

Characterization of plasticized PMMA–LiBF₄ based solid polymer electrolytes

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Abstract. Polymer electrolyte films prepared from poly(methyl methacrylate) and LiBF₄ with different concentrations of plasticizer (DBP) are described. The formation of polymer–salt complex has been confirmed by FTIR spectral studies. The temperature dependence of conductivity of polymer films seems to obey the VTF relation. Values of conductivities of the polymer complexes are presented and discussed.

Keywords. Polymer electrolyte; PMMA–LiBF₄–DBP; FTIR; impedance studies.

1. Introduction

Many types of ionically conducting polymers, generally classified as polymer electrolytes or polymer ionics (Croce *et al* 1994), have been developed and characterized in recent years. Special interest today is focused on polymer systems having high ionic conductivity at ambient and subambient temperatures, since they find unique applications, such as separators in high power, versatile and rechargeable lithium batteries. Among the most promising examples are gel-type electrolytes obtained by the immobilization of liquid solutions (e.g. propylene carbonate–ethylene carbonate, PC–EC solutions) of lithium salts in a polymer matrix (Abraham 1993). Additionally if these gel electrolytes have high transparency, they become more attractive. The gel properties are governed by all the three components viz. polymers, salt and solvent, and studies on various combinations of these have been reported. PMMA as a host polymer was first reported by Iijima *et al* (1985) and Bohnke *et al* (1993). Wixwat *et al* (1990) reported the properties of a gel made of poly (methyl methacrylate)–poly (ethylene glycol)–LiClO₄. Appetecchi *et al* (1995) studied the kinetics and stability of lithium electrode in PMMA-based gel electrolytes. Sekhon *et al* (1998) reported the transport properties of lithium electrolytes gelled with PMMA.

In an attempt to look for good lithium ion conducting polymer electrolytes, a new plasticized polymer electrolyte composed of PMMA as the host polymer, LiBF₄ as a salt and dibutyl phthalate (DBP) as a plasticizer has been studied. The ionic conductivity of these gels at room temperature is of the order of 10⁻³ to 10⁻⁴ S cm⁻¹ and is comparable with values reported for similar systems.

2. Experimental

Thin films of PMMA–LiBF₄–DBP in different mole ratios were prepared by solution cast technique. PMMA with an

average molecular weight of 1.7 × 10⁵ (Aldrich) and LiBF₄ (Aldrich) were dried by heating them under vacuum at 100 and 70°C for 12 and 24 h, respectively. DBP (dibutyl phthalate) (Aldrich) was used without further purification. The appropriate weights of PVC and LiBF₄ (table 1), were dissolved in THF (tetrahydrofuran) followed by the addition of plasticizer. The solution was then stirred continuously until the mixture took a homogeneous viscous liquid appearance. The solution of different compositions were poured into identical Teflon moulds and THF was allowed to evaporate in air at room temperature. This procedure provided mechanically stable, free-standing and flexible films with thickness between 110–200 μm. The films formed were again dried in a vacuum oven at 323 K with a pressure of 10⁻³ torr for 24 h. Impedance of the film was studied over the frequency range 40 Hz–100 kHz using a LCZ meter (Model 3330, Keithley Instruments Inc., USA). The conductivity was obtained from the bulk resistance found in the complex impedance diagram (figure 2). Perkin-Elmer Paragon 500 Grating IR spectrophotometer was used for IR measurement.

3. Results and discussion

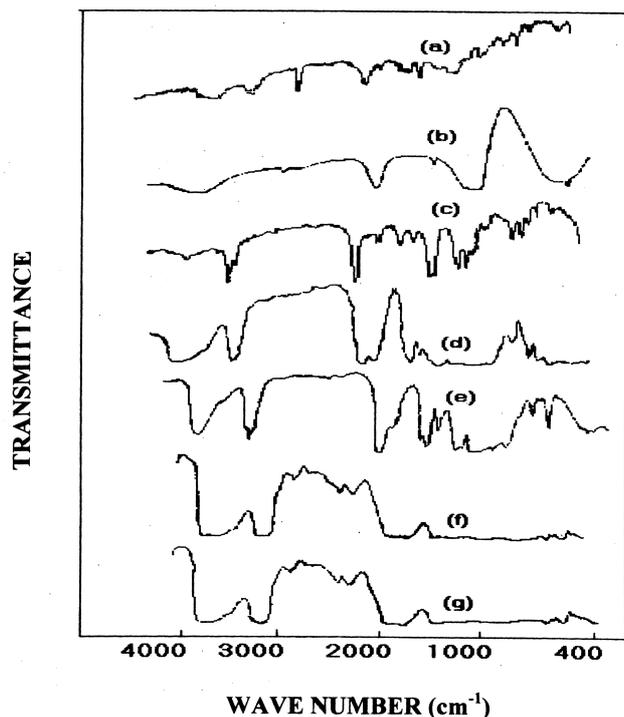
3.1 FTIR spectroscopic studies

The infrared spectra of PMMA, LiBF₄, DBP and polymer complexes are shown in figure 1. IR would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase. The absorption peaks of PMMA (2927, 1559, 1458, 1384, 990, 840, 750 and 483 cm⁻¹), LiBF₄ (3563, 1633, 1305, 1083 and 521 cm⁻¹) and DBP (2961, 2874, 1728, 1578, 1385, 1120 and 1038 cm⁻¹) get shifted in the polymer complexes. The vibrational bands of PMMA (3446 and 668 cm⁻¹) and DBP (3435 cm⁻¹) are found to be absent in the polymer complexes. The band at 1734 cm⁻¹ of PMMA is replaced by two bands at 1728 and 1731 cm⁻¹ in the complexes.

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Table 1. Conductivity values of PMMA–LiBF₄–DBP polymer complexes.

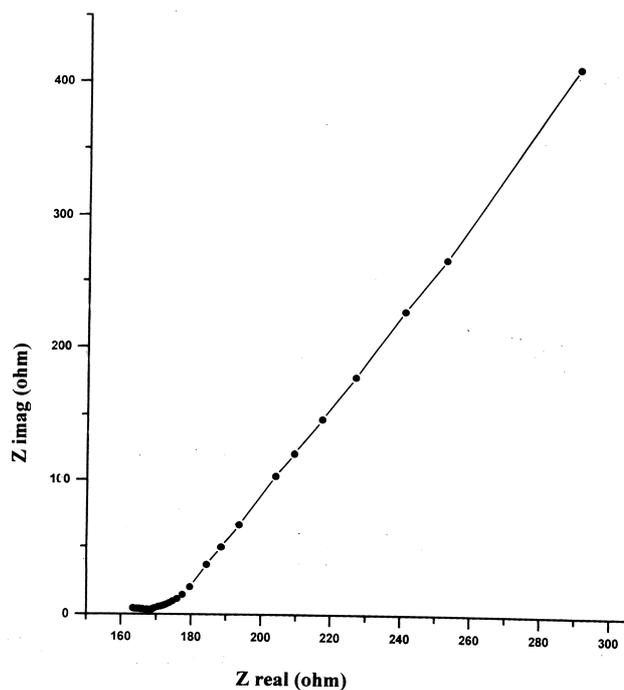
Film	Polymer complex	σ values ($\times 10^{-3}$ S cm ⁻¹)					
		304 K	328 K	338 K	348 K	358 K	373 K
F1	10–5–85	4.538	6.262	7.162	9.865	14.797	73.987
F2	15–5–80	2.493	5.232	5.717	7.848	10.464	12.556
F3	25–5–70	1.649	3.737	4.312	4.359	4.671	5.096
F4	35–5–60	0.327	0.862	1.221	1.832	2.093	2.349

**Figure 1.** FTIR plots for PMMA, LiBF₄, DBP and the complexes: (a) PMMA; (b) LiBF₄; (c) DBP; (d) PMMA–LiBF₄–DBP (10–5–85 mole%); (e) PMMA–LiBF₄–DBP (15–5–80 mole%); (f) PMMA–LiBF₄–DBP (25–5–70 mole%); (g) PMMA–LiBF₄–DBP (35–5–60 mole%).

The peaks at 2927 and 1734 cm⁻¹ are assigned to C–H stretching and C=O stretching vibrations, respectively in PMMA. The peaks at 2953, 1731, 1485 and 1247 cm⁻¹ are assigned to C–H stretching, C=O stretching, CH₂–stretching and O–CH₃ stretching vibrations, respectively in the polymer electrolyte systems (Vien *et al* 1991). The above analysis establishes the formation of polymer–salt complexes.

3.2 Conductivity measurements

The conductivity values of PMMA–LiBF₄–DBP systems are given in table 1. Iijima *et al* (1985) reported the conductivity value as 10⁻³ S cm⁻¹ at 25°C for PMMA based system with an average molecular weight of 7000. Bohnke *et al* (1993) dissolved PMMA, up to 20 weight% in

**Figure 2.** Impedance diagram of PMMA–LiBF₄–DBP (10–5–85 mole%) at 304 K.

a LiClO₄ (1M)–PC electrolyte at room temperature to obtain a homogeneous and transparent gel. They reported that the resulting gel electrolyte possessed a conductivity of 2.3 $\times 10^{-3}$ S cm⁻¹ at 25°C. Sekhon *et al* (1998) reported the ionic conductivity for PMMA–LiCF₃SO₃–PC–EC polymer electrolytes in the range 0.6–5.5 $\times 10^{-3}$ S cm⁻¹ at room temperature.

In the present work, the conductivity value of PMMA–LiBF₄–DBP system (film F1) is found to be 4.5 $\times 10^{-3}$ S cm⁻¹ at 304 K (table 1). This value compares well with those values already reported (Bohnke *et al* 1993; Sekhon *et al* 1998). The presence of the high molecular weight PMMA imparts a very high macroscopic viscosity (≈ 335 Pas) to the system without significantly diminishing the conductivity, i.e. the conductivity of the gel remains very close to that of a liquid electrolyte. It is concluded that PMMA acts primarily as a stiffener, that fast ion transport occurs through a continuous conduction path which does not affect the electrochemical stability of the

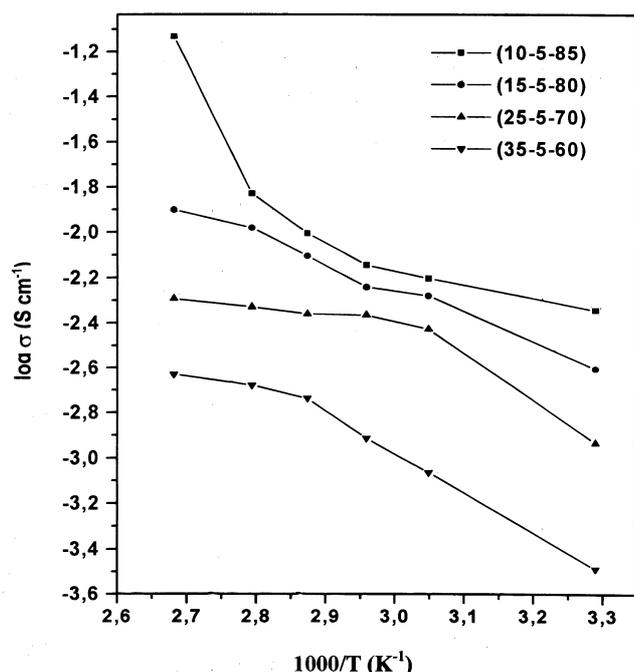


Figure 3. Arrhenius plot of log conductivity against reciprocal temperature for PMMA–LiBF₄–DBP polymer complexes: (a) PMMA–LiBF₄–DBP (10–5–85 mole%); (b) PMMA–LiBF₄–DBP (15–5–80 mole%); (c) PMMA–LiBF₄–DBP (25–5–70 mole%); (d) PMMA–LiBF₄–DBP (35–5–60 mole%).

electrolyte. In later studies, Bohnke *et al* (1993) revealed that the ionic conductivity of PMMA–LiClO₄ (1 M)–PC system decreases with increasing amount of polymer and lies between 5×10^{-3} and 5×10^{-5} S cm⁻¹ at room temperature.

In the present investigation, the conductivity values for PMMA–LiBF₄–DBP are found in the range 4.5×10^{-3} – 3.3×10^{-4} S cm⁻¹ for various mole ratios of PMMA and DBP (table 1) at 304 K. It is seen from table 1, that the conductivity decreases with increase in concentration of PMMA. This behaviour is also reported by Bohnke *et al* (1993). It is also observed that the conductivity increases with concentration of DBP. This may be due to the lowering of viscosity with increasing plasticizer concentration. It is also observed from table 1 that as the temperature increases, conductivity values also increase for all the compositions. This behaviour is in agreement with theory (Armand *et al* 1979).

Figure 3 represents the Arrhenius plot of the ionic conductivity for the polymer electrolytes. The overall features of the Arrhenius plot are quite similar for the electrolyte systems that no linear dependence could be obtained seems to suggest that ion conduction follows the Williams–Landel–Ferry (WLF) mechanism (Williams *et al* 1955). In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion (Okamoto *et al* 1993). Thus, the results may be more effectively represented by

the empirical Vogel–Tamman–Fulcher (VTF) equation (Vogel 1922; Fulcher 1925; Tamman and Hesse 1926):

$$S = AT^{-1/2} \exp[-B/T - T_g],$$

where A and B are constants and T_g the reference temperature taken as the glass transition temperature here. Constant A in the VTF equation is related to the number of charge carriers in the electrolyte system and constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. It supports the idea that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e. plasticizer-rich phase, involves the plasticizer, the salt and PMMA, the characteristics of the viscous matrix are brought out.

4. Conclusion

The complex formation in PMMA–LiBF₄–DBP system has been confirmed from IR studies. Ionic conductivity increases with the concentration of plasticizer. Conductivity greatly changes from 10^{-4} to 10^{-3} S cm⁻¹ as the mole ratio of DBP increased from 60 to 85. This may be due to the lowering of viscosity with increasing plasticizer concentration.

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