 20°C/min. under nitrogen atmosphere.

Conductivity measurements

The appropriate tetrahydrofuran (THF) solutions of the polymers and $LiCF_3SO_3$ were mixed to form the polymer-Li complexes with the ratio of the ether oxygen to lithium ions being 10/1. After removing THF, the samples were dried at 60°C under 0.05 mm Hg for 24 hours. The polymer-Li complexes with triethylene oxide chains were found to be solid, but other complexes—pentaethylene oxide and heptaethylene oxide were sticky viscous materials. The sample was placed between two nickel electrodes in a nitrogen dry box. The conductivity measurements were carried out using a Hewlett-Packard 4192A Impedance Analyzer in the frequency range from 5 Hz to 13 MHz.

RESULTS AND DISCUSSION

The results of the viscosity measurements and the estimated molecular weights of the polymers are summarized in Table I.

The molecular weights of the polymers were found to be in the same range as the poly(n-alkyl isocyanates) prepared previously.[12] The DSC results of the uncomplexed polymers are shown in Figure 1. The *Tg* of the polymers decreased with increasing length of the ethylene oxide side chains. For PNCO3, in addition to the glass transition at −17°C, it showed a sharp endothermal peak at 95.4°C which corresponds to the melting point of the polymer. PNCO5 and PNCO7 did not exhibit any endothermal peaks. These results suggest that PNCO5 and PNCO7 are amorphous while PNCO3 contains some crystalline domains. By complexing the polymers with Li salts the *Tg* increased by 20–30°C and a small exothermal peak around 50–80°C

TABLE I

Estimated molecular weights of oligo(ethylene oxide) substituted poly(phenyl isocyanate).

Polymer	(η) dl/g	$Mv \times 10^{-5}$
PNCO3	0.467	1.19
PNCO5	0.516	1.37
PNCO7	0.592	1.68

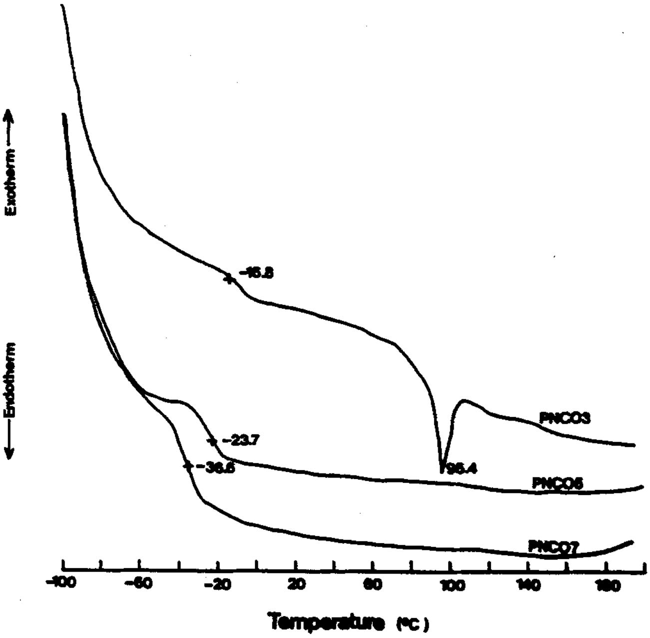


FIGURE 1 DSC scans of oligo(ethylene oxide) substituted nylon-1.

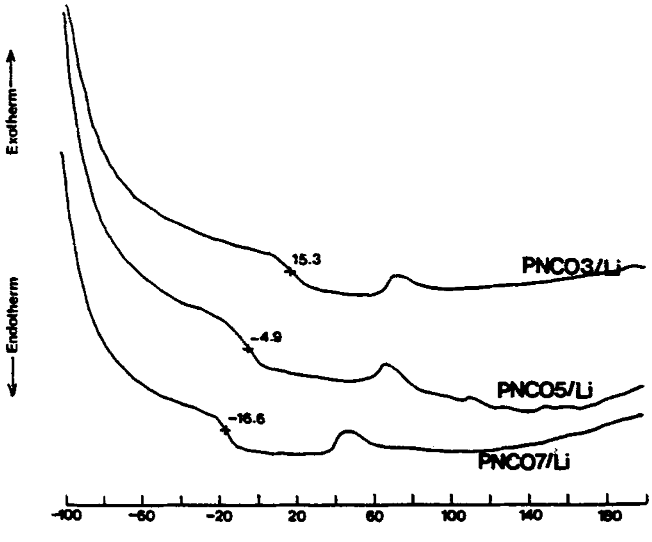


FIGURE 2 DSC scans of oligo(ethylene oxide) substituted nylon-1 complexed with CF_3SO_3Li at O/Li ratio of 10/1.

was observed for all polymer-Li complexes (Figure 2). The nature of this exothermal peak is not clear at present.

The ionic conductivities of the polymer-Li complexes increased with increasing the ethylene oxide side chains (Figure 3). For PNCO7 with O/Li being 10/1, the conductivity at ambient temperature was 2.4×10^{-6} S cm^{-1}.

The conductivity data showed a slight deviation from Arrhenius behavior (Figure 4). The curvature in the conductivity data is typical for amorphous polymer-Li salt complexes and is usually explained in terms of free volume. Thus, when the temperature dependence of the conductivity was plotted according to the VTF expression (Equation 1),[13] a linear relationship was obtained (Figure 5), which indicated that the PNCO7-Li complex is essentially amorphous.

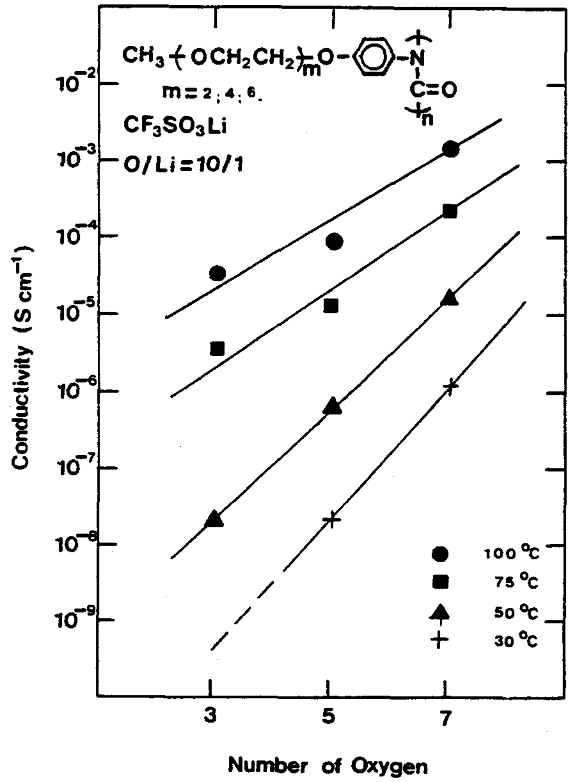


FIGURE 3 Conductivity versus ethylene oxide side chain length for the nylon-1 at different temperatures.

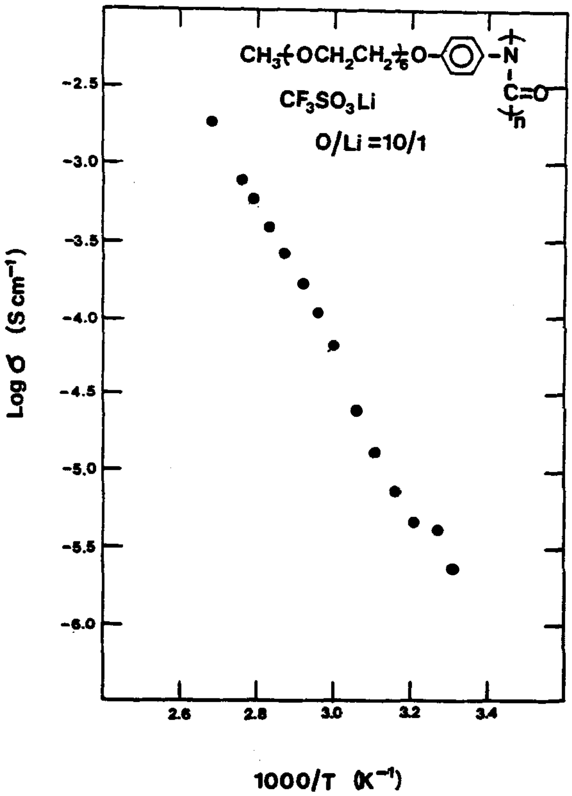


FIGURE 4 Log α versus 1000/*T* for the nylon-1 with seven oxygens at the side chains.

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

where T_0 is the thermodynamic glass transition temperature, which was calculated using $Tg - T_0 = 50$ K.[14]

Ea is the apparent activation energy and *A* is proportional to the number of carriers. *k* is Boltzmann's constant.

The conductivity values obtained for PNCO7 (O/Li = 10/1) are comparable to those polymers with flexible backbones such as polymethylsiolxane[6] and polymethacryalte.[3] The structure of poly(aryl isocyanate) is considered to be rather stiff as compared to the olefinic polymer polysiloxane. Thus our results suggest that the backbone rigidity does not affect the conductivity significantly as long as the ethylene oxide side chains are long enough to provide an amorphous region through which the Li ions can move.

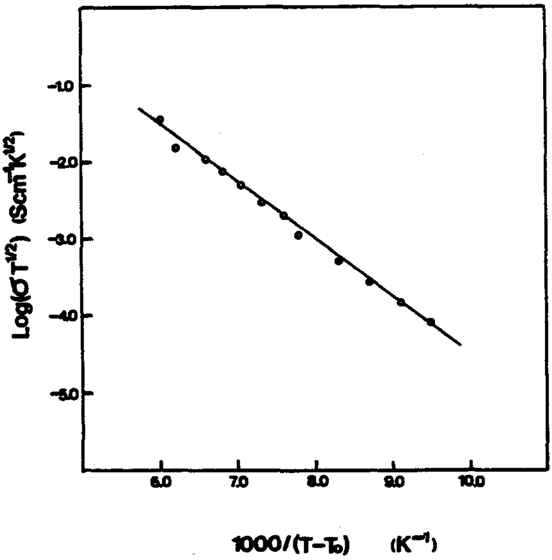


FIGURE 5 Data from Figure 4 for PNCO7/CF_3SO_3Li complex are plotted according to the V.T.F. equation with $T_0 = T_g - 50$ K, O/Li = 10/1.

Acknowledgments

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