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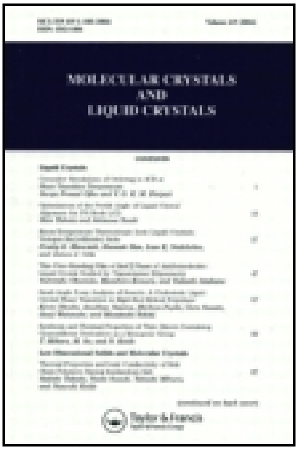

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Ion Interaction in (Ethylene Oxide) Based Polymer Electrolyte

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ION INTERACTION IN (ETHYLENE OXIDE) BASED POLYMER ELECTROLYTE

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Abstract A new polymer electrolyte based on ethylene oxide unit was synthesized and complexed with lithium salts for high ionic conductivity at room temperature. The salts used were lithium perchlorate and lithium triflate. FTIR and FTRaman spectrosocpies were used to characterize ion-ion or ion-polymer interaction and to determine the relative amount of ions present in the complexes. The spectroscopic analysis was performed as a function of $[EO]/[Li^+]$ ratio (20 ~ 5) and temperature (up to 120 °C). The free ion percentages in the lithium perchlorate-complexes rapidly decreased to $[EO]/[Li^+]$ ratio of 10 and then levelled off. But its ionic conductivity linearly decreased over the salt concentration range studied. The negative temperature dependence of free ion concentration was observed for the lithium triflate-complexes.

INTRODUCTION

Solid polymer electrolytes are highly conductive at solid states and formed by the dissociation of salts in ion-solvating polymers.[1] Ion solvating polymers of high ionic conductivity are required to have chain flexibility for facilitated ion movement through the solid polymer electrolyte and high solvating power for maximum dissociation of lithium salts (small lattice energy). But the amount of charge carrier, especially free ion responsible for the ionic conduction may be reduced due to ion-ion interaction such as the formation of neutral ion pairs and ion multiples.[2] In this study FTRaman and FTIR have been used to investigate the degree of ion dissociation as a function of salt concentration and how it is related to ionic conductivity. Poly[oligo(oxyethylene) oxysebacoyl] (called PES) was used as a solvating polymer.

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EXPERIMENTAL

Synthesis of Polymer

Poly[oligo(oxyethylene)oxysebacoyl] was synthesized by reacting poly(ethylene glycol) (PEG, molecular weight = 1,000) with sebacoyl chloride. PEG was dissolved in benzene and then triethylamine (TEA) was added as a catalyst. Sebacoyl chloride dissolved in benzene was dropped into the PEG solution which was maintained at 5 °C using dropping funnel. After complete dropping the reaction temperature was raised to 60 °C and kept for 10 hr. And then the reaction product was filtered and freeze-dried for 24 hr.

Characterization of Complexes

Polymer-salt complexes were prepared of $[EO]/[Li^+] = 5 \sim 20$ by dissolving stoichiometric amount of the polymer and lithium salt in anhydrous acetonitrile and then allowing the solvent to evaporate. The FTIR measurements were performed with Midac Prospect spectrometer at room temperature, 40, 60, 80, 100 and 120 °C. The complexes were mixed with KBr and pelletized. FTRaman spectra were also obtained with Perkin Elmer Sys 2000 by averaging 128 scans with a resolution of 4 cm^{-1}. Model studies of lithium salts in acetonitrile were performed for the concentration of 0.05, 0.5, 0.8 mole and pure salts.

Complex impedance measurements over frequency range of 10 Hz to 100 kHz were performed using Solartron 1255 frequency response analyzer with an applied potential of 5 mV. All the impedance measurements were done using stainless steel blocking electrodes in a glove box.

RESULTS AND DISCUSSION

Figure 1 shows the deconvoluted FTIR spectrum of PES-$LiClO_4$ complex whose salt concentration is $[EO]/[Li^+] = 5$. The frequency window is in the range of the ClO_4 stretch vibration. The two distinct components in the peak indicate two different environments for the anions. The two peaks at ~625 cm^{-1} and ~637 cm^{-1} are assigned to the free ions and ion pairs through the model compound study. The relative amounts

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of free ions and ion pairs are determined from the deconvoluted peak area. Such analysis result in terms of free ion percentage is presented in Figure 2 along with ionic conductivity. Free ion percentage drops rapidly to salt ratio of 0.1, where the amount of ion pairs becomes significant and then levels off. This may imply that the increment of total free ions with salt ratio may be offset by the hindered chain mobility due to strong ion-polymer association.

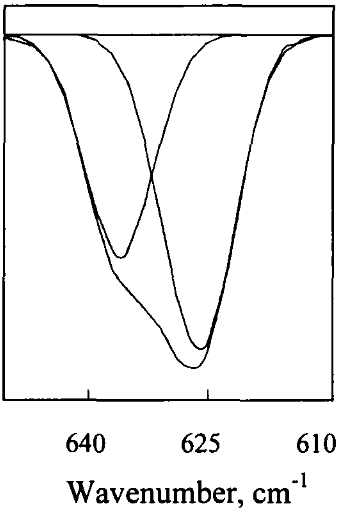

FIGURE 1 Deconvoluted FTIR spectrum of $LiClO_4$ complex for $[EO]/[Li^+] = 5$.

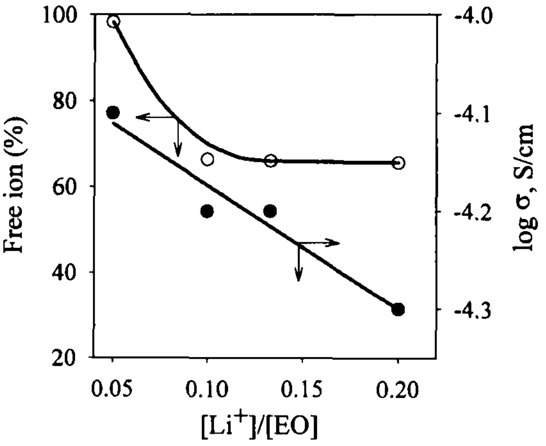

FIGURE 2 Free ion percentage and conductivity of $LiClO_4$ complex as a function of salt concentration.

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FTRaman spectra of PES-$LiClO_4$ complexes for $[EO]/[Li^+] = 5$ and 20 were also obtained to compare with FTIR spectra. As shown in Table I there is a good agreement between them. The ion multiples are not found even at the salt ratio of 5.

TABLE I Comparison of peak deconvolution result by FTIR and FTRaman.

Salt concentraion $[EO] / [Li^+]$	FTIR free ion (%) / ion pair(%)	FTRaman free ion (%) / ion pair(%)
20	98.3 / 1.7	97.8 / 2.2
10	67.0 / 33.0	NA
7.5	66.0 / 34.0	NA
5	65.6 / 34.4	66.4 / 34.4

In the case of PES-$LiCF_3SO_3$ complexes FTRaman spectra were obtained as a function of salt concentration and are presented in Figure 3 in the frequency range of SO_3 symmetric stretch. There are two distinct peaks at ~1032 and ~ 1042 cm^{-1}. The modes at ~1032 and ~1042 cm^{-1} are attributed to free ions and ion pairs.[3, 4] With increasing salt ratio the percentage of free ions becomes less and a small shoulder appears at ~1052 cm^{-1} for $[EO]/[Li^+] = 5$ complex. The highest frequency at 1052 cm^{-1} is assigned to ion multiples. The peak deconvolution results are summarized in Table II. When Table II is compared with Table I, $LiCF_3SO_3$ complexes have much lower free ion percentage and small amount of ion multiples.

To study the effect of temperature on ion-dissociation both complexes for $[EO]/[Li^+] = 10$ were analyzed by FTIR spectrometer. The free ion percentage is shown in Figure 4 with ionic conductivity of $LiClO_4$-complexes only. The conductivity of the $LiClO_4$-complexes increases almost linearly with temperature up to 60 °C but the increment of the free ion percentage is negligible. Thus the conductivity increase may result from the facilitated chain segmental motion. Above 60 °C the small increase conductivity may due to the strong ion-polymer interaction, which results from the more free ions. The negative temperature dependence of free ion concentration was observed in the PES-CF_3SO_3 complexes. The same behavior was also found by Jacobsson[5] and explained by volume changes in the solvation process.

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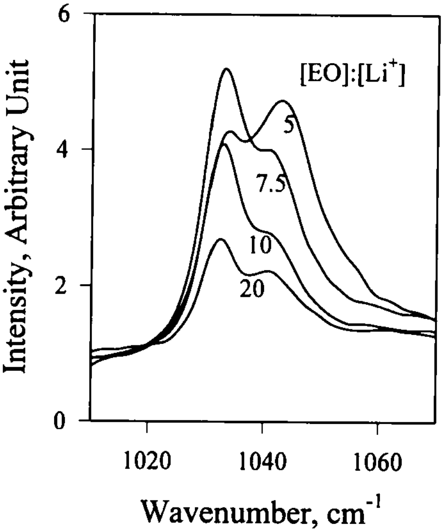

FIGURE 3 FTRaman spectra of PES-LiCF$_3$SO$_3$ complexes.

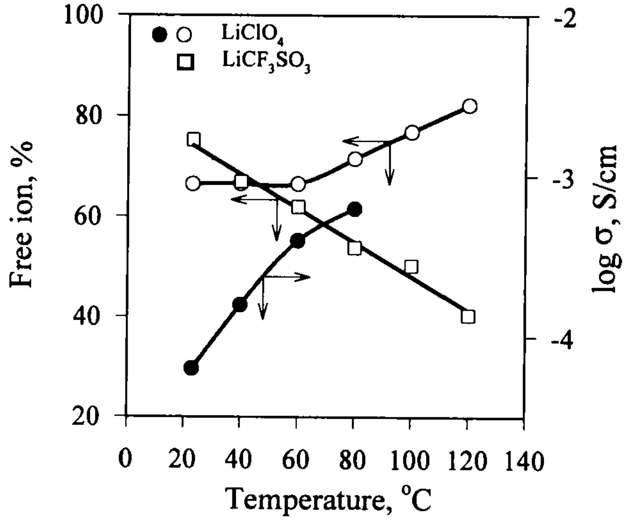

FIGURE 4 Effect of temperature on ion dissociation and conductivity.

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TABLE II Results of peak deconvolution as a function of salt concentration.

Salt concentration [EO] / [Li$^+$]	FTRaman (%) free ion / ion pair / ion aggregates
20	55.4 / 44.6 / 0.0
10	52.7 / 41.3 / 0.0
7.5	44.6 / 50.4 / 5.0
5	31.3 / 63.4 / 5.3

CONCLUSIONS

The ion-ion or ion-polymer interaction of PES complexed with lithium perchlorate or triflate was characterized. The interaction was dependent on the salts complexed and [EO]/[Li$^+$] ratio. In PES-$LiClO_4$ complexes the concentaration of free ions levelled off at salt ratio of 0.1, where ion pairs became significant. But the conductivity linearly decreased with salt ratio because of the reduced chain mobility. PES-$LiCF_3SO_3$ complexes have less free ions and another multiple aggregates, which was not present in PES-$LiClO_4$ complexes. Negative temperature dependence of free ion concentration was found in the PES- $LiCF_3SO_3$ complexes, which needs further study.

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