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POLYMER ELECTROLYTE BASED ON POLY(ETHYLENE IMINE) AND  
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GAITHERSBURG MD POLYMERS DIV C K CHIANG ET AL.

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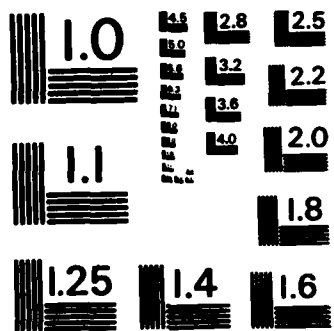
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The dissolution of lithium salts in linear poly(ethylene imine) has been investigated because of its possible role as a solid electrolyte in lithium batteries. Lithium salts included in the study are LiF, LiCl, LiBr, LiI, LiSCN, LiClO<sub>4</sub>, and LiBF<sub>4</sub>. When cast from solution in a common solvent, a uniform mixture is obtained (except for the case of LiF). Interaction of the salt and polymer can be characterized by observing a loss in crystallinity of the polymer and an increase in the glass transition temperature. At concentrations of salt below 10 mole percent, the polymer can slowly recrystallize at room temperature.

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but at higher concentrations, the mixture remains amorphous for an indefinite period of time. DC conductivity at room temperature is about  $1 \times 10^{-8}$  S/cm but increases to  $1 \times 10^{-3}$  S/cm at 150°C.

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POLYMER ELECTROLYTE BASED ON POLY(ETHYLENE IMINE)  
AND LITHIUM SALTS

by

C. K. Chiang, G. T. Davis, C. A. Harding and T. Takahashi

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## POLYMERIC ELECTROLYTE BASED ON POLY(ETHYLENE IMINE) AND LITHIUM SALTS

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The dissolution of lithium salts in linear poly(ethylene imine) has been investigated because of its possible role as a solid electrolyte in lithium batteries. Lithium salts included in the study are LiF, LiCl, LiBr, LiI, LiSCN, LiClO<sub>4</sub>, and LiBF<sub>4</sub>. When cast from solution in a common solvent, a uniform mixture is obtained (except for the case of LiF). Interaction of the salt and polymer can be characterized by observing a loss in crystallinity of the polymer and an increase in the glass transition temperature. At concentrations of salt below 10 mole percent, the polymer can slowly recrystallize at room temperature but at higher concentrations, the mixture remains amorphous for an indefinite period of time. DC conductivity at room temperature is about  $1 \times 10^{-6}$  S/cm but increases to  $1 \times 10^{-3}$  S/cm at 150 °C.

### 1. INTRODUCTION

The dissolution of alkali metal salts in oxygen-containing polymers such as poly(ethylene oxide)<sup>1-4</sup>, poly(propylene oxide)<sup>4-6</sup>, and poly(ethylene succinate)<sup>7</sup> is believed to involve strong interaction between the cation and the unshared electron pairs of the oxygen. We have examined linear poly(ethylene imine),  $(-\text{CH}_2\text{CH}_2\text{NH}-)_n$  as a host polymer for electrolytes<sup>8</sup> because of the unshared electron pair on nitrogen. Many of the phenomena observed are analogous to those of poly(ethylene oxide)-salt systems. For example, the imine polymer (PEI) dissolves many of the same alkali metal salts as the ether polymer as evidenced by a loss in crystallinity of the polymer, the absence of x-ray diffraction from the added salt, and an increase in the glass transition temperature. In the case of sodium iodide in PEI, a new crystal phase is formed which melts near 150 °C rather than near 68 °C which is the melting point of the unadulterated polymer. The molar ratio of Na/N in the complex is about 1/3 rather than the 1/4 ratio

usually observed for Na/O in the PEO complex<sup>4,8</sup>. Ionic conductivity of the PEI-salt mixtures in most cases is comparable to that reported for PEO-salt mixtures. Results obtained for a variety of lithium salts in linear poly(ethylene imine) will be presented in this report.

### 2. EXPERIMENTAL

#### A. Preparation of polymer and complexes

The poly(ethylene imine) which is available commercially is highly branched, non-crystalline, and available only as an aqueous solution. Linear poly(ethylene imine) was prepared following the procedure of Saegusa et al<sup>9,10</sup> which involves hydrolysis of poly-(N-acetyl ethylene imine) which in turn was polymerized by the methyl iodide-initiated ring-opening polymerization of 2-methyl oxazoline in dimethyl formamide solution.

Lithium salts of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> were dehydrated by heating in a vacuum. Dried linear PEI and an appropriate amount of anhydrous salt to yield

a molar ratio of salt to monomer of 0.1 were dissolved in spectra grade acetonitrile at reflux temperature (ca. 82 °C). The resulting uniform solution was then evaporated to dryness by evacuating for several days at 100 °C.

#### B. Differential Scanning Calorimetry

DSC scans were measured using a Perkin-Elmer DSC-II equipped with a data station<sup>11</sup>. Samples were hermetically sealed in an argon-filled dry box and heating and cooling rates were usually 20 °C/min. Melting temperatures reported herein refer to the peak temperature of the endothermic peak at the normal scanning rate and glass transition temperatures are reported as the mid point of the change in heat capacity.

#### C. Conductivity Measurements

To avoid measurement problems associated with polarization at the electrodes, DC conductivity was deduced from Cole-Cole plots of AC impedance data obtained over the frequency range from 100 Hz to 13 MHz<sup>12</sup>. AC impedance was determined using a computerized Hewlett-Packard model 3470 network analyzer<sup>11</sup>. The sample cell consisted of two thin stainless steel electrodes and a glass sample cup. When loading the sample into the conductivity cell, it was exposed to atmospheric conditions for about 10 minutes and was subsequently dried by evacuating overnight followed by heating to the highest measuring temperature (usually 140°) with continued evacuation for another 20 to 40 hours. Impedance data were first obtained upon cooling from the highest temperature in steps of five to ten degrees, allowing 30 minutes for thermal equilibrium at each temperature. Impedance data were also obtained during subsequent heating and cooling cycles.

### 3. RESULTS

Typical DSC traces of PEI containing a mo-

lar ratio of Li/(-CH<sub>2</sub>CH<sub>2</sub>NH-) of 1/10 are shown in Figure 1 for PEI-LiCF<sub>3</sub>SO<sub>3</sub>. Trace (a) was obtained when heated at 20 °C/min for the first time. It shows an indication of a glass transition at -13 °C and an endothermic peak at 52.8 °C attributed to the melting of PEI crystals. Upon cooling from the molten state at 20 °C/min, one obtains trace (b) which shows only the glass transition with no evidence of a crystallization exotherm. [The same polymer without the addition of salt exhibits a sharp exotherm upon cooling.] Subsequent heating and cooling cycles, traces (c) and (d), show only a change in heat capacity; no first order transitions. If stored at room temperature for several days, crystallization does occur and the characteristics of trace (a) can be reproduced.

The same DSC characteristics were observed

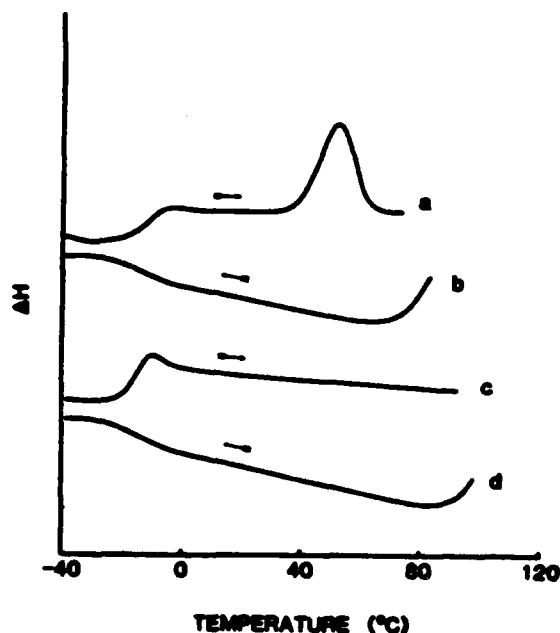


FIGURE 1  
DSC Traces of PEI-LiCF<sub>3</sub>SO<sub>3</sub> complexes.

for all of the lithium salts listed above except LiF. In this case, there was essentially no change in the melting point of the PEI crystals, crystallization of the polymer was observed upon cooling, and evidence for a glass transition in the temperature range examined was absent. The only indication we have so far that LiF has dissolved in the polymer is that the degree of crystallinity has been reduced.

The DC conductivity results for PEI containing 0.1 mole of  $\text{LiClO}_4$  per mole of monomer repeat are shown as a function of reciprocal temperature in Figure 2 for both cooling and heating cycles. Conductivity data obtained during the cooling cycle exhibit a smooth but curved variation with reciprocal temperature.

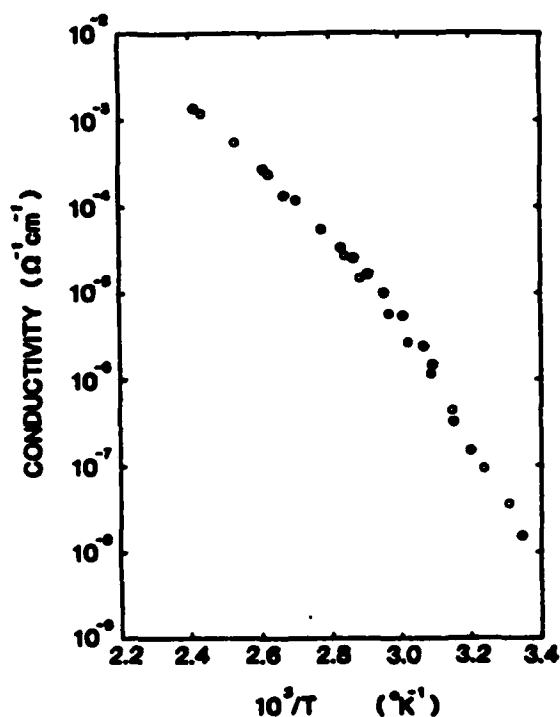


FIGURE 2  
Conductivity of PEI- $\text{LiClO}_4$  complex as a function of inverse temperature. (○ heating; ● cooling)

Data obtained from the same sample upon heating exhibit an abrupt change between 45 and 50 °C which is the region in which uncomplexed polymer undergoes a phase change. Recall that crystallization is not observed upon cooling this system at 20 °C/min in the DSC but the cooling rates used for the conductivity measurements are necessarily much slower and some crystallization may be occurring. The activation energy for ionic conduction seems to depend upon the presence or absence of polymer crystals - much as in the case of poly(ethylene oxide) - salt systems<sup>1-3</sup>. Below 45 °C, the apparent activation energy is 1.35 eV but decreases to 0.72 eV for temperatures above 80 °C. Both the values of conductivity and activation energies are similar to those

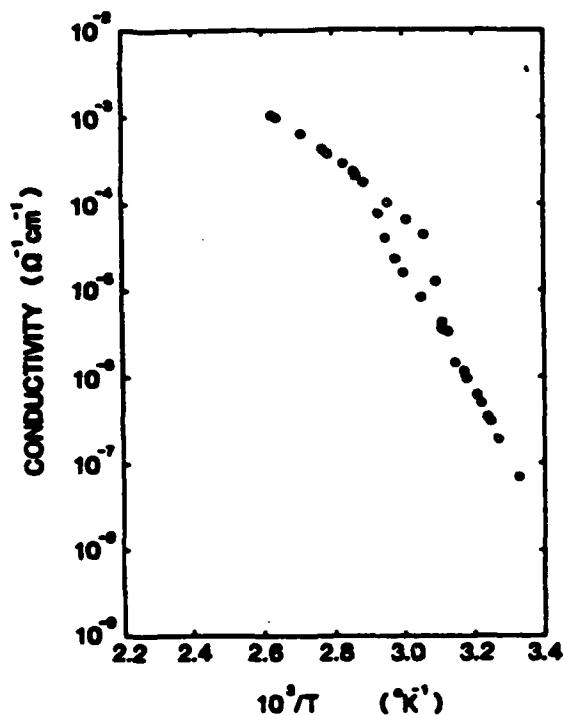


FIGURE 3  
Conductivity of PEI- $\text{LiBF}_4$  complex as a function of inverse temperature. (○ heating; ● cooling)

reported for comparable levels of  $\text{LiClO}_4$  in PEG<sup>13</sup>.

DC conductivity as a function of reciprocal temperature is shown in Figure 3 for PEI containing 0.1 mole of  $\text{LiBF}_4$  per mole of monomer repeat. Hysteresis in conductivity upon heating and cooling in the region of melting and crystallization of the polymer is much more pronounced in this system. Apparent activation energies above and below the crystallization region are 0.56 eV and 1.64 eV, respectively.

#### 4. DISCUSSION

The poly(ethylene imine) prepared by the procedure described is of rather low molecular weight, about 2,000, and crystallizes readily into a brittle material. Broad line NMR proton resonance spectra can be resolved into a narrow line component which we attribute to protons in the amorphous region and a broad component attributable to protons within the crystalline phase. A sample whose degree of crystallinity was 80% as determined by NMR exhibits a heat of fusion (by DCS) of 55.3 cal/g (231.5 J/g). From these data we deduce that the heat of fusion of the crystalline phase is 69.1 cal/g (289.3 J/g) which we use in subsequent estimates for degree of crystallinity in PEI to which lithium salts have been added. As mentioned previously, a reduction in degree of crystallinity implies that the added salt interacts strongly with the polymer and at least some of it must be dissolved. Heats of fusion were obtained on the first heating cycle following removal of the acetonitrile; except for the case of  $\text{LiF}$ , there is no endothermic peak if reheated immediately. The DSC results are summarized in Table I where the observed enthalpies are expressed in grams of polymer (i.e. corrected for salt content). The  $\text{CF}_3\text{SO}_3^-$  (triflate) salt has the

greatest effect on crystallinity which is consistent with the idea that salts of low lattice energy are most readily dissolved<sup>2</sup>. According to the lattice energies compiled by Shriver et al<sup>2</sup>,  $\text{LiBF}_4$  has the lowest lattice energy of the salts examined here but its effect on crystallinity (as cast from acetonitrile) is not as great as most of the other salts. When cooled at 20 °/min from above the melting point of the polymer however, all the salts except  $\text{LiF}$  prevented crystallization of the polymer.

The glass transition temperature of poly(ethylene imine) was not observed directly in our measurements. It is probably below -40 °C which is the lower range of our present DSC equipment. The presence of 80% crystallinity also makes it difficult to determine. However, in other work, we have cross-linked the PEI with varying levels of diepoxyoctane which prevents crystallization and introduces a clearly observed  $T_g$  within the range of our DSC. Extrapolation of these data to zero concentration of cross-links yields -35 °C as an estimate of  $T_g$  which is listed in Table I. Again, all of the salts except  $\text{LiF}$  cause an

Table I  
Complex Formation of PEI and Lithium Salts

| Composition                |                        | Thermodynamic Data  |                   |                       |                   |
|----------------------------|------------------------|---------------------|-------------------|-----------------------|-------------------|
| Lithium Salt               | Concentration (mole %) | Melting Temperature | Enthalpy (cal/gm) | Percent Crystallinity | Glass Temperature |
| None                       | 0                      | 76.4                | 55.35             | 80.0                  | -35               |
| $\text{LiF}$               | 10                     | 76.7                | 55.05             | 80.7                  | none              |
| $\text{LiCl}$              | 10                     | 68.5                | 27.95             | 40.5                  | -16               |
| $\text{LiBr}$              | 10                     | 65.1                | 20.65             | 20.8                  | -15               |
| $\text{LiI}$               | 10                     | 61.5                | 15.65             | 21.8                  | -15               |
| $\text{LiSCN}$             | 10                     | 58.2                | 19.75             | 20.6                  | -20               |
| $\text{LiClO}_4$           | 10                     | 64.7                | 19.75             | 20.6                  | -9                |
| $\text{LiBF}_4$            | 10                     | 58.6                | 27.15             | 20.3                  | -23               |
| $\text{LiCF}_3\text{SO}_3$ | 10                     | 58.8                | 6.17              | 8.8                   | -13               |

increase of  $T_g$ . Presumably,  $Li^+$  ions act as cross-links by interacting with unshared electron pairs on the nitrogens of neighboring chains. An increase in  $T_g$  is further evidence for the dissolution of salt by the polymer<sup>14</sup>.

All of the lithium salts examined (except LiF) have about the same effect on the glass transition temperature as obtained from DSC scans at 20°/min. Conductivity data shown in Figures 3 and 4 for  $LiClO_4$  and  $LiBF_4$  represent the highest and lowest  $T_g$ 's of the very limited range. The system containing  $LiBF_4$  exhibits a larger conductivity than that of  $LiClO_4$  over the whole range of temperature which is consistent with greater mobility in the system of lower  $T_g$ . The conductivities are in the same range as those reported for poly(ethylene oxide) - salt systems<sup>13,15</sup>, especially above the melting point of the PEI.

The pronounced hysteresis in conductivity between heating and cooling in the PEI- $LiBF_4$  system of Figure 3 is associated with the melting and crystallization of polymer crystals. Super cooling and slow crystallization are phenomena usually observed in polymers but the dissolution of salt in the polymers discussed here enhances these effects. When cooled from above the melt, the conductivity decreases smoothly with decreasing temperature until about 50 °C where it suddenly decreases over a narrow temperature range and then assumes a smooth decrease again with a higher activation energy than at higher temperatures. The rapid decrease coincides with polymer crystallization. Upon reheating, the polymer crystals persist until about 70° and the conductivity is consequently lower between 50 and 70° than it was during cooling through this same region. The reasons for reduced conductivity in the presence of polymer crystals have not been determined but one can speculate on possibilities. Certainly the presence of

crystallites through which the ions cannot move will require that the ions migrate through a more tortuous path which will reduce conductivity but one would not expect this to greatly influence the apparent activation energy for conduction. Since the ions are dissolved in the amorphous regions of this polymer, the removal of part of this phase by crystallization will increase the concentration of ions in the remaining amorphous phase which in turn can cause an increase in  $T_g$  and reduce mobility of ions in the polymer. Furthermore, if the motion of ions bound to a polymer chain depends upon the segmental mobility of the polymer chain, such motion can be expected to be greatly inhibited by incorporation of a part of the chain in a polymer crystal.

Conductivity data obtained upon cooling the PEI containing  $LiClO_4$  covers a large temperature range over which the polymer remains almost completely amorphous. When plotted as a function of reciprocal temperature, the data are represented by a curved line reminiscent of the temperature dependence of viscosity which has been noted for other polymer-salt systems<sup>4</sup>. Assuming that conductivity varies inversely with viscosity, the data can be fit very well to a form of the WLF equation<sup>16,17</sup>:

$$\sigma = \sigma^* \exp[-C_1 C_2 / (T - T_0)] \quad (1)$$

where  $\sigma$  is conductivity,  $T$  is temperature,  $C_1$  and  $C_2$  are constants related to fractional free volume and its variation with temperature,  $\sigma^*$  is the conductivity at  $T_g$  times  $e^{C_1}$ , and  $T_0$  is a temperature parameter.  $T_0$  is related to the glass transition temperature through the relation:

$$T_0 = T_g - C_2 \quad (2)$$

Values of the parameters obtained from a least squares fit to the data are  $T_0 = 198$  K and  $C_1 C_2 = 930$  K. From the value of  $T_g$  in Table 1, we deduce that  $C_2 = 66^\circ$  and  $C_1 = 14.1$  which

are close to the "universal" values of 51.6 and 17.4, respectively. The data can be fit equally as well to empirical equations of the form:

$$\sigma = (A/T) \exp [-B/(T-T_0)] \quad (3)$$

or

$$\sigma = (A/T^{1/2}) \exp [-B/(T-T_0)] \quad (4)$$

where A, B, and  $T_0$  are constants.

## 5. CONCLUSIONS

Linear poly(ethyleneimine) has been shown to dissolve the lithium salts of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{CF}_3\text{SO}_3^-$  at concentrations of 1 mole of salt to 10 moles of monomer repeat. If LiF dissolves, it is to a lesser extent than the other salts. Dissolution is evidenced by a decrease in crystallinity of the normally semicrystalline polymer, an increase in the glass transition temperature and large increases in conductivity. No evidence for a high-melting specific crystalline complex between the linear PEI and Li salts has been observed. Temperature dependence of DC conductivity as deduced from AC impedance analysis shows a change in slope at the melting point of the PEI crystals. Hysteresis between heating and cooling is observed in some cases in the region of crystallization and melting showing greater conductivity in an undercooled sample than in a semicrystalline sample at the same temperature. For polymer-salt systems in which crystallization is suppressed during the time scale of the electrical measurements, the conductivity data as a function of temperature are well-represented by an empirical equation similar to the MLF equation which describes the temperature dependence of viscosity. The parameters deduced from a least squares fit to the data yield constants similar to those of the MLF equation.

## ACKNOWLEDGEMENT

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