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Conductivity studies on poly(MEEMA)-LiCF$_3$SO$_3$ polymer–electrolyte systems

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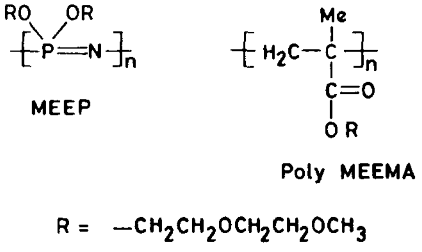
Poly (methoxy ethoxy ethyl methacrylate) (poly(MEEMA)), an acrylate polymer containing a short oligo oxyethylene side chain, readily dissolves alkali metal salts. Ionic conductivity studies on poly(MEEMA)-LiCF$_3$SO$_3$ complexes at different compositions and temperatures have been carried out. The highest conductivity observed for the poly(MEEMA)-LiCF$_3$SO$_3$ (O:Li, 20:1) complex is 2.98×10^{-5} S cm^{-1} at 298 K. I.r. SEM and XRD studies have also been carried out. The complexes are amorphous and the conductivity behaviour follows the Vogel–Tammann–Fulcher equation.

(Keywords: poly(MEEMA); polymer electrolytes; ionic conductivity)

INTRODUCTION

We have recently described the design and synthesis of a new short chain oligo etheroxy side group containing polymethacrylate poly(methoxy ethoxy ethyl methacrylate) (poly(MEEMA)), which can function as a polymer electrolyte in its complexes with alkali metal salts[1,2].



Scheme 1

Among the various new polymers that have been tried out in recent years as candidates for polymer electrolytes, the polyphosphazene MEEP, $-[(OR)_2P{=}N]_n-$, has shown the greatest promise[3,4]. However, MEEP suffers from serious drawbacks such as low dimensional stability, hydrophilicity and consequent solubility in water[5,6]. We felt that these disadvantages in MEEP could be overcome by changing the backbone structure of the polymer. A short etheroxy side chain on a methacrylate backbone was also chosen to see if the conductivities of the resulting polymer electrolytes are affected, because polymer electrolytes with a methacrylate backbone and long etheroxy side chains exhibit low conductivity values[7–10]. As expected, poly(MEEMA) has been found to be completely amorphous and hydrophobic. In addition to being easily synthesized, poly(MEEMA) forms a number of metal salt complexes which form homogeneous phases. We here describe detailed conductivity studies on the poly(MEEMA)-LiCF$_3$SO$_3$ system.

EXPERIMENTAL

Materials

Methacrylic acid (Merck, Germany) and 2-[2-(methoxy ethoxy)ethanol] (Aldrich, USA) were used as received. Thionyl chloride and triethylamine (S.D. Fine Chemicals, India) and other organic solvents were purified before use[11]. LiCF$_3$SO$_3$ (Aldrich, USA) was dried in an oven at 100°C for 24 h before use. AIBN (Aldrich, USA) was recrystallized from methanol and vacuum dried prior to use.

MEEMA and poly(MEEMA) were prepared as described earlier[1]. Poly(MEEMA) is a high-molecular-weight polymer ($\bar{M}_w$ 2.4×10^5) soluble in several organic solvents and it is completely amorphous (T_g -26.5°C).

Measurements

I.r. spectra were recorded neat or as films in chloroform on a Perkin–Elmer 1600 series model spectrophotometer. Thermal data were obtained on a Perkin-Elmer DSC 7 thermal analyser and on a Dupont 9900 thermal analyser at a heating rate of 10°C min^{-1}. G.p.c. measurements were carried out on a Maxima 820 instrument using THF as the eluent and polystyrene as a standard calibrant. X-ray diffraction (XRD) patterns of all the samples were recorded on a Rich Seifert (ISO Debye Flex 2002 D) counter diffractometer using Cu Kα radiation and operating at 30 kV. All XRD studies were done at room temperature. The electron micrographs were taken with a Jeol scanning microscope (JSM 840A). Each sample was silver coated using a sputtering unit (International Scientific Instruments PS-2 coating unit) before loading in the system. The photographs were taken at 10 kV accelerating voltage.

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Thin film preparation

Appropriate amounts of poly(MEEMA) and $LiCF_3SO_3$ were dissolved in dry THF and allowed to form a homogeneous solution of the polymer–salt complex by stirring at room temperature for 8–20 h. The solution was concentrated and cast on a Teflon sheet and the solvent was removed at room temperature. The samples were dried completely under vacuum (10^{-1} Torr) at 40°C for 48 h. The dried thin films (thickness 0.2–0.8 mm) were used for the conductivity measurements.

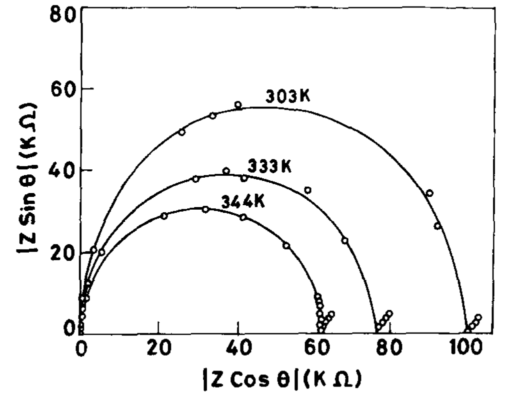

Figure 1 Complex impedance plot for a poly(MEEMA)–$LiCF_3SO_3$ complex (O:Li, 24:1) at three different temperatures

Conductivity measurements

The conductivity studies were carried out using a HP 4194A impedance/gain phase analyser with a slow heating rate. A dynamic vacuum of $\sim 10^{-3}$ Torr was maintained throughout the experiment to exclude moisture and solvent that might be present in the samples. The bulk resistances of the complexes were obtained using the complex impedance spectra at different temperatures and were analysed using a software package[12].

RESULTS AND DISCUSSION

Characterization of poly(MEEMA)–$LiCF_3SO_3$ complexes

Seven polymer–salt complexes were prepared by varying the Li:O ratios. I.r. data pertaining to the C=O and C–O–C stretching frequencies for the selected compositions are given in *Table 1*. The peak positions due to C=O stretching are split and/or shifted to lower energy in the metal salt complexes. The C–O–C stretching frequencies considerably broaden upon complexation. Based on the above observations it is reasonable to suggest that both the ether oxygens and the carbonyl oxygen are involved in coordination to the metal.

XRD studies on the polymer–salt complexes have shown a complete absence of crystallinity, indicating that they are amorphous in nature. SEM studies on the pure

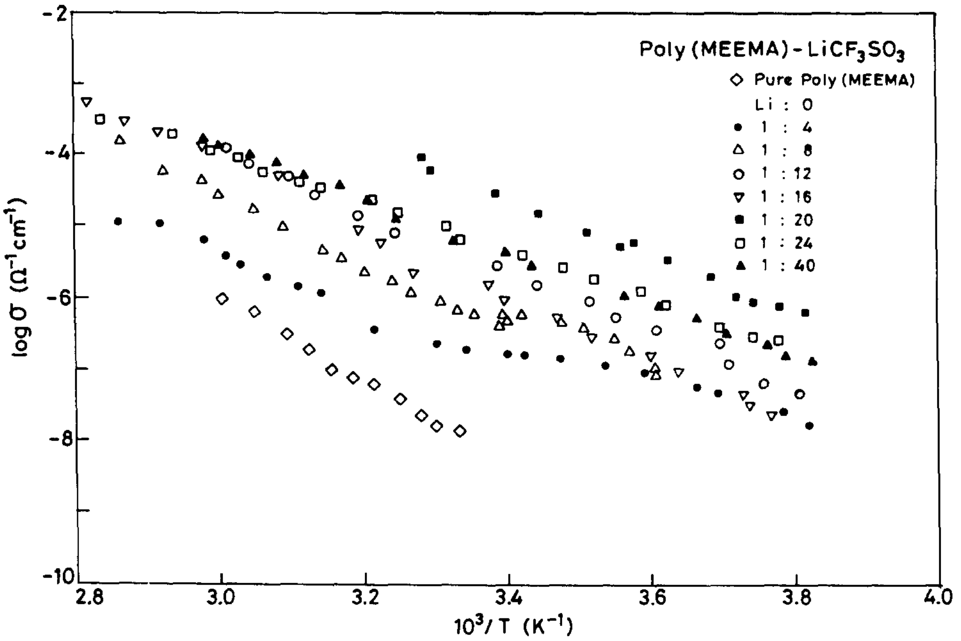

Figure 2 Conductivity plots (log σ vs. $10^3/T$) for poly(MEEMA)–$LiCF_3SO_3$ complexes

Table 1 Stretching frequencies for poly(MEEMA)–$LiCF_3SO_3$ complexes

Sample	Li:O ratio	C=O stretching frequency (cm^{-1})	C–O–C stretching frequency (cm^{-1})
Poly(MEEMA)	0	1733.8 (vs)	1110.1 (vs)
Poly(MEEMA)–$LiCF_3SO_3$	1:8	1729.8 (vs)	1164.9; 1037.3 (b)
	1:12	1731.7 (vs); 1714.6 (vs)	1167.7 (b)
	1:20	1724.1 (vs)	1113.1 (b)
	1:24	1731.9 (vs); 1715.4 (vs)	1108.8 (b)

vs, Very strong; b, broad

polymer, poly(MEEMA) and its salt complexes further support their amorphous nature.

Conductivity studies on poly(MEEMA)–$LiCF_3SO_3$ salt complexes

Conductivity studies were carried out on the thin films of the polymer–salt complexes by impedance spectroscopy. D.c. conductivity of each composition at different temperatures was measured by complex impedance analysis of the strong frequency-dependent impedances of the samples. *Figure 1* shows a typical plot for the complex with an Li:O ratio of 1:24 at three different temperatures. The d.c. resistance of each sample at different temperatures was obtained and the conductivity was computed.

Figure 2 shows the conductivity plots ($\log \sigma$ vs. $10^3/T$) obtained for pure poly(MEEMA) and the various poly(MEEMA)–$LiCF_3SO_3$ complexes. As can be seen from the plot, the polymer–salt complex with a Li:O ratio of 1:20 has the highest conductivity. *Figure 3* shows the conductivity isotherm of various poly(MEEMA)–$LiCF_3SO_3$ complexes along with that of the virgin polymer at 303 K. The most conductive complex (Li:O, 1:20) has a conductivity of the order of $10^{-5}\,S\,cm^{-1}$, as compared to $10^{-8}\,S\,cm^{-1}$ for pure polymer at 303 K. Thus an enhancement in conductivity of about three orders of magnitude is seen.

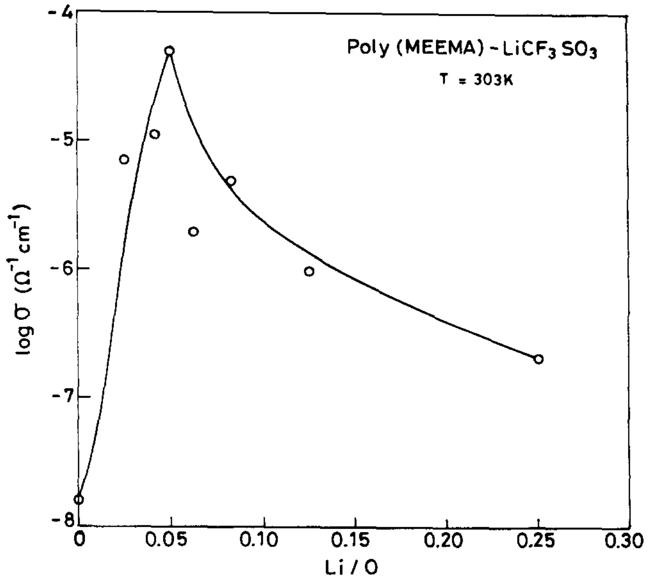

Figure 3 Conductivity isotherm plots for poly(MEEMA)–$LiCF_3SO_3$ complexes at 303 K

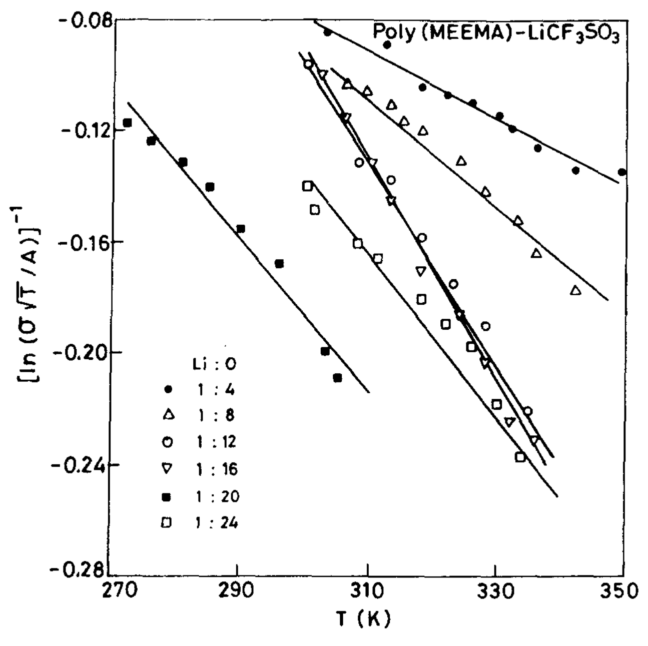

Figure 4 VTF plots for poly(MEEMA)–$LiCF_3SO_3$ complexes

Table 2 Values computed using *Figure 4*

Composition (Li:O ratio)	B (eV)	T (K)	T_g, T_0+50 (K)	A
1:4	7.32×10^{-2}	232	282	0.500
1:8	4.58×10^{-2}	252	302	0.333
1:12	2.41×10^{-2}	273	323	0.250
1:16	2.22×10^{-2}	276	326	0.200
1:20	3.13×10^{-2}	232	282	0.166
1:24	2.95×10^{-2}	254	304	0.143

Another interesting feature of the conductivity plots is that they are gentle curves and not perfectly straight lines. This behaviour, which is explained by the free volume or the configurational entropy model[13–15], obeys the Vogel–Tammann–Fulcher (VTF) equation,

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

where σ and T are the conductivity and temperature values respectively, k is the Boltzmann constant, A is proportional to the number of charge carriers, the T_0 term in the exponential is closely related to the glass transition temperature of the samples and B is the activation energy.

A plot of $\ln(\sigma\sqrt{T}/A)^{-1}$ vs. T for all polymer–salt complexes affords straight lines as expected (*Figure 4*). T_0, T_g and B values computed from the plots are listed in *Table 2*.

In general, it can be seen that for the highest conducting composition the T_0 value is the lowest. Since the T_g values are related to the T_0 values it is not unreasonable to find that the T_g of the highest conducting composition is also the lowest.

The conductivity trends observed in the poly(MEEMA)–$LiCF_3SO_3$ system are consistent with literature trends on other amorphous polymer electrolytes[16]. Briefly, increased addition of the salt, while increasing the conductivity, also enhances the T_g; this latter feature is counterproductive for ionic conductivity. Thus, the conductivity increases gradually with addition of metal salt and after attaining a maximum, falls off due to possible increase in T_g (ref. 3).

CONCLUSION

In conclusion it is to be noted that poly(MEEMA)–$LiCF_3SO_3$ complexes exhibit ionic conductivity comparable to one of the best polymer electrolytes, the MEEP–$LiCF_3SO_3$ system[4]. In view of the many desirable features of poly(MEEMA) it is quite likely that polymer electrolytes based on this new polymer system may find use in practical electrochemical devices.

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