Ionic Conductivity of Polymer Electrolytes

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Summary: In this work, the effect of different salts: $LiCF_3SO_3$ (lithium triflate, LiOTf) and LiCl in 1:1 mole ratio in a methacrylate-type polymer with zwitterionic pendant groups (PMBS-4) used as host polymer, are evaluated. By means of X-ray diffraction patterns, the formation of a homogeneous solution is observed in the case of PMBS-4/LiCl and PMBS-4/LiOTf. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) allows determination of glass transition temperatures (T_g) and thermal stability of the polymers. T_g values of the two polymer electrolytes are 293 ± 2 K against PMBS-4 which is 291 K. The initial decomposition temperatures (IDT) for PMBS-4 and PMBS-4/Lithium salt are 483 K and 460 K, respectively. The *ac* ionic conductivity (σ) was obtained using the electrochemical impedance spectroscopy (EIS). It was found that σ increases as temperature rises following a simple Arrhenius behavior and reaches a value of $\sim 6 \times 10^{-4}$ S/cm in the case of PMBS-4/LiCl and $\sim 2 \times 10^{-2}$ S/cm in the case of PMBS-4/LiOTf, both measured at 343 K.

Keywords: dielectric properties; polymer electrolytes; polymer-salt complexes; zwitterionic polymers

Introduction

Ionically conducting polymer electrolytes have been considered in recent years as candidates for a number of applications including high energy density and power lithium batteries. That the cation of the inorganic salt coordinates with polymer and that ionic transport occurs in amorphous region of materials are common features of so-called traditional polymer electrolytes.[1] Most research activities on polymer electrolytes have focused on systems related to poly(ethyleneoxide) (PEO). In the early 70 s, the first measurement of ionic conductivity in polymer electrolytes, PEO-salt complexes were carried out by Wright[2] and Armand,[3] who were the first to use polymer-salt complexes as electrolytes in lithium batteries. A polymer electrolyte with high value of conductivity ($\sim 10^{-3}$ Scm^{-1}) at room temperature is the key requirement for these applications. The ability of a polymer material to dissolve salts can be studied with the dielectric parameters associated with relaxation processes in ion conducting polymers where the dielectric constant plays a fundamental role.[4,5]

On the other hand, the synthesis, structure and dielectric properties of zwitterionic polymers have been extensively studied by Cardoso et al.[6–9] and by Rozanski et al.[10] These polymers have shown interesting properties; particularly those related to electrical conductivity and associated phenomena. Their applications in the production of solid-state batteries are potentially suitable. In the absence of salts, the presence of zwitterionic structures of two opposed sign charges joined by covalent

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bonds provides specific dipole-dipole interactions which induce conductivity levels comparable to those of salt-polyether systems. However, this behavior is observed in a very narrow temperature range and for temperatures higher than 473 K.

According to Cardoso et al.,[8] the flexibility of the polymethacrylate lateral chains with zwitterionic pendant groups brings the glass transition temperature (T_g) down up to 298 K with respect to that of the parent polymer. There are some reports[11,12] indicating that polymethacrylates with grafted POE groups render conductivity values as high as 10^{-4} S/cm. There is also evidence of strong dipole effects of the ionic side groups which allow the formation of complex salts up to stoichiometric ratios, resulting in the generation of a high concentration of ion carriers. High conductivity in zwitterionic polymers has been measured and reported by Cardoso et al.[8]

In this work, polymer electrolytes containing two different salts have been studied. Poly(methacrylate sulfobetaine) was chosen as the host polymer. The different salts i.e. $LiCF_3SO_3$ (lithium triflate, LiOTf) and LiCl in 1:1 mole ratio are chosen as dopant salts. Figure 1 shows the polymer electrolyte structure. The effect of different salts is discussed mainly based on the ionic conductivity of the electrolyte films, which is measured by ac impedance experiments. Conductivity values were measured under different atmospheres.

Experimental Part

Sample Preparation

Sulfobetaine of 12-Ethyl-3,6,9-trioxa-12-azatetradec-1-yl-2-methylacrylate (named MBS-4) was synthesized following the method disclosed in ref. [8]. MBS was polymerized at 60 °C, 50 mmHg for 24 h. AIBN was used as radical initiator. The polymer (PMBS4) was washed twice with ethanol, dissolved in trifluoroethanol, precipitated in cold acetone and dried in a vacuum oven at 50 °C for 48 h.

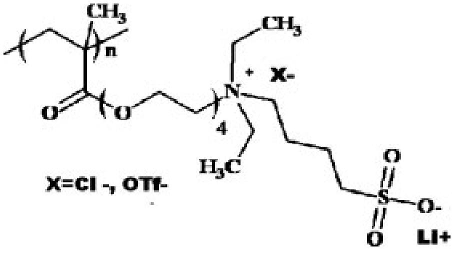

Figure 1.
Sulfobetaine polymer electrolyte structure.

PMBS-4 and LiCl or $LiCF_3SO_3$ (Aldrich Chemical Co.) 1:1 in mole were dissolved in deionized water (18.3 MΩ-cm). The solution was continuously stirred for 24 h at room temperature and then dropped into a circular Teflon mold. Residual water was slowly evaporated and thereafter the sample was vacuum-dried. The film was then kept in a desiccator for further drying until characterizations were carried out. The systems obtained were named PMBS-4/ LiCl or PMBS-4/ $LiCF_3SO_3$, respectively.

Sample Characterization

PMBS-4 structure was verified by ^{1}HNMR in 5–10% weight solution of D_2O with 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt as an internal reference. δ units were recorded. Elemental analysis was used to verify the chemical composition of the polymers. Light-scattering experiments were performed at room temperature on a Dawn-F (Wyatt Tech.) apparatus at $\lambda = 6320$ Å in trifluoroethanol. The refractive index increment dn/dc was calculated as 0.211 mL/g in the same solvent at the same former wave length. The thermal behavior was determined on a TA Differential Scanning Calorimeter and on a Thermal Analysis Thermogravimetry instrument linked to a Thermal Analyzer 2100 microprocessor at a heating rate of 10 °C/ min under 50 mL/min of nitrogen within the range of 223 to 453 K. X-ray diffraction patterns for PMBS-4, PMBS-4/LiOTf, and PMBS-4/LiCl were obtained in a Siemens D500 diffractometer using $Cu_{k\alpha}$ radiation. Sweeps from 2 to 70° at 1°/min.

Impedance Measurements

The conductivity experiments were carried out in a hermetic cell, under vacuum, as shown in Figure 2. The cell allowed variation of temperature. The samples were sandwiched between stainless steel electrodes. Once connected to the potentiostat by using a two-electrode configuration the samples were dried overnight by means of a vacuum mechanical pump. The experiments were carried out in the temperature range of 298–343 K. A Potentiostat / Galvanostat, E&GG, PAR, model 283, was used to apply potentials and a frequency response analyzer (FRA) Solartron, model IF 1260, for impedance measurements in the frequency range of 0.1 Hz–300 kHz.

Results and Discussion

Elemental Analysis and ^{1}H-NMR analysis, confirmed the proposed structure (see Figure 1). The molecular weight of PMBS-4 was obtained from light-scattering measurements using the classical Zimm plots. The calculated value was 28,000 g/mole. Since PMBS-4 has 4 ethylene glycol residues, its semicrystalline character is weak, as confirmed by the absence of ordered domains in the X-ray diffraction patterns shown in Figure 3. Here, the curves provide information on the absence of domains made of correlated aggregated chains. The formation of a homogeneous solution was observed in the case of PMBS-4/LiCl and PMBS-4/LiOTf (not shown in Figure 3), which indicated the complete dissolution of the salt in the polymer matrix up to 1:1 ratio. These results revealed that the neutralization of zwitterionic groups by the salts had occurred and that the formed complexes were amorphous. Berhier et al.[13] established that ionic conductivity in polymer electrolytes is associated with the amorphous phase of the studied samples. Therefore, these results could be related to a high ionic conductivity.

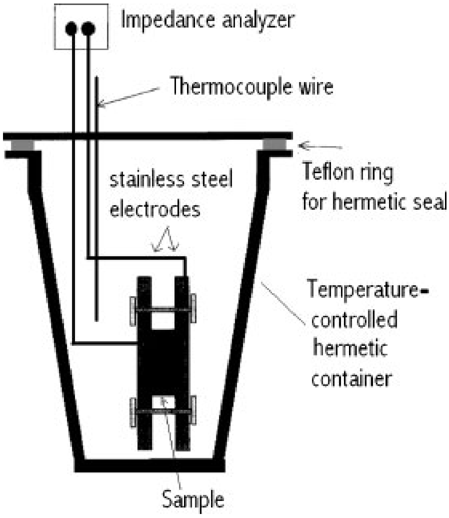

Figure 2.
Schematic view of the hermetic cell used in conductivity tests.

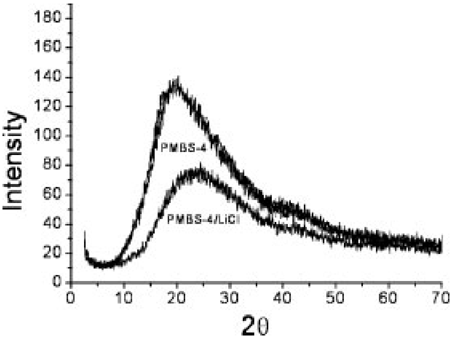

Figure 3.
Wide-angle X-ray patterns for the mixture 1:1 of polymer and ionic salt (indicated in the figure).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the glass transition temperatures (T_g) and thermal stability of the polymers. T_g values of the two polymer electrolytes were essentially the same (293 ± 2 K) as that of PMBS-4 which is 291 K. Katiyar and coworkers[14] have observed in PEO/LiOTf that an increment of Tg with increasing amounts of salt is common, meanwhile there have been reports where Tg variation was not very smooth and even Tg decreased with increasing amount of salt content in the polymer electrolytes.[15] This is explained by assuming that the elevation of Tg with salt addition arises from the transient crosslinking between Li^+ ions and O atoms in the polymer chains and the anions (Cl^- and OTf^-) might also interact with the ammonium nitrogen due to the zwitterionic character. So, the elevation of Tg could be mainly correlated to the number of free Li^+ ions. The larger the number of free Li ions, the higher the elevation of Tg for polymer salt complexes. In a polymer with a higher Li salt content, the number of free Li ions might not increase because they interact to generate ion-pairing (anion complex-cation interaction) and keep the number of free Li ions, which are responsible for the transient crosslinking to the polymer chains, more or less constant. Hence, for polymer electrolytes with high salt content, the Tg remained almost the same.

Initial decomposition temperatures (IDT) for PMBS-4 and PMBS-4/Lithium salt were 483 K and 460 K, respectively. The presence of Li^+ ions in the PMBS-4 polymer did not influence the T_g values of the samples. IDT decreased due to an instable complex formation with the lithium ions.

Conductivity Characterization

In order to obtain the ionic resistance of the polymers, several sets of measurements were performed using EIS. The measurements were carried out in the frequency range of 0.1 Hz–300 kHz at the open circuit potential and different temperatures. In Figure 4a*i* and 4b*i*, the impedance spectra show depressed semicircles at room temperature (298 K). The depressed semicircles, in the higher frequency range, are associated to the ionic resistance (*R*) of the polymer electrolyte and the capacitance of the double layer, at lower frequencies the response is an inclined line, which is the typical response of blocking electrodes.[16,17] The ionic resistance (*R*) of the polymer electrolyte can be readily obtained from the high-frequency intercept of the Cole-Cole plot on the real-axis or the intercepting point of the inclined line with the real axis. Since at high temperatures the semicircles disappear. The *ac* ionic conductivity (σ) of a) PMBS-4/LiCl and b)

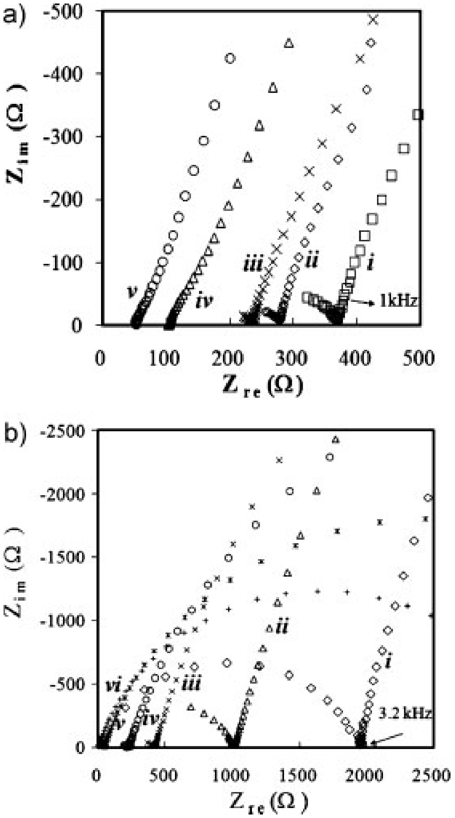

Figure 4.
Impedance spectra at the open circuit potential, in vacuum of *a)* PMBS-4/LiCl, (*i*) 298 K, (*ii*) 308 K, (*iii*) 313 K, (*iv*) 323 K and (*v*) 343 K. and *b)* PMBS-4/LiOTf, (*i*) 298 K, (*ii*) 303 K, (*iii*) 308 K, (*iv*) 313 K, (*v*) 323 K and (*vi*) 343 K.

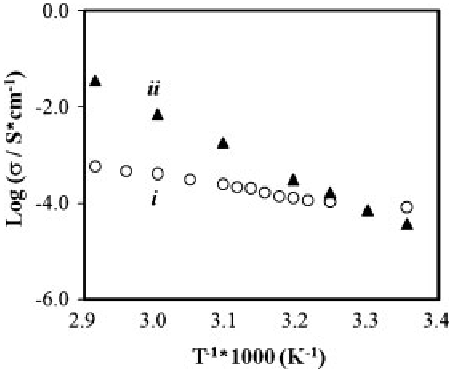

Figure 5.
Variation of log ionic conductivity with the inverse of absolute temperature. Experiments made in vacuum of: (*i*) PMBS-4/LiCl and (*ii*) PMBS-4/LiOTf.

Table 1.
Thermal and dielectric characterization of PMBS-4/Li salt.

Sample	Salt type	Atmosphere	Tg (°C)	IDT (K)	Bulk conductivity at 25 °C	Ea (eV)
PMBS-4	–	N_2	291	483	3.3 E-7	1.11
PMBS-4	LiCl	air	292	460	2.0 E-3	2.03
PMBS-4	LiCl	vacuum	292	460	1.0 E-4	1.74
PMBS-4	LiOTf	air	293	453	2.2 E-4	–
PMBS-4	LiOTf	vacuum	293	453	3.6 E-5	1.37

PMBS-4/LiOTf polymer electrolytes can be calculated from the intercept of the Cole-Cole plot on the real-axis (*R*) and using equation 1.

$$\sigma = \frac{l}{AR} \tag{1}$$

Where: *l* is the thickness of the polymer; *A* is the area and *R* the ionic resistance.

The ionic conductivity (σ) measurements versus the inverse of temperature are presented in Figure 5. Temperature (T) was varied from 298 to 343 K. In Figure 5 the ionic conductivity increases as the temperature rises. It reaches a value of $\sim 6 \times 10^{-4}$ S/cm at 343 K for PMBS-4/LiCl (Figure 5*i*) and $\sim 2 \times 10^{-2}$ S/cm for PMBS-4/LiOTf (Figure 5*ii*). $LiCF_3S0_3$ is easily dissociated by the polymeric matrix compared to LiCl. This results in the triflate sample being more conductive. For temperatures higher than Tg (Table 1), the increases in conductivity with temperature can be explained due to the increased flexibility and bond rotations on the polymer chain, which may cause segmental motion, favoring the movement of hopping inter-chain and intrachain ionic motion.

In Figure 5, the temperature dependence follows a simple Arrhenius behavior. The equation $\sigma = \sigma_o e^{-Ea/kT}$ (where σ_o is a pre-exponential factor, E_a is the apparent activation energy, k is the Boltzmann constant and T is the absolute temperature) approximates its behavior in the temperature range fairly well. The bulk activation energy was calculated from this equation and reported in Table 1. Atmosphere influence on ionic conductivity is shown in Table 1. Ionic conductivity increases in air and decreases in vacuum, due to the effect of humidity.

Conclusions

The effect of different salts: $LiCF_3SO_3$ (lithium triflate, LiOTf) and LiCl in 1:1 in mole ratio in a methacrylate-type polymer with zwitterionic pendant groups (PMBS-4) used as host polymer, was evaluated. The Elemental Analysis and ^{1}H-NMR analysis, confirmed the proposed structure. Since PMBS-4 has 4 ethylene glycol residues, its semicrystalline character is weak, as confirmed by the absence of ordered domains in the X-ray diffraction patterns. The formation of a homogeneous solution is observed for PMBS-4/LiCl and PMBS-4/LiOTf. T_g values of the two polymer electrolytes were measured as $\sim 293 \pm 2$ K against PMBS-4 which was 291 K. The initial decomposition temperatures (IDT) for PMBS-4 and PMBS-4/Lithium salt were 493 K and 460 K, respectively. The presence of Li^+ ions in the PMBS-4 polymer did not influence the T_g values of the samples. The ionic resistance (*R*) of the polymer electrolyte was obtained from the high-frequency intercept of the Cole-Cole plot on the real-axis, but at high temperatures the semicircles disappeared. The *ac* ionic conductivity (σ) increased as the temperature rose following a simple Arrhenius behavior and at 343 K reached a value of $\sim 6 \times 10^{-4}$ S/cm for PMBS-4/LiCl and $\sim 2 \times 10^{-2}$ S/cm for PMBS-4/LiOTf.

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