Analysis of P(VdCl-co-AN-co-MMA)-LiClO₄-EC triblock copolymer electrolytes

D INBAVALLI^{1,2,*}, S SELVASEKARAPANDIAN², C SANJEEVIRAJA³, R BASKARAN⁴,
S NITHYA^{2,5}, JUNICHI KAWAMURA⁴ and YOSHITAKE MASUDA⁶

¹Research and Development Centre, Bharathiar University, Coimbatore 641 046, India

²Materials Research Centre, Coimbatore 641 045, India

³Department of Physics, Alagappa University, Karaikudi 630 003, India

⁴Institute of Multi Disciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

⁵SRNM College, Sattur 626 203, India

⁶National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan

MS received 13 October 2013; revised 8 March 2014

Abstract. The lithium ion conducting copolymer electrolytes based on poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate) P(VdCl-co-AN-co-MMA)-lithium per chlorate (LiClO₄) (P(VdCl-co-AN-co-MMA):LiClO₄) and poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate)P(VdCl-co-AN-co-MMA)-lithium per chlorate (LiClO₄)-ethylene carbonate (EC) (P(VdCl-co-AN-co-MMA):LiClO₄:EC) of different compositions were prepared by solution-casting technique. Structural and surface morphological characterizations were studied by X-ray diffraction analysis and scanning electron microscopy measurements, respectively. Thermal and conductivity behaviour of copolymer-salt and copolymer-salt-plasticizer complexes were studied by employing differential scanning calorimetry and AC impedance measurements, respectively. The highest bulk conductivity was found to be $1.94 \times 10^{-4} \text{ S cm}^{-1}$ at 303 K for the plasticized sample. The dielectric behaviour and relaxation parameters of the samples have been presented and discussed.

Keywords. Copolymer; SEM; XRD; DSC; LiClO₄.

1. Introduction

The science of polymer electrolytes has attracted ever increasing interest for the past two decades due to the potentially promising applications of such electrolytes in all solid-state batteries and electrochemical devices. The study of polymer electrolytes was launched by Fenton *et al*¹ in 1973 and their work inspired intense research and development on the synthesis of new polymer electrolytes.² Since the discovery that a number of polymer-salt complexes exhibited considerable conductivity, much research efforts have been directed to find the optimal combination of host polymer and dopant salt for fast ionic transport. Various methods have been applied to increase the conductivity of electrolytes. One of the approaches relied upon the addition of plasticizer to the polymer complex known as gel polymer electrolytes (GPEs).

The GPEs with the polymer matrices such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO) exhibited high ionic conductivity, usually over $10^{-3} \text{ S cm}^{-1}$ at room temperature.³ However, the stability of the GPE was poor. With the aim of improving stability and ionic

conductivity, the researches later focused on copolymer electrolytes.

Raghavan Prasanth *et al*⁴ have reported on the blend copolymer electrolyte based on PAN, PMMA and poly(styrene) (PS). Jian-Huo Cao *et al*⁵ have analysed the influence of additives on the morphology, structure, electrolyte uptake of porous membranes and lithium ion conductivity for the diblock copolymer electrolytes based on poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)). Phani Kumar *et al*⁶ have reported on the self-aggregation characteristics of triblock copolymer poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) (PEO-PPO-PEO). Though many works have been done on various copolymer electrolytes, it is interesting to note that so far no work has been reported on the triblock copolymer electrolytes based on P(VdCl-co-AN-co-MMA).

In the present study, the new triblock copolymer P(VdCl-co-AN-co-MMA) has been doped with various concentrations of LiClO₄ and for the same system, the plasticizer EC has been added for various compositions and the conductivity behaviour of all the copolymer complexes has been analysed. The presence of large number of polar groups such as oxygen, nitrogen and chlorine in the copolymer, as seen in scheme 1, has been a great advantage to enhance the ionic mobility. The plasticizer EC has been selected due to its high dielectric constant (95.3), which would easily

*Author for correspondence (inbavalli.d@gmail.com)

dissociate the salt into ions thereby easily enhancing the conductivity.⁷ The morphological, thermal, conductivity and dielectric behaviour of this new triblock copolymer-based electrolytes has been discussed.

2. Experimental

P(VdCl-co-AN-co-MMA) (Himedia) and LiClO₄ (Himedia) were dried by heating under vacuum at 100 and 120°C for 12 and 10 h, respectively, and tetrahydrofuran (THF, SD Fine. Chem. Ltd) was used as the solvent. Copolymer electrolyte samples of P(VdCl-co-AN-co-MMA):LiClO₄ and the plasticized samples of P(VdCl-co-AN-co-MMA):LiClO₄:EC in

different weight ratios have been prepared by solution-casting technique. Appropriate weights of P(VdCl-co-AN-co-MMA) and LiClO₄ (table 1) were dissolved in THF. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. Similarly, appropriate weights of P(VdCl-co-AN-co-MMA) and LiClO₄ (table 1) were dissolved in THF followed by the addition of EC. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. These solutions of different compositions were poured into identical Petri glass dishes of 10 cm diameter. The films were dried in a vacuum chamber at room temperature for 24 h. The copolymer films were further dried in a vacuum chamber at 60°C for 5 h to remove any traces of solvent (THF), and then were stored in sealed containers in a desiccator. Gel-like and solvent-free polymer electrolyte films with thickness of 1–2 mm were obtained.

The Cu-K_α line was used for XRD measurements by the usual θ – 2θ scan. SEM micrographs of samples were observed with a field emission scanning electron microscope (FE-SEM; JSM-6335F, JEOL Ltd). The glass transition temperature (T_g) of different samples were obtained from DSC measurements performed using a MAS-5800, model DSC 200 differential scanning calorimeter with a heating rate of 5°C min^{–1}. The electrical conductivity, dielectric behaviour and relaxation parameter studies were carried out on the copolymer electrolyte films by using a computer-controlled HIOKI model 3532 LCZ metre of frequency range 42 Hz–5 MHz at 303 K.

3. Results and discussion

3.1 X-ray diffraction analysis

XRD measurements were conducted to examine the nature of crystallinity of the copolymer electrolyte P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC films with respect to that of pure copolymer P(VdCl.) and LiClO₄ to investigate the occurrence of complexation. XRD patterns of pure P(VdCl.),

Scheme 1. Structure of poly(vinylidene chloride-co-acrylonitrile-co-methylmethacrylate).

Table 1. Compositions, calculated T_g , ionic conductivity and dielectric relaxation parameters for the triblock copolymer complexes.

Sample composition	Used hereafter as	T_g (°C)	σ from nyquist plot (S cm ^{–1})	Relaxation frequency log ω_m (Hz)	ω_m (Hz)	Relaxation time τ (s)
P(VdCl-co-AN-co-MMA) — pure copolymer	P(VdCl.)	144.7	—	—	—	—
70m% P(VdCl.):30m% LiClO ₄	70m% P(VdCl.):30m% LiClO ₄	146.2	4.89×10^{-9}	2.04	1.11×10^2	9.05×10^{-3}
50m% P(VdCl.):50m% LiClO ₄	50m% P(VdCl.):50m% LiClO ₄	147.6	1.21×10^{-7}	2.71	6.00×10^2	1.67×10^{-3}
45m% P(VdCl.):45m% LiClO ₄ :10m% EC	45m% P(VdCl.):45m% LiClO ₄ :10m% EC	150.7	1.49×10^{-5}	3.99	9.93×10^3	1.01×10^{-4}
25m% P(VdCl.):25m% LiClO ₄ :50m% EC	25m% P(VdCl.):25m% LiClO ₄ :50m% EC	151.5	1.94×10^{-4}	5.87	7.46×10^5	1.34×10^{-6}

P(VdCl₂):LiClO₄ complexes and P(VdCl₂):LiClO₄:EC complexes of different compositions have been depicted in figure 1a–e. The XRD pattern of pure LiClO₄ showed intense, sharp peaks at angles $2\theta = 21.78^\circ, 27.5^\circ, 32.99^\circ$ and 36.58° , and they revealed crystalline nature of the ionic salt [JCPDS: 30-0751].⁸ The pure copolymer showed two broad diffraction peaks at 32.34° and 38.56° , and another two sharp peaks at 24.88° and 15.8° as seen in figure 1a.

For the P(VdCl₂):LiClO₄ complexes as seen in figure 1a and b, it was found that the incorporation of LiClO₄ into the copolymer matrix has caused slight increase in the amorphous nature of the sample, which was observed from the increase in broadness and decrease in intensity of the peaks with respect to that of the pure copolymer. The amorphous nature has produced greater ionic diffusivity leading to high ionic conductivity. Also, it was observed that in the XRD patterns of P(VdCl₂):LiClO₄, there were no peaks corresponding to pure LiClO₄.

The diffractograms of P(VdCl₂):LiClO₄:EC complexes have been presented in figure 1d and e. It was seen that the broadness and the intensity of the same peaks mentioned above have been further increased and decreased, respectively, when compared with those of the P(VdCl₂):LiClO₄ complexes that have further enhanced the conductivity of the plasticized copolymer complexes.

3.2 DSC analysis

DSC was employed to determine the thermal behaviour of P(VdCl₂):LiClO₄ complexes and P(VdCl₂):LiClO₄:EC plasticized complexes with respect to that of P(VdCl₂).

Figure 2a–e show the DSC thermograms obtained for P(VdCl₂), P(VdCl₂):LiClO₄ and P(VdCl₂):LiClO₄:EC gel copolymer electrolytes of different compositions. The results obtained are shown in table 1. Figure 2a shows that the T_g of the pure copolymer P(VdCl₂) was 144.7°C .

With the addition of LiClO₄, T_g has been increased to 146.2 and 147.6°C for 70m% P(VdCl₂):30m% LiClO₄ and 50m% P(VdCl₂):50m% LiClO₄, respectively. This increase in T_g has been attributed to the interaction of Li⁺ ion with the copolymer. Similarly, for the plasticized system, with the addition of LiClO₄ and EC, T_g has increased significantly to 150.7 and 151.5°C for 45m% P(VdCl₂):45m% LiClO₄:10m% EC and 25m% P(VdCl₂):25m% LiClO₄:50m% EC, respectively. This is evident from the thermograms in figure 2d and e. This increase in T_g might be due to the restriction of the molecular movement of EC by the copolymer chains due to which the molecules get trapped within the cages formed by the polar groups in the copolymer P(VdCl₂).⁹

3.3 Morphological characteristics

SEM of P(VdCl₂), P(VdCl₂):LiClO₄ complexes and P(VdCl₂):LiClO₄:EC copolymer electrolyte films, are shown in figure 3a–e. Figure 3a shows smooth and non-porous morphology of pure P(VdCl₂). For 70m% P(VdCl₂):30m% LiClO₄, many number of minute pores were observed as seen from figure 3b. When the concentration of LiClO₄ was increased to 50m%, there were more number of pores with increased pore size as evident from figure 3c.

Figure 1. XRD diffractograms of (a) P(VdCl₂), (b) 70m% P(VdCl₂):30m% LiClO₄ (c) 50m% P(VdCl₂):50m% LiClO₄, (d) 45m% P(VdCl₂):45m% LiClO₄:10m% EC and (e) 25m% P(VdCl₂):25m% LiClO₄:50m% EC.

Figure 2. DSC thermograms of (a) P(VdCl.), (b) 70m% P(VdCl.):30m% LiClO₄ (c) 50m% P(VdCl.):50m% LiClO₄, (d) 45m% P(VdCl.):45m% LiClO₄:10m% EC and (e) 25m% P(VdCl.):25m% LiClO₄:50m% EC.

In the micrograph of 45m% P(VdCl.):45m% LiClO₄:10m% EC, a large number of ring-like structures with porosity were observed as seen from figure 3d, which might be due to the addition of plasticizer EC. The pore size was further increased and a small well-like structure was seen from each pore for 25m% P(VdCl.):25m% LiClO₄:50m% EC. This is evident from figure 3e with the increase in plasticizer EC content. This large amount of pores in the porous membrane and increase in the size of the pores with small well-like structure have enlarged the contact areas between copolymer and solvent such that the electrolyte solution was well retained in the membrane by copolymer–solvent interactions which, in turn, have enhanced the ionic conductivity.¹⁰ Hence, the conductivity was more for the copolymer complex 25m% P(VdCl.):25m% LiClO₄:50m% EC, which was in good agreement with the SEM micrographs.

3.4 AC impedance analysis

The ionic conductivity of P(VdCl.):LiClO₄ system and P(VdCl.):LiClO₄:EC plasticized system was derived from the complex impedance plots. The Nyquist plots for P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC copolymer electrolytes of different compositions at 303 K are presented in figure 4a–d. The plots consisted of a high-frequency depressed semicircle represented by a capacitor (C_g) parallel to a bulk resistor (R_b) and a low frequency spike represented by a constant phase element (CPE). The high-frequency part of impedance plots was related to bulk relaxation processes, according to Armstrong's model of a solid electrolyte.¹¹ The low-frequency spur resulted from the electrode/electrolyte interfacial

properties. It was noted that the semicircle depression decreased as the content of LiClO₄ increased. This is seen from figure 4a–c.

The EQ software program developed by Boukamp¹² was used to extract the bulk electrical resistance (R_b) of the copolymer electrolytes from the impedance plot of the low-frequency side intercept on the Z' axis. The ionic conductivity was calculated using the equation,

$$\sigma = L/R_b A \text{ (S cm}^{-1}\text{)}, \quad (1)$$

where L and A represent the thickness of the copolymer electrolyte film and surface area of the film, respectively.

From the impedance spectra of 70m% P(VdCl.):30m% LiClO₄ and 50m% P(VdCl.):50m% LiClO₄, as seen from figure 4a and b, it was observed that the value of the bulk resistance decreased with increase in LiClO₄ content, which in turn enhanced the ionic conductivity. It was seen from table 1 that the ionic conductivity for 70m% P(VdCl.):30m% LiClO₄ and 50m% P(VdCl.):50m% LiClO₄ was 4.89×10^{-9} and 1.21×10^{-7} S cm⁻¹, respectively. As the LiClO₄ content was increased from 30m% to 50m%, there was an increase in conductivity due to the increase in charge carrier concentration.

Similarly, from the impedance spectra of 45m% P(VdCl.):45m% LiClO₄:10m% EC and 25m% P(VdCl.):25m% LiClO₄:50m% EC, as seen in figure 4c and d, it was observed that the semicircle slowly disappeared and only the spur remained for the high concentration of EC. Also from table 1, the conductivity value for 45m% P(VdCl.):45m% LiClO₄:10m% EC and 25m% P(VdCl.):25m% LiClO₄:

Figure 3. (a) SEM micrograph of P(VdCl..), (b) SEM micrograph of 70m% P(VdCl.):30m% LiClO₄, (c) SEM micrograph of 50m% P(VdCl.):50m% LiClO₄, (d) SEM micrograph of 45m% P(VdCl.):45m% LiClO₄:10m% EC and (e) SEM micrograph of 25m% P(VdCl.):25m% LiClO₄:50m% EC.

50m% EC was found to be 1.49×10^{-5} and 1.94×10^{-4} S cm⁻¹, respectively. There was considerable increase in conductivity when compared with that of the P(VdCl.):LiClO₄ system. This might be due to the enhancement of the ionic mobility and number of carrier ions due to the plasticizing effect of EC, as reported by previous researchers.^{13,14}

3.5 Dielectric spectra

The complex permittivity (ϵ^*) or dielectric constant of a system was defined by the equation,

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon' - j(\sigma/\omega\epsilon_0), \quad (2)$$

Figure 4. Nyquist plot of (a) 70m% P(VdCl.):30m% LiClO₄, (b) 50m% P(VdCl.):50m% LiClO₄, (c) 45m% P(VdCl.):45m% LiClO₄:10m% EC and (d) 25m% P(VdCl.):25m% LiClO₄:50m% EC at 303 K.

Figure 5. Dielectric spectra of (a) 70m% P(VdCl.):30m% LiClO₄, (b) 50m% P(VdCl.): 50m% LiClO₄, (c) 45m% P(VdCl.):45m% LiClO₄:10m% EC and (d) 25m% P(VdCl.):25m% LiClO₄:50m% EC at 303 K.

where ϵ' , ϵ'' , σ , ω , ϵ_0 represented real part of dielectric constant of the material, imaginary part of dielectric constant of the material, conductivity, angular frequency and permittivity of free space, respectively. Figures 5 and 6 show ϵ' vs. $\log f$ and ϵ'' vs. $\log f$ plots, respectively, for P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC copolymer complexes. It was seen from figures 5 and 6 that for both the P(VdCl.):LiClO₄

and P(VdCl.):LiClO₄:EC systems, the dielectric permittivity rose sharply towards low frequencies, which was due to the electrode polarization effects.¹⁵ The low frequency dispersion region was attributed to the contribution of charge accumulation at the electrode–electrolyte interface. At high frequencies, due to high periodic reversal of the field at the interface, the contribution of charge carriers (ions) towards

the dielectric constant decreased with increased frequency. Hence ϵ' has decreased with increased frequency.

From figure 6, it was observed that the dielectric loss (ϵ'') became very large ($\sim 7 \times 10^5$) at lower frequencies due to free charge motion within the material.¹⁶ These values did not correspond to the bulk dielectric processes, but were

due to the free charges built up at the interface between the material and the electrodes. At very low frequencies, there was time for charges to build up at the interfaces before the field changes the direction and this contributed to very large apparent values of ϵ'' . This phenomenon lead to the so called 'conductivity relaxation'.¹⁷

Figure 6. Dielectric spectra of (a) 70m% P(VdCl.):30m% LiClO₄, (b) 50m% P(VdCl.): 50m% LiClO₄, (c) 45m% P(VdCl.):45m% LiClO₄:10m% EC and (d) 25m% P(VdCl.):25m% LiClO₄:50m% EC at 303 K.

Figure 7. Loss tangent spectra of (a) 70m% P(VdCl.):30m% LiClO₄, (b) 50m% P(VdCl.): 50m% LiClO₄, (c) 45m% P(VdCl.):45m% LiClO₄:10m% EC and (d) 25m% P(VdCl.):25m% LiClO₄:50m% EC at 303 K.

3.6 Loss tangent spectra

The dielectric relaxation parameter of the copolymer complexes P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC was obtained from the plot of Tan δ as a function of frequency. The dielectric loss tangent (Tan δ) was defined by the equation,

$$\text{Tan } \delta = \varepsilon''/\varepsilon'. \quad (3)$$

The variation of Tan δ with frequency has been presented in figure 7 for all the copolymer complexes P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC at 303 K. It was observed that, for all the copolymer complexes, as seen from figure 7, Tan δ increased with increasing frequency thereby reaching a maximum, and then, decreased with further increase of frequency. For the maximum dielectric loss, the loss tangent peak was described by the relation,

$$\omega\tau = 1, \quad (4)$$

where τ and ω represented the relaxation time and angular frequency of the applied electric field.¹⁸ The relaxation parameters for all the copolymer complexes at 303 K were calculated and tabulated (table 1).

From table 1, it is seen that the relaxation time (τ) decreased from 9.05×10^{-3} s for 70m% P(VdCl.):30m% LiClO₄ to 1.67×10^{-3} s for 50m% P(VdCl.):50m% LiClO₄. The relaxation time further decreased from 1.01×10^{-4} s for 45m% P(VdCl.):45m% LiClO₄:10m% EC to 1.34×10^{-6} s for 25m% P(VdCl.):25m% LiClO₄:50m% EC. This decrease in relaxation time τ enhanced the ionic conductivity. From table 1, it is noted that the relaxation time was lowest for 25m% P(VdCl.):25m% LiClO₄:50m% EC and hence exhibited highest ionic conductivity. This was in good agreement with the result of Nyquist plots.

4. Conclusion

The copolymer electrolyte of P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC complexes of various compositions were prepared by solution-casting method. XRD studies revealed the increase in amorphous nature of the copolymer-salt complexes of P(VdCl.):LiClO₄:EC and thereby produced greater ionic diffusivity when compared with that of P(VdCl.):LiClO₄ complexes. The SEM micrographs revealed the increase in porosity and size of the pores for P(VdCl.):LiClO₄ complexes. There was further increase in porosity, size of the pores and a small well-like structure for the P(VdCl.):LiClO₄:EC complexes.

DSC measurements revealed increase in T_g with increase in LiClO₄ content for the P(VdCl.):LiClO₄ system because of the interaction of Li⁺ with the polar groups of the copolymer. The T_g increased further for P(VdCl.):LiClO₄:EC

complexes due to the restriction of the molecular movement of the EC by the copolymer chains. Because of this, the molecules got trapped within the cages formed by the polar groups in the copolymer P(VdCl.). The ionic conductivity was found to exhibit an increasing trend with increasing salt concentration. For the P(VdCl.):LiClO₄ systems, the maximum conductivity was 1.21×10^{-7} S cm⁻¹ for 50m% P(VdCl.):50m% LiClO₄. However, the highest conductivity of 1.94×10^{-4} S cm⁻¹ was obtained for 25m% P(VdCl.):25m% LiClO₄:50m% EC for the plasticized system.

The low frequency dispersion of dielectric constant for both P(VdCl.):LiClO₄ and P(VdCl.):LiClO₄:EC complexes revealed the space charge effects arising from the electrodes. From the loss tangent spectra, it was found that the relaxation time (τ) was lowest for 25m% P(VdCl.):25m% LiClO₄:50m% EC and hence exhibited highest ionic conductivity.

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