Research Article

Structural and Electrochemical Analysis of PMMA Based Gel Electrolyte Membranes

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New gel polymer electrolytes containing poly(vinylidene chloride-co-acrylonitrile) and poly(methyl methacrylate) are prepared by solution casting method. With the addition of 60 wt.% of EC to PVdC-AN/PMMA blend, ionic conductivity value 0.398×10^{-6} S cm^{-1} has been achieved. XRD and FT-IR studies have been conducted to investigate the structure and complexation in the polymer gel electrolytes. The FT-IR spectra show that the functional groups C=O and C≡N play major role in ion conduction. Thermal stability of the prepared membranes is found to be about 180°C.

1. Introduction

During the past two decades, solid-state polymer and polymer gel electrolytes have attracted great interest because of the possibility of their usage in lithium batteries because polymer gel electrolytes are leakage-free and have much higher ionic conductivity. The dissolution of low lattice energy salts into a solvating polymer leads to the formation of polymer electrolyte. These can conduct ions and the mobility of these ions can be improved by the addition of plasticizers [1]. A number of methods have been reported for improving the ionic conductivity and mechanical stability of polymer electrolytes including copolymerization, grafting, physical cross-linking, blending, plasticization, and the addition of inert ceramic oxides to the matrix. Numerous studies have been carried out on polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) [2], poly(vinyl acetate) (PVAc), poly(ethylene oxide) (PEO), and so forth. Although these polymer electrolytes exhibit high ionic conductivities exceeding 10^{-5} S cm^{-1} after blending, most of them have various deficiencies preventing them from being used in commercial lithium batteries [3].

Optimized PVdC-AN/PMMA blend ratio on the basis of electrochemical analysis has been reported as 50/50 wt%

in our previous work [4]. It has been reported that the addition of plasticizer can enhance the polymer flexibility and hence the better ionic conduction. In order to provide a detailed description about the effect of plasticizer on the poly(vinylidene chloride-co-acrylonitrile) (PVdC-AN) membranes, three different formulations of PVdC-AN electrolyte films have been prepared and analysed using various techniques such as FT-IR, Electrochemical Impedance analysis, and X-ray diffraction. LiBF$_4$ has been chosen as ionic salt in this present study since it has low lattice energy. The dielectric constant of the plasticizer is an important parameter that affects the ionic conduction. Higher dielectric constant results in better dissociation of the salt as the number of free mobile charge carriers increased. The researchers who initiated the study on LiBF$_4$ mentioned the multiple advantages of LiBF$_4$ as compared with other lithium salts (e.g., less toxicity than LiAsF$_6$ and higher safety than LiClO$_4$). In the present study one of the host polymers used is PMMA, since it is an amorphous polymer with excellent mechanical property and is less reactive towards the lithium electrode and it induces favourable passivation of ions [5]. Also, PVdC-AN and PMMA help better electron pair formation of C≡N, C=O, and C−O−C which can coordinate with cations from lithium salt to form polymer-salt complexes and hence provide ionic conduction [6].

2. Materials and Methods

Poly(vinylidene chloride-co-acrylonitrile) (PVdC-AN; Avg M_w 150,000, Aldrich, USA), poly(methyl methacrylate) (PMMA; Avg M_w 120,000, Aldrich, USA), plasticizer ethylene carbonate, EC (Alfa Aesar, India), and electrolyte salt lithium tetrafluoroborate (LiBF$_4$; Aldrich, USA) were used as received. All electrolyte membranes were prepared by solution casting technique. Appropriate weights of PVdC-AN, PMMA, and LiBF$_4$ were dissolved separately in the organic solvent tetrahydrofuran (THF; Merck, India) at room temperature. The polymer and salt solutions were mixed and then stirred continuously for 12 h to obtain a homogeneous solution. The plasticizer ethylene carbonate was added to the polymer solution with ratios 20, 40, 60, and 80 wt%. The obtained homogeneous, highly viscous solution was allowed degassing to remove air bubbles and cast onto the well-cleaned petri-dishes to get the desired thin film membranes. Then the solvent was allowed to evaporate slowly at 60°C for about 6 h using vacuum oven. Finally, the harvested electrolyte membranes were analysed using various techniques. The PVdC-AN/PMMA blend electrolyte membrane with 80 wt% ethylene carbonate could not form a freestanding film and was in the form of a gel at room temperature. The membranes with 20, 40, and 60 wt% of EC were denoted as R1, R2, and R3, respectively.

The X-ray diffraction patterns were recorded with a computer controlled X'pert PRO PANalytical diffractometer in the scanning range $2\theta = 10$ to $80°$ using Cu-Kα (wavelength, $\lambda = 1.541$ Å) radiation as a source. The Fourier Transform Infrared (FT-IR) spectra of the samples were recorded with Thermofisher Nicolet iS10 FT-IR Spectrometer in the range of 4000–400 cm^{-1} in the transmittance mode. The electrochemical analysis of the polymer electrolytes was carried out by sandwiching the electrolyte film between stainless steel blocking electrodes using μ-Autolab Type-III Potentiostat/Galvanostat in the frequency range 1 Hz–1 MHz. The measurements were taken between 303 K and 353 K. The value of bulk resistance R_b was found to be the intercept on the x-axis of the impedance plot. The conductivity (σ) was calculated using

$$\sigma = \frac{l}{R_b A}, \tag{1}$$

where l is the thickness of the polymer electrolyte film, R_b is the bulk resistance, and A is the surface area of the polymer electrolyte film [7].

All the polymer complexes were subjected to thermal analysis, which was carried out using Perkin Elmer Pyris-6 TG/DTA Analyzer. The thermogravimetric curves were recorded in nitrogen atmosphere from room temperature to 600°C. The heating rate was 10°C/min. From TG plots, temperature of maximum process rate, temperature at the end of decomposition, and weight loss were determined.

3. Results and Discussion

3.1. Structural Analysis.
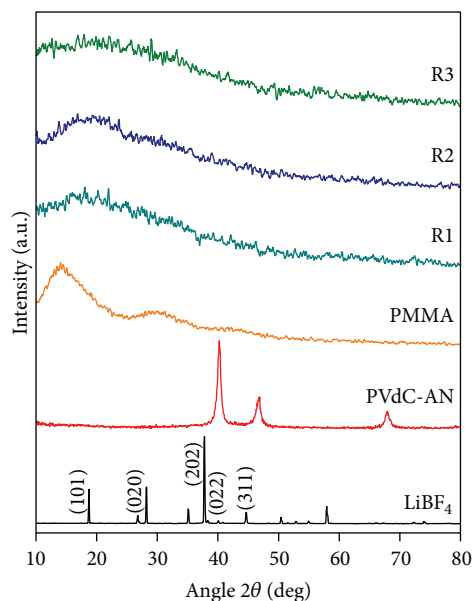Structural analysis of the prepared polymer complexes was carried out using X-ray diffraction

Figure 1: XRD patterns of PVdC-AN/PMMA/EC/LiBF$_4$ membranes.

method. The diffraction pattern of PVdC-AN/PMMA/-EC/LiBF$_4$ based membranes is shown in Figure 1. The graphs show that PVdC-AN exhibits semicrystalline peaks at angles $2\theta = 40.25$, 46.76, and 67.94° and PMMA shows an amorphous nature. The intense peaks of LiBF$_4$ in Figure 1 at angles $2\theta = 18.7$, 26.7, 28.1, 37.7, 44.6, 52.8, and 57.93° reveal the crystalline nature of the ionic salt. All of these crystalline peaks are found to have disappeared when the polymer, plasticizer, and salt were mixed together. Thus, XRD patterns of the prepared polymer membranes in Figure 1 reveal the amorphous nature which is essential for a polymer electrolyte. The interaction between the polymer atoms, plasticizer, and lithium ions disturbed the polymer network, which leads to a decrease in crystallinity. The amorphous nature of complexes indicates that the lithium salt is not crystallized in the film but rather molecularly dispersed within the polymer in the presence of EC. With the increase in the content of EC, complexes became completely amorphous, without any trace of diffraction halos. It is known that high intensity diffraction peaks are associated with high crystallinity and broader diffraction humps for their semicrystalline/amorphous nature. Hence, the broadening of diffraction peaks reveals the enhancement of the amorphous nature of PVdC-AN/PMMA/LiBF$_4$/EC polymer electrolyte membranes. In addition, the absences of diffraction peaks of both polymer and salt in prepared complexes reveal the good miscibility of polymer and salt, with plasticizer at the molecular level. These results suggest that the incorporated lithium salts were dissolved in the amorphous region of polymer in the presence of plasticizer and the ionic conductivity of polymer electrolyte given by the amorphous phase of the complex [8].

3.2. Functional Group Analysis.
The FT-IR spectra of PVdC-AN/PMMA electrolyte membranes are shown in Figure 2. The spectra of pure samples such as PVdC-AN, PMMA, EC,
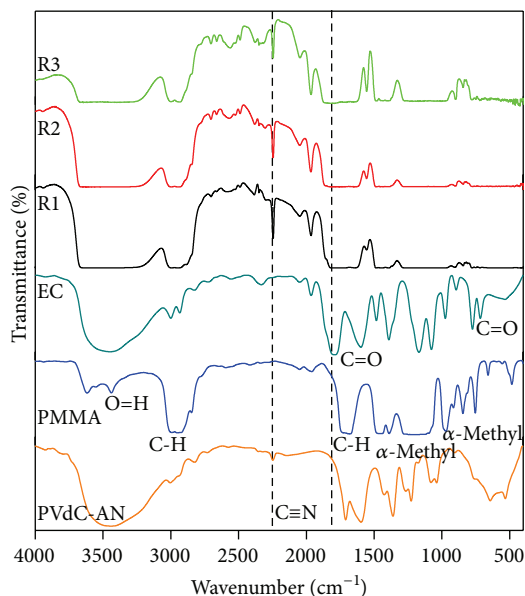
FIGURE 2: FT-IR transmission spectra of PVdC-AN/PMMA/EC/-LiBF$_4$ membranes.

FIGURE 3: Variation of ac conductivity with respect to frequency for PVdC-AN/PMMA/EC/LiBF$_4$ membranes.

and LiBF$_4$ are also included in both graphs for the comparison purpose. The –CH$_2$ asymmetric stretching, C(Cl$_2$) symmetric stretching, and the C(Cl$_2$) bending of vinylidene chloride in pure PVdC-AN were observed at 1038–1073 cm^{-1}, 751–656–606 cm^{-1}, and 568–446 cm^{-1}, respectively, in the spectrum of the copolymer. However, in the spectra of polymer electrolytes, these bands are found shifted in complexes as ethylene carbonate (EC) ratio decreases which is due to the structural reorganization of the polymer. The strong stretching vibration of the Nitrile group C≡N of PVdC-AN is observed at 2247 cm^{-1} in the complexes [9]. In acrylonitrile-based electrolytes, the Li$^+$ ions associate with the nitrogen atoms since the Nitrile is a strong electron dopant whereas, in methacrylate-based electrolytes, the lithium ions associate with oxygen atoms. It is clear that when the composition of EC is increased, the transmittance intensity of the C≡N group in PVdC-AN is decreased and can be explained by the interaction between functional groups of both polymers and it may vary with the composition. This signifies the strong interaction of Li$^+$ ions with the Nitrile group. It is clear that as the plasticizer composition increases, the free volume between the polymer chains and the segmental mobility increases; hence, the vibrational intensity in the spectra gets reduced. These two conditions enhance the faster conduction of mobile ions. Also the symmetrical stretching of the carbonyl group, μ(C=O) at 1725 cm^{-1}, and ether group (C–O–C) at 1100–1200 cm^{-1} in PMMA [10] had been found to be broadened and intensity is reduced significantly in the complexes. It can be observed that the C=O bending band which appears at 718 cm^{-1} in the spectrum of pure EC has shifted to higher wavenumber region in all the complexes and has become more intense as EC composition increases. This may be due to the interaction between Li$^+$ of the salt and C=O bending band [11]. The vibrational band at 1073 cm^{-1} of
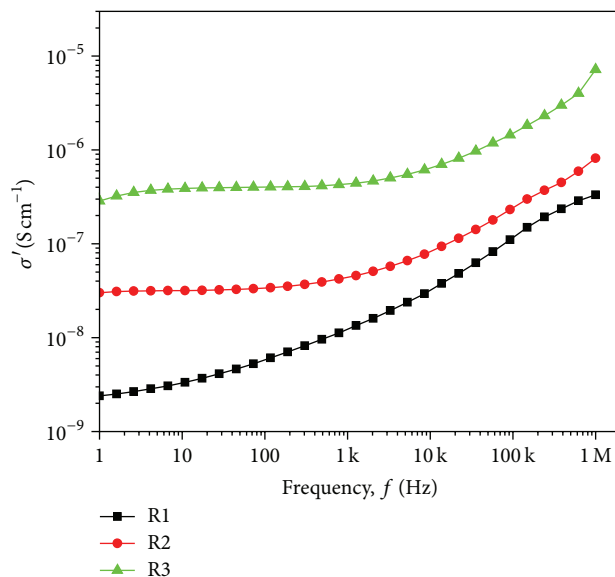
BF$_4^-$ anion observed in the polymer complexes indicates the dissociation of LiBF$_4$ in the polymer [12]. It is very clear that the characteristic peak C≡N is more intense in the spectra of polymer complex than in pure PVdC-AN which reveals the good miscibility and strong bonding between PVdC-AN and PMMA. The vibrational peaks at 1388 cm^{-1} and 754 cm^{-1} can be attributed to the α-methyl group vibrations and the peak at 1444 cm^{-1} can be assigned as bending vibration of the C–H bonds of the –CH$_3$ group in PMMA and are found shifted in the complexes [13]. Based on this finding, we believe that the oxygen atom from PMMA contributed to the stronger interaction with lithium cation than the nitrogen atom from PVdC-AN in blend membranes while Nitrile group alone makes good interaction with lithium cation in single polymer membranes. The presence of –OH group around 3500 cm^{-1} in the spectra of membranes may be due to the absorption of moisture during sample loading for FT-IR analysis.

3.3. Conductance Spectra. The variation of σ_{ac} with frequency of different compositions of PVdC-AN/PMMA at room temperature has been given in Figure 3. Generally, the electrode polarization, direct current conductivity, and the dielectric relaxation phenomena could be distinguished at low, intermediate, and high frequencies, respectively [14]. From the figure, it can be seen that the low frequency electrode effects represented by the deviation from flat conductivity are completely absent in all the films. The ac conductivity patterns show frequency independent plateau in the low frequency region and exhibit dispersion at higher frequencies owing to the contribution of polymer segmental motion. This behaviour obeys Jonscher power law $\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n$, where σ_{dc} is the dc conductivity (frequency independent plateau in the low frequency region), A is the preexponential
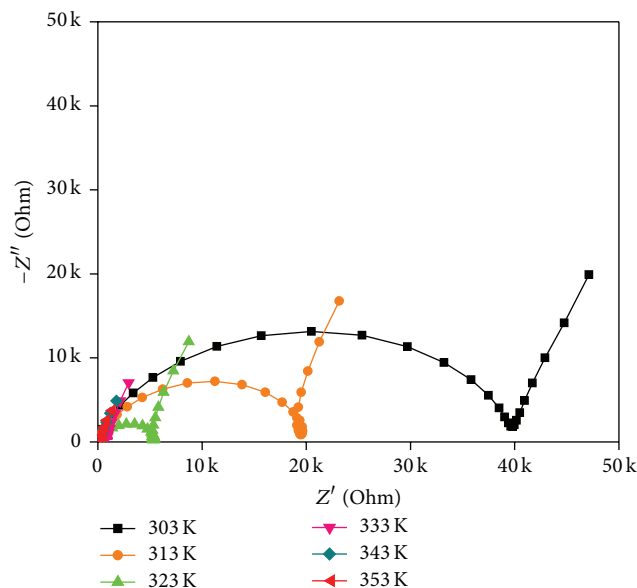
FIGURE 4: Impedance response of R3 = PVdC-AN/PMMA/EC/-LiBF$_4$ polymer electrolyte membranes at different temperature.

FIGURE 5: Plot of temperature versus log conductivity for PVdC-AN/PMMA/EC/LiBF$_4$.

factor, ω is the angular frequency ($\omega = 2\pi f$), and n is the fractional exponent [15]. The values of σ_{dc}, A, and n are determined by fitting the $\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n$ and are tabulated in Table 1. Generally, for ionic conductors, power law exponents (n) can be between 1 and 0 indicating the ideal long-range pathways and diffusion limited hopping (tortuous pathway), respectively. The highest dc conductivity of the ionically conducting polymer electrolytes is found in the order of 10^{-6} S cm^{-1} for R3 (EC = 60 wt%) in Figure 3.

3.4. Ionic Conductivity Studies. In conductance spectra, the highest ionic conductivity has been observed for R3 = PVdC-AN(46)/PMMA(46)/LiBF$_4$(8)/EC(60) membranes in the overall range of temperatures studied. The typical impedance plot for the polymer membrane R3 from room temperature to 353 K is shown in Figure 4. It is found that as the plasticizer ratio increases, the ionic conductivity values also increase, which is due to the increment of the mobility of charge carriers in the polymer-salt complexes. This may be due to the plasticizer which enhances the polymer segmental mobility and the number of free volumes between the polymer chains and hence leads to greater conduction of mobile ions. The maximum ionic conductivity is found to be for the membrane with 60 wt% of plasticizer. This may be due to the oxygen atom from PMMA contributing to the strong interaction with lithium cation when plasticizer ratio increased which is in accordance with FT-IR spectra.

The variations of log σ with the inverse of absolute temperature for all the prepared polymer electrolyte films are presented in Figure 5. The figure shows that the increase of temperature increases the conductivity of polymer electrolytes over the temperature range studied. The nonlinear behaviour of the temperature dependence of the ionic conductivity can be explained using VTF (Vogel-Tamman-Fulcher) expression $\sigma = AT^{-1/2} \exp(-B/K(T - T_0))$ where A is a constant
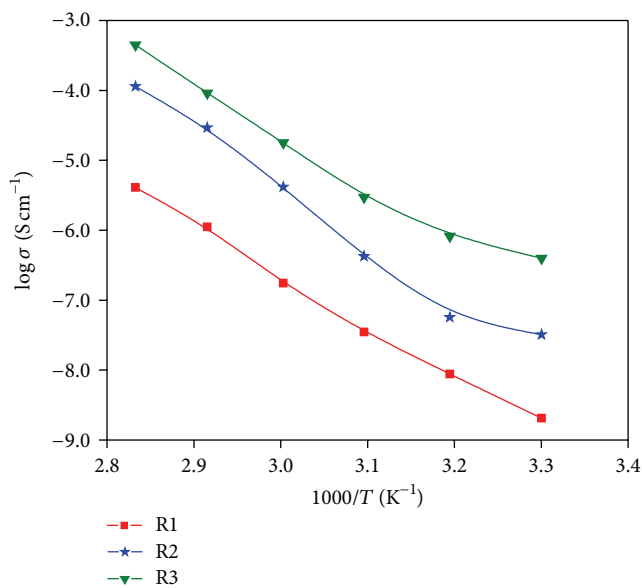
proportional to the number of charge carriers, B is a constant, and T_0 is the temperature at which configurational entropy becomes zero. This reveals that the ionic conductivity and viscoelastic properties of polymer electrolytes are closely related to each other. Due to the addition of the plasticizing agent ethylene carbonate (EC) to polymer combinations, the viscosity of complex gets reduced. Since both macroscopic flow of polymer and local segmental motion are possible for viscous solutions, it is suggested that the local segmental motion plays an important role in ion-migration in the polymer electrolytes [16].

The diffusion theory can explain well the change in conductivity with respect to temperature. The diffusion coefficient of small particles in such amorphous polymer electrolyte media can be expressed as $D = gd\nu \exp(-\gamma V^*/V_f)$, where $g \cong 1/6$, d is the distance through which the particles are transported (effectively a molecular diameter), ν is the velocity of the particle (proportional to $T^{1/2}$), γ is a factor to allow for overlap of free volume, V^* is the critical volume required for migration of the particle, and V_f is the free volume of the medium. The basic concept of diffusion theory is that transport of the particles in a medium depends upon the formation of holes large enough for diffusive displacement. The statistical redistribution of the free volume results in hole formation and its probability is given by the exponential term of the diffusion coefficient [17]. The diffusion coefficient and ionic conductivity can be related by Nernst-Einstein relation. Therefore, a good fit of the conductivity data of plasticized electrolytes to VTF relation implies that the conductivity change with temperature is dominated by the change in the diffusion coefficient (ionic mobility), which can be explained by free volume mechanism. The carrier lithium ions in the polymer electrolyte move from one site to another and will be redistributed around the site, when the free volume is large enough for their diffusive

TABLE 1: Comparison of parameters obtained from fitting the experimental data to power law, $\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n$ of PVdC-AN/PMMA/EC/LiBF$_4$ at room temperature.

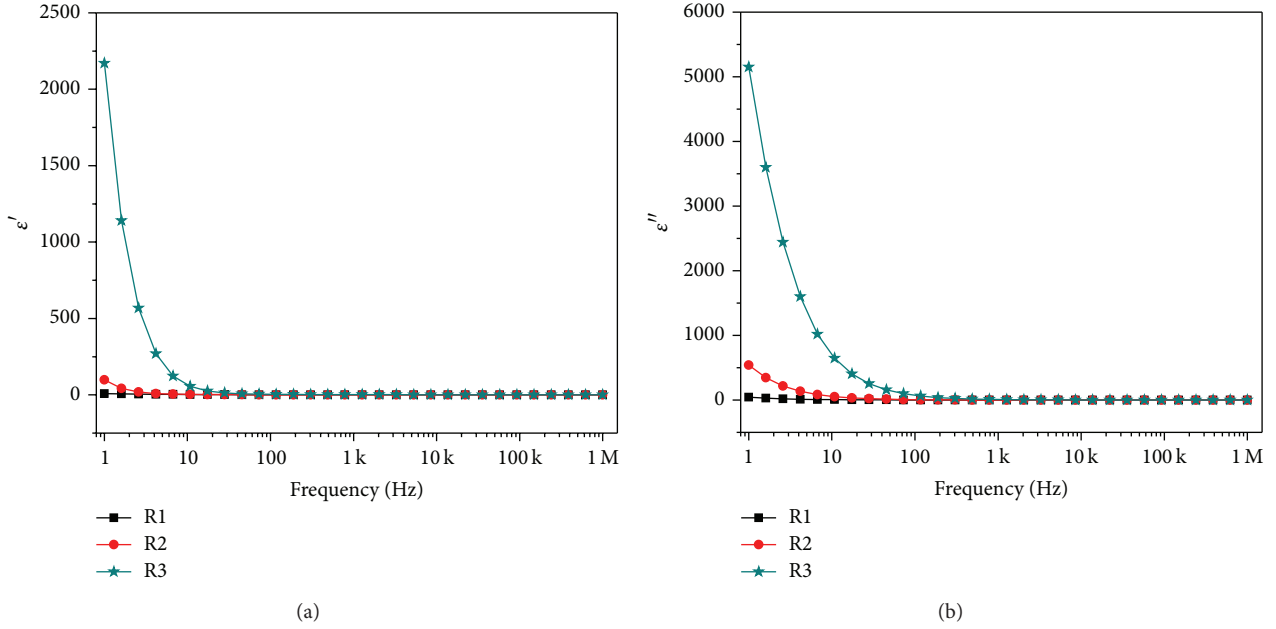| Serial number	PVdC-AN/PMMA/LiBF$_4$/EC (wt.%)	σ_{dc} (10^{-7}) (S cm^{-1})	A	n
R1	46/46/8/20	0.0025	$4.11E-10$	0.49
R2	46/46/8/40	0.0308	$2.45E-10$	0.58
R3	46/46/8/60	0.4371	$3.63E-11$	0.87

FIGURE 6: Dielectric constant (a) and dielectric loss (b) versus frequency.

displacement ($<V_i^*>$). The polymer segments associated with ions continuously rearrange because the electrolytes are in a rubbery state. This redistribution of free volume is mainly caused by the segmental motion in polymer electrolytes and this rearrangement changes the local position of the carrier ions. Thus, it can be seen that the ion-migration does not happen by itself. Thus, the repeating of the association of the carrier ions to the polymer segments, the segmental motion with associated ions, and the dissociation from the polymer segments may result in ionic transport. Therefore, it is proved that the temperature dependence of ionic conductivity and segmental mobility closely correlate with each other.

3.5. Dielectric Studies. The dielectric response is generally described by the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where real ε' (or the dielectric constant, ε_r) and imaginary ε'' (or dielectric loss, ε_i) components are the storage and loss of energy in each cycle of applied electric field. Figures 6(a) and 6(b) show the variation of dielectric constants (ε' and ε'') with frequency for different EC value of PVdC-AN/PMMA based polymer blend electrolytes. It can be seen that both ε' and ε'' are dispersed at lower frequency and they are independent at higher frequency. The dielectric constant is found decreased with the increase in frequency for all concentrations which may be due to relaxation process [18].
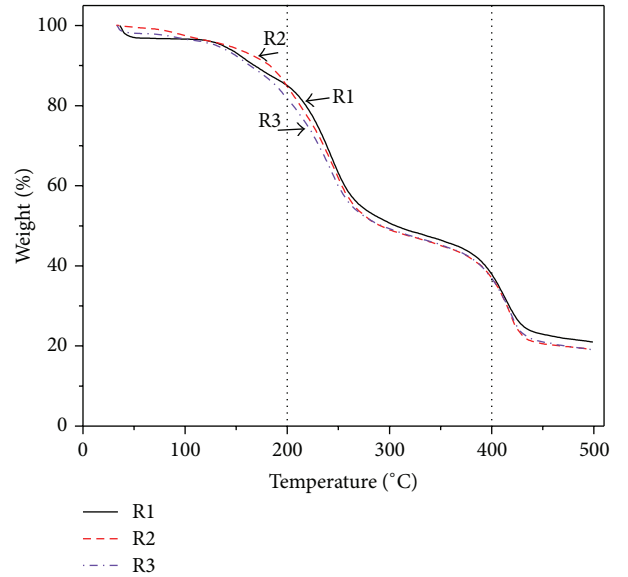

FIGURE 7: Thermogravimetric (TG) curves of polymer membranes.

3.6. Thermogravimetric Analysis. It is noted from **Figure 7** that the TGA of polymer complexes R1, R2, and R3 exhibit two-step degradation. All the samples almost completed the

decay (weight loss is about 80%) at the end of the process, that is, at 500°C. The samples R1, R2, and R3 show weight loss of about 3, 2, and 3%, respectively, at 90°C and this weight loss may be due to the moisture or by the evaporation of residual solvent which is used in the sample preparation. The two-degradation steps at 200 and 383°C are generally attributed to scissions at the chain-end initiation and random internal scission of the polymer chain, respectively. During thermal degradation of PMMA, the production of free radicals at low temperature participates in the further depolymerization at high temperatures through chain transfer processes. Even though vinylidene chloride polymers are extremely resistant to biodegradation, oxidation, and permeation of small particles, they are extremely durable under most conditions. However, when these types of polymers are heated above 120°C, they are thermally unstable and undergo a degradative dehydrochlorination [19]. The significant change in the polymer's original, highly ordered structure at 170°C in TGA plot can be observed which indicates the breakage of CH_2 bonds in the polymer chain and the expansion of the C–Cl carbon-halogen bonds which leads to the elimination of the halogen atoms at sites along the polymer chain [20]. Thus, the loss of the chlorine atoms from the polymer chain results in a significant change in the stability of the polymer electrolyte. Since degradation apparently begins in VDC units adjacent to comonomer units, acrylonitrile copolymers release a small amount of ammonia and hydrogen cyanide (HCN) as well as hydrogen chloride (HCl) and methyl methacrylate polymers release methyl chloride in addition to hydrogen chloride on thermal degradation [21]. All the prepared samples incorporating different ratios of ethylene carbonate exhibit maximum thermal stability of about 180°C and show appreciable weight losses of about 12, 10, and 12%, respectively, at 180°C. The weight loss observed in the temperature range 180–270°C is mainly due to the degradation of polymer, lithium salt, and plasticizer. The second-step degradation of membranes shows weight losses of 58, 59, and 59% at 383°C. The residual mass of about 20% at 600°C can be assigned to the carbonaceous residue formed in both previous stages. The results obtained show that the degradation process of the polymer electrolyte complexes depends not only on their composition, but also on the chemical structure of the components, whereby the components of various concentrations exhibit mutual interactions [22].

4. Conclusion

PVdC-AN-based polymer electrolytes were prepared by solvent casting technique. The polymer electrolytes with plasticizer EC and PMMA have been subjected to EIS, FT-IR, and also XRD studies. With the addition of 60 wt% of EC to PVdC-AN/PMMA blend, ionic conductivity of 0.398×10^{-6} S cm^{-1} has been achieved. The increase of temperature nonlinearly increases the ionic conductivity of polymer complex over the studied temperature range. XRD results suggest that the incorporated lithium salts were dissolved in the amorphous region of polymer in the presence of plasticizer and the ionic conductivity of polymer electrolyte is

given by the amorphous phase of the complex. The complex formation of polymer electrolyte was confirmed from FT-IR spectra. The thermal analysis leads to the conclusion that degradation process of gel polymer electrolyte depends not only on the chemical structure of the components, but also on their composition, where the components of the various ratios exhibit mutual interactions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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