

Research Article

Development of Bright Fluorescent Poly(1-vinyl-2-pyrrolidone-co-acrylonitrile) and Its Polysalts with HCl and HNO₃: Materials for Solid State Electrical Applications

Samiran Upadhyaya, Rajumani Sarma, Abdul Barik, and Neelotpal Sen Sarma 

Advanced Materials Laboratory, Institute of Advanced Study in Science and Technology, Guwahati, Assam 781035, India

Correspondence should be addressed to Neelotpal Sen Sarma; neelot@iasst.gov.in

Received 17 October 2018; Accepted 24 January 2019; Published 25 February 2019

Academic Editor: Tamilselvan Mohan

Copyright © 2019 Samiran Upadhyaya et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Herein, we have reported the synthesis, characterization, and ionic conductivity analysis of fluorescent poly(1-vinyl-2-pyrrolidone-co-acrylonitrile) and its salts with 10% HCl and HNO₃ in solid state. The synthesized polymers and their polysalts were characterized using Fourier-transformed infrared spectroscopy, UV-visible, Cyclic Voltammetry, Thermogravimetric analysis, Differential Scanning Calorimetric, X-ray diffraction, and spectrofluorometric techniques. The AC conductivities were measured in the frequency ranging from 42 Hz to 1 MHz and temperature from 30°C to 70°C in solid state. Ionic conductivities of the salts of the copolymer with hydrochloric acid and nitric acid were found to be 2.145×10^{-5} and 2.349×10^{-5} S cm⁻¹, respectively, which are nearly 1000 times more than that of poly(1-vinyl-2-pyrrolidone-co-acrylonitrile). The activation energies for the copolymer and the polyelectrolytes were found to be 0.454, 0.6288, and 0.659 eV, respectively. The transport number of the copolymers was found to be 0.0278, and that of the polysalts was found to be 0.7596 and 0.7424, respectively. The copolymer showed distinct fluorescent when irradiated with UV light and can be used as acid vapor sensor in solid state.

1. Introduction

Materials synthesis and device fabrication have been in tremendous demand since last few decades. Use of cost-effective and advanced materials for applications in electronics is the need of the hour. Conducting polymers with conducting and semiconducting properties can be employed in fuel cell and lithium-ion battery applications as diodes and super-capacitors, etc. [1–3]. Solid state polyelectrolytes have paved the way for wide range of applications because of their ease of synthesis, stability, and ability to be moulded to desired shapes and films [4–6]. The first polyelectrolytes reported were the complexes of poly(ethylene oxide) (PEO) with alkali metal salt [7]. Use of acids to increase the ionic conductivity of polymers has been in demand owing to its stability and applicability. For example, the solid state conductivity of the polymer of 2-vinyl pyridine, i.e., poly(2-vinyl pyridine), was found to be enhanced by the use of dilute

(10%) hydroiodide acid [8], because of the increase in the ionic character of the polymer due to the presence of protons incorporated via acids. Apart from acids, nanomaterials, such as carbon nanotubes [9] and graphene [10], for the fabrication of electronic devices have been widely explored. Fabricated electronic devices have also found their applicability as sensors for biomolecules detection, like urea [11] and cholesterol [12].

It is evident from the literature that research based on exploration of ionic characters of various proton conducting solid electrolytes of poly-n-vinyl pyrrolidone have caught the attention of many researchers around the globe [13], owing to the easy synthesis of the polymers of n-vinyl pyrrolidone moiety and its biocompatible nature. Polyelectrolytes contain charged groups either cations or anions, covalently attached to the polymer, so only the counter ion is mobile [14]. Most of these materials have been quaternized by using ammonium salt or other alkali metal ions [15–17]. But the quaternization

of the polymers based on 1-vinyl-2-pyrrolidone using acids has not been explored much. Moreover, the solid state conductivity of the polyelectrolytes of the fluorescent copolymers based on 1-vinyl-2-pyrrolidone with other monomers is also yet to be explored. These polymers may serve as potential materials for photodynamic therapy, photovoltaic devices, sensors, etc. [18, 19].

The synthesis of salts of the 1-vinyl-2-pyrrolidone-co-acrylonitrile copolymer with dilute hydrochloric (HCl) and nitric acid (HNO₃) has not yet been carried out. In this work, we have attempted the synthesis and characterization of these copolymer salts and to study their conductivities in the solid state, along with optical analysis. The most important advantage of our work, unlike other similar works, is that we have not used metal salts [20] or other conducting polymers like PEO [21, 22] or polyaniline [23, 24]. Only the virgin copolymer and its salts have been used for conductivity measurement, which gives us a route to the easy synthesis of polysalts, without going through difficult and multistep preparatory processes.

2. Experimental

2.1. Materials. 1-Vinyl-2-pyrrolidone was purchased from Merck. It was purified before use by distillation under moderate vacuum [25]. Acrylonitrile was procured from Merck. Azobisisobutyronitrile (AIBN) was obtained from Spectrochem. HCl, HNO₃, acetone, carbon tetrachloride, dimethylformamide (DMF), and chloroform were purchased from Merck. All these materials were of analytical grade and were used without further purification.

2.2. Preparation of Copolymer. To 0.05 mol (5.34 mL) of the purified monomer 1-vinyl-2-pyrrolidone (VP), 0.05 mol (3.274 mL) of the purified monomer acrylonitrile (AcN) was added drop wise initially and stirred well. The reaction flask was then evacuated by a vacuum pump and heated for 15 hours at 60°C. After completion of the reaction, the copolymer of VP and AcN, poly(1-vinyl-2-pyrrolidone-co-acrylonitrile) [denoted by P(VP-co-AcN)] was formed. The copolymer so formed was dissolved in chloroform and then precipitated in benzene. The copolymer was then heated up to 75°C and connected to a vacuum pump to remove excess chloroform and unreacted monomer that may be present in the copolymer. The copolymer was again dissolved in chloroform for the second time, and the process was repeated to remove the last traces of unreacted VP and AcN. The product obtained was then dried in an oven and stored in a vacuum desiccator over anhydrous calcium chloride.

2.3. Preparation of the Copolymer Salts. Concentrated solutions of the copolymer in chloroform were taken in two different test tubes and were treated with 10% HCl and 10% HNO₃, respectively, at room temperature and kept overnight. The salts poly(1-vinyl-2-pyrrolidone-co-acrylonitrile)-hydrochloric acid [P(VP-co-AcN)-HCl] and poly(1-vinyl-2-pyrrolidone-co-acrylonitrile)-nitric acid [P(VP-co-AcN)-HNO₃] were then precipitated by carbon

tetrachloride. The obtained salts of the corresponding acids used were then stored in a desiccator over anhydrous calcium chloride for later use.

3. Characterization

The Fourier transform infrared (FT-IR) spectra were recorded by using a NICOLET-6700 spectrophotometer in transmission mode over 32 scans. The FT-IR spectra were recorded in ATR mode. The samples were handled carefully and always stored in a desiccator to avoid contact with moisture.

The thermal properties of the copolymer and its corresponding salts were examined by thermogravimetric analysis (TGA) using a PerkinElmer TGA 4000 thermogravimetric analyzer at a heating rate of 10°C min⁻¹ in a nitrogen environment with a gas flow rate of 20 ml min⁻¹. The differential scanning calorimetric (DSC) studies were recorded with the help of PerkinElmer DSC 6000 instrument with a heating rate of 10°C min⁻¹ in nitrogen atmosphere. The X-ray diffraction (XRD) patterns were collected from an XRD D8 Advance Bruker instrument at a scan rate of 2 s per step.

Electronic transitions of the solutions of the copolymer and the electrolytes were observed by monitoring the room temperature UV-Vis spectra using Shimadzu (UV1601PC) spectrophotometer. The fluorescence spectra were taken by JASCO (FP-8300) spectrofluorometer with a slit width of 2.5 nm at a constant scan speed of 240 nm/s and with a detector voltage of 450.

Cyclic voltammetry data were recorded on CH instruments cyclic voltammetry (Model No. CHI660E), with a typical three-electrode system, using glassy carbon as working electrode, Ag/AgCl as reference, and platinum as the counter electrode with 0.1M KCl as the electrolyte.

4. AC Conductivity Measurement

Using alternating current (AC), the impedance of the samples was recorded. The readings were taken at different temperatures from 30 to 70°C with regular interval of 10°C using HIOKI 3532-50 frequency response analyzer in the frequency range from 42 Hz to 5 MHz at a constant voltage of 0.1 V. The bulk ionic conductivities of the samples were evaluated from the complex-impedance plots or Nyquist plots using the data recorded from impedance analyzer. The samples were taken in the form of thin films sandwiched in between two symmetric stainless steel (SS) anvils which acted as electrodes. The geometry of the cell for measurement of conductivity was SS|polymer sample|SS where SS stands for stainless steel. The experiments were carried out under a relative humidity of 55 %. Before recording the data, each of the samples was preheated at 50°C for at least 1 hour to ascertain the interface contact between the electrolyte sample and the electrodes.

5. Transport Number Determination

The total ionic transport numbers, t_{ion} , were evaluated by the standard Wagner polarization technique. The

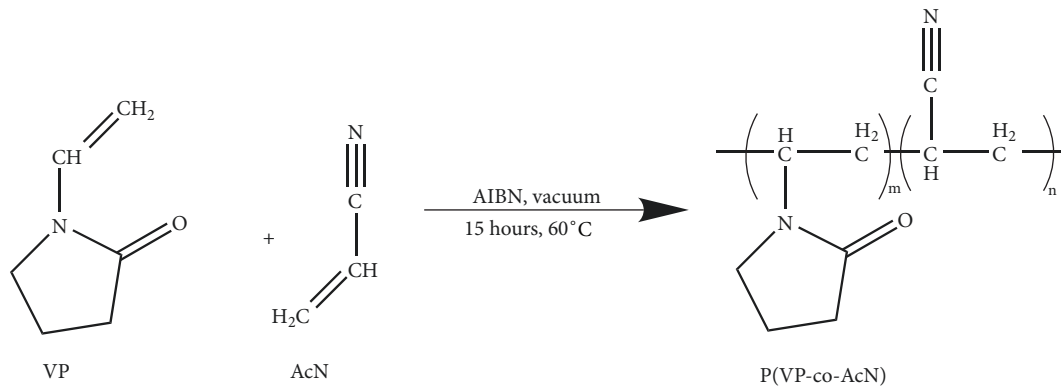
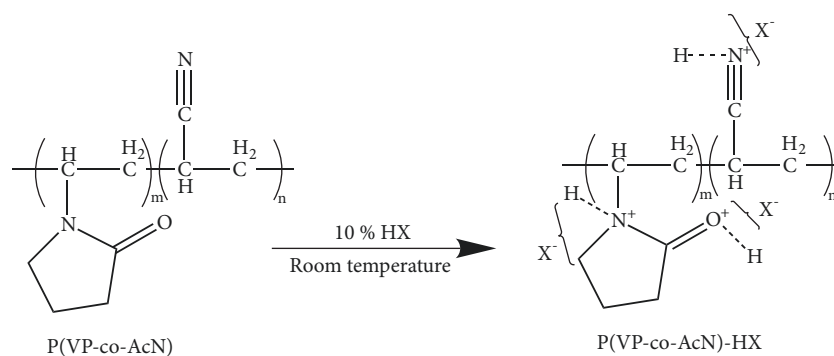


FIGURE 1: Schematic representation for the synthesis of the copolymer, P(VP-co-AcN).



where HX= HCl or HNO₃

FIGURE 2: Schematic representation for the synthesis of the polyelectrolytes, P(VP-co-AcN)-HCl/HNO₃.

cells SS|P(VP-co-AcN)|SS, SS|P(VP-co-AcN)-HCl|SS, and SS|P(VP-co-AcN)-HNO₃|SS were polarized by a step potential of about 1 V and the resulting potentiometric current was monitored as a function of time. The SS acted as blocking electrodes for the above cell. t_{ion} was evaluated by using the following:

$$t_{ion} = \frac{(i_T - i_e)}{i_T} \quad (1)$$

where i_T and i_e are the total and residual currents, respectively.

6. Results and Discussion

6.1. Chemical Synthesis. It may be assumed that the reaction proceeds in the following way: VP is a basic molecule due to the electron donating nature of the N-vinyl pyrrolidone moiety. AcN is also a weak base. But, in P(VP-co-AcN), the polymeric character predominates [Figure 1]. It has been found earlier that doping of acid in a polymer moiety increases the conducting properties [26, 27], because of the charged particles made available to the system by the acid. In our case, with the involvement of the acids, which get ionized to H⁺ and the corresponding negative fragments, denoted by X⁻ [explained in schemes as in Figures 1 and 2], the nitrogen

present in the copolymer readily forms a new N-H bond with the proton of the acid and behaves like a positive ion. Similarly, the carbonyl group adjacent to the N atom forms a new O-H bond, and the oxygen here behaves as a positive ion. These positive ions then form stable salt with the negative counter ion of the acid [Figure 2]. In this process, the ionic character of the copolymer was found to be increased, which results in the formation of good polyelectrolyte [28]. The whole reaction schemes have been explained in Figure 3.

The above reaction (Figure 2) was carried out at higher temperature (70°C) as well, to check the interaction of the CN group with acids. The reaction vessels were kept for 4 hours, until the solvents get evaporated and polymer lumps were obtained in both cases. Interestingly, the results were different to that of the reactions done at room temperature. This may be because at higher temperature the reactions lead to the hydrolysis of the CN group of the polymer [29, 30]. The interaction of P(VP-co-AcN) with HCl leads to the formation of amide, and the interaction with HNO₃ forms acid. The interactions can be confirmed by FT-IR spectra shown in Figure 4. The acid hydrolysis reaction might have followed the scheme shown in Figure 3(a) [31].

6.2. FT-IR Analysis. The synthesized compounds were characterized with the help of FT-IR spectra. The FT-IR spectra of

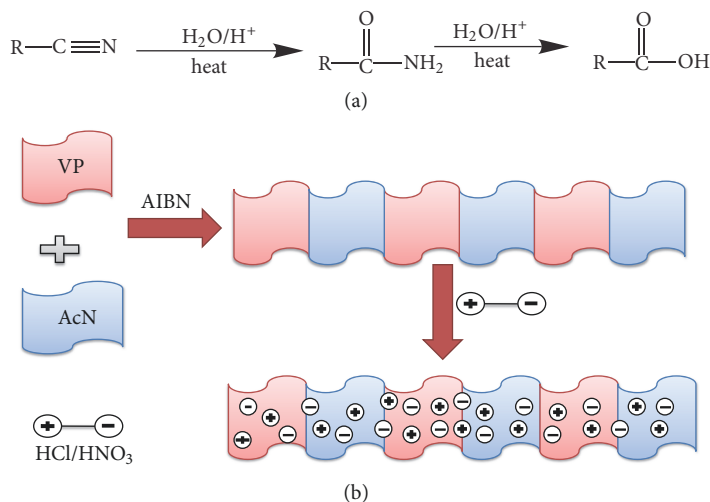


FIGURE 3: Diagrammatic representation of the series of reactions and the underlying mechanisms involved.

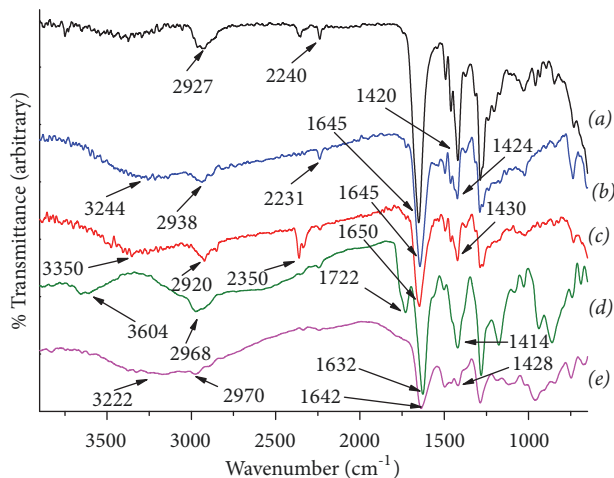


FIGURE 4: FT-IR spectra of the copolymer and the polyelectrolytes: (a) P(VP-co-AcN); (b) P(VP-co-AcN)-HNO₃ at room temperature; (c) P(VP-co-AcN)-HCl at room temperature; (d) P(VP-co-AcN)-HNO₃ at 70°C; (e) P(VP-co-AcN)-HCl at 70°C.

the copolymer and the polyelectrolytes are shown in Figure 4. For the copolymer, the peak at 2927 cm⁻¹ corresponds to C-H stretching, 2240 cm⁻¹ to that of C-N (triple bond) stretching, 1645 cm⁻¹ to carbonyl group of amide and 1420 cm⁻¹ to C-H bending modes. The corresponding salts of the copolymer, P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃, show additional broad peaks at 3350 (c) and 3244 cm⁻¹ (b), respectively, which were not present in the polymer. These peaks may be because of the formation of new O-H and N-H bonds in the salt, which hints the interaction of the acidic protons with the polar groups of the copolymer. The interactions between the copolymer and the acids do not change the overall backbone of the polymer. Other significant peaks are all retained by the salts as that in the polymer.

Effect of Temperature. The interactions of P(VP-co-AcN) with the acids at higher temperature can be analyzed by

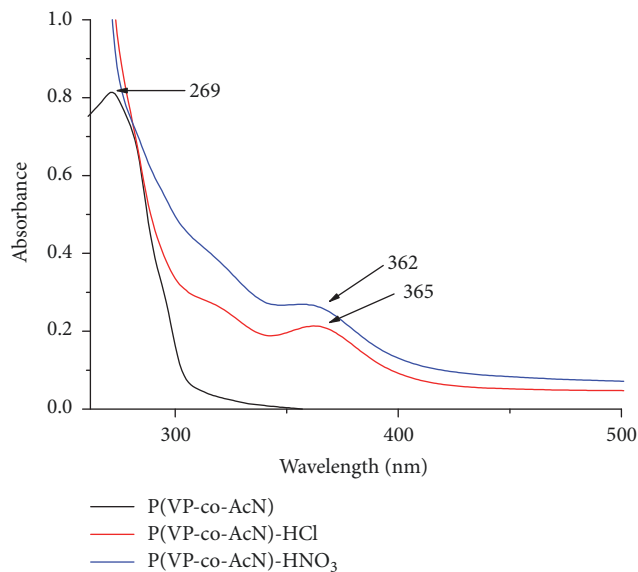


FIGURE 5: UV-Visible spectra of copolymer and its polyelectrolytes.

the spectra shown in Figures 4(d) and 4(e). The interaction of HCl with the CN group of the copolymer leads to the formation of amide (e) and that with HNO₃ forms acid (d). This can be confirmed by an additional peak at 1722 cm⁻¹, which can be attributed to the carbonyl C=O stretching of carboxylic acids and a broad peak at 3604 cm⁻¹, which corresponds to carboxylic OH stretching.

The interactions of the acids and the copolymer at room temperature do not change the overall fragment of the polymer and yield materials as required, so the reaction for the polyelectrolytes formation was preferably carried out at room temperature.

6.3. UV-Visible Spectroscopy. The UV-visible spectra of the copolymer and the corresponding polyelectrolytes, shown in Figure 5, were taken by preparing a dilute solution

TABLE 1: The different energy levels and the band gap of the copolymer and the polyelectrolytes.

Material	Band gap (in eV)	HOMO (in eV)	LUMO (in eV)
P(VP-co-AcN)	3.47	-5.32	-1.85
P(VP-co-AcN)-HCl	1.76	-5.29	-3.53
P(VP-co-AcN)-HNO ₃	1.52	-5.29	-3.75

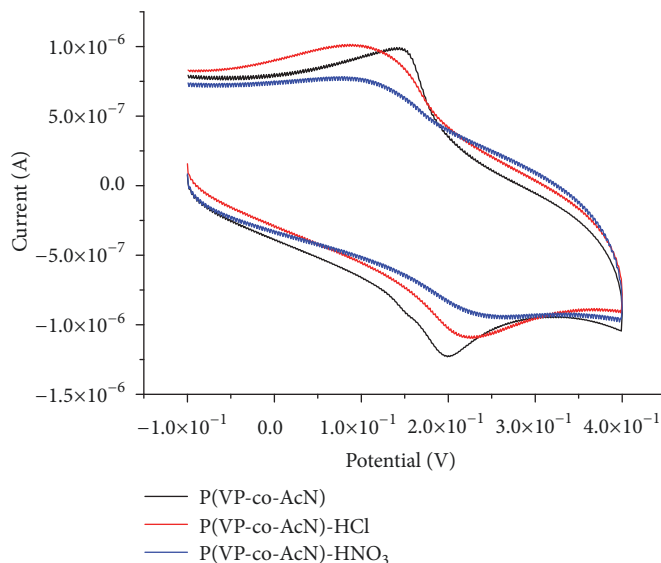


FIGURE 6: Cyclic voltammogram of copolymer and the polyelectrolytes.

of the copolymer in chloroform and the solutions of the polyelectrolytes in DMF, respectively. The presence of peak at a 269 nm for P(VP-co-AcN) and peaks at 362 nm and 365 nm, respectively, for P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃ confirms the formation of the materials. These peaks can all be attributed to n to π^* transitions. There is an increase in absorption wavelength (red shift) observed in the case of the polysalts. The increase in wavelength signifies the decrease in energy of transition. In other words, there is a decrease in the band gap of the polymer after the formation of the polyelectrolytes, thus giving semiconductor characteristics.

The band gap of the copolymer and the salts were calculated by the Tauc plots obtained from UV-visible spectra [32]. The calculated band gaps of P(VP-AcN), P(VP-AcN)-HCl and P(VP-AcN)-HNO₃ were found to be 3.4728 eV, 1.7583 eV, and 1.5362 eV, respectively. The band gaps of the polysalts fall under the semiconductor range.

6.4. Cyclic Voltammetry. Cyclic voltammetry for the polymer and the salts were taken by drop-casting the solutions of the materials on the working electrode, and the experiments were carried out with a scan rate of 0.1V/s, as shown in Figure 6.

The HOMO and the LUMO of the copolymer and the salts were calculated from the cyclic voltammetry and also referring the Tauc plots from UV-visible spectra. The energy levels and the band gap hint the polyelectrolytes to be semiconducting [33]. The obtained values are given in Table 1.

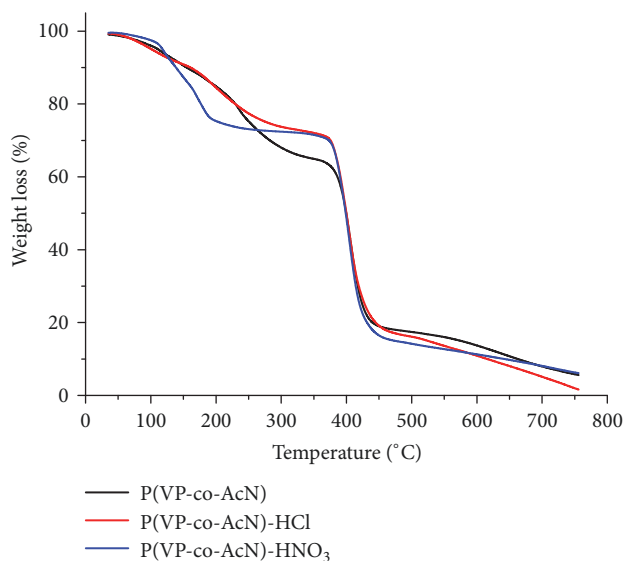


FIGURE 7: TGA spectra of the copolymer and the polyelectrolytes.

6.5. TGA. The TGA thermograms of the copolymer and the salts are shown in Figure 7. For P(VP-co-AcN), there is an initial loss of around 5% weight up to 110°C due to the removal of moisture present in the molecule. Again, there is a loss of another 21% weight below 236°C which may be attributed due to the loss of some fractions of pyrrolidone group present in the molecule. The significant weight loss occurred from

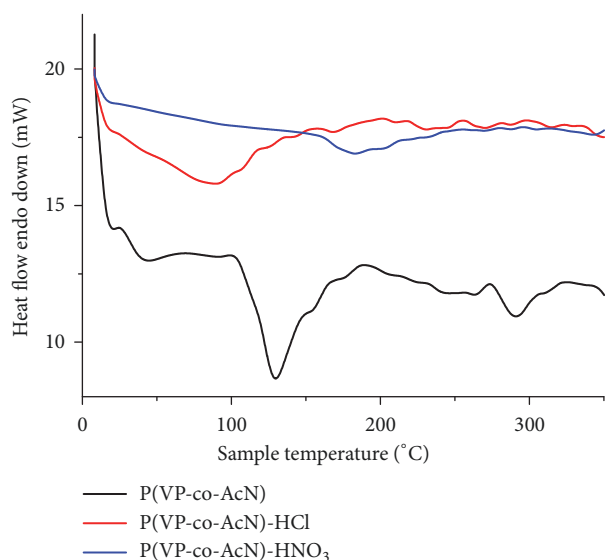


FIGURE 8: DSC spectra of the copolymer and the polyelectrolytes.

372 to 455°C (another 59 % loss) which results from the degradation of the copolymer backbone. The copolymer is wholly decomposed above 700°C.

In the TGA thermogram of P(VP-co-AcN)-HCl, the initial weight loss of 4 % occurred at 98°C, which may be due to the removal of the moisture absorbed. The next weight loss of 21 % up to 265°C can be assumed to be due to the loss of the HCl molecule. The significant weight loss (57 %) occurred from 370 to 448°C, due to the degradation of the copolymer backbone causing the removal of the NH₃ and CO₂ molecules. The copolymer salt decomposed entirely above 640°C.

The TGA thermogram of P(VP-co-AcN)-HNO₃ shows an exciting trend and is not very similar to that of P(VP-co-AcN)-HCl. It gives an initial weight loss of 4 % at around 109°C, and this weight loss may correspond to the removal of moisture. Next, a loss of about 23 % up to 273°C, is assumed to be due to the loss of HNO₃ molecule and is much faster compared to that of corresponding HCl salt. The second degradation occurred from 362 to 450°C, which is the primary degradation of around 60 % may be due to the decomposition of the copolymer backbone with the removal of NH₃ and CO₂ molecules. The salt wholly decomposed above 650°C. From TGA it is evident that P(VP-co-AcN)-HNO₃ loses its HNO₃ molecules earlier than HCl of P(VP-co-AcN)-HCl and so is thermally less stable.

6.6. DSC. DSC thermograms of P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃ are shown in Figure 8. Their corresponding glass transition temperatures (T_g) were found to be 25, 18, and 17°C, respectively. The T_g values of the salts are lower than that of the copolymer. This may be probably due to the new N–H and O–H bonds formed between the copolymer and the acids. The formation of salts increases the flexibility of the copolymer and hence increases of their ionic conductivity [34]. From DSC it can also be concluded

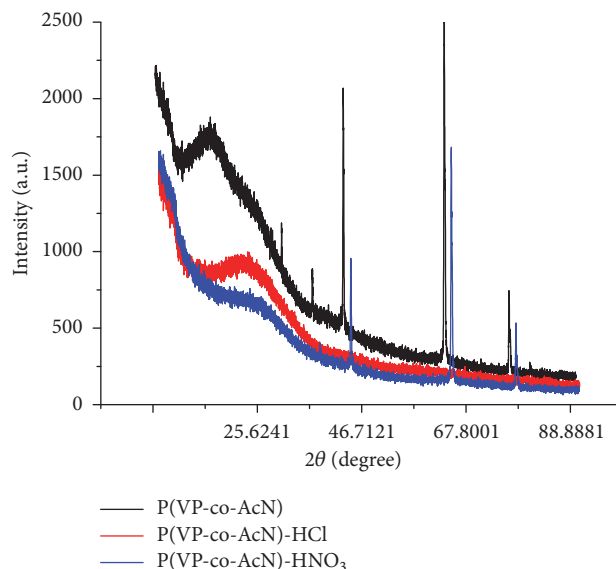


FIGURE 9: XRD spectra of the copolymer and the polyelectrolytes.

that the copolymer is more crystalline (corresponding peak at 129°C) compared to the corresponding salts.

6.7. XRD. The XRD plots for the copolymer and the polysalts are shown in Figure 9, which reveals that the copolymer and also the salts are polycrystalline, as is also evident from the DSC curve. But, the crystalline nature of the copolymer is lost after the formation of the polysalts due to the deformation of the crystal lattice of the polyelectrolytes. The (VP-co-AcN)-HCl is least crystalline. The peaks, i.e., 2θ values, shift towards the right after the interaction of the polymer with the acids, which signifies the increase in ionic interaction on formation of the new compounds [27]. For instance, the peak at 16.06 of the copolymer shifts to 22.68 and 25.16 for (VP-co-AcN)-HCl and (VP-co-AcN)-HNO₃, respectively. The decrease in crystallinity (increasing amorphous nature) facilitates better ionic diffusivity and subsequently ionic conductivity is enhanced [35]. The increase in amorphous nature causes a reduction in the energy barrier of the segmental motion of the polymer electrolyte, resulting in high ionic conductivity [36].

6.8. Fluorescence Spectroscopy. A known amount of the polymer (approximately 0.05g) was dissolved in 3 mL of chloroform, and the same amount of the salts was dissolved in DMF, respectively, to observe the fluorescence properties. The polymer emits bright bluish-white light, which was quenched after the incorporation of HCl and HNO₃. This quenching may be possibly due to the interaction of the polymer with the acids. The photographic images of the copolymer and the polysalts are shown in Figure 10.

Fluorescence spectra of the solutions of copolymer and electrolytes are plotted in Figure 11.

The response of the copolymer towards the vapor of HCl and HNO₃ was also observed. The copolymer solution was poured in a petridish and kept overnight at 60°C to form a thin film. The thin film was peeled out and cut into small

TABLE 2: Conductivity data at 30°C obtained at different frequencies.

Frequency	P(VP-co-AcN)	P(VP-co-AcN)-HCl	P(VP-co-AcN)-HNO ₃
100 Hz	5.62×10^{-9}	5.26×10^{-7}	7.82×10^{-6}
1 kHz	1.06×10^{-8}	6.97×10^{-7}	8.78×10^{-6}
10 kHz	8.32×10^{-8}	9.39×10^{-7}	1.6×10^{-5}
100 kHz	1.04×10^{-7}	1.42×10^{-6}	2.05×10^{-5}
1 MHz	2.57×10^{-6}	1.63×10^{-6}	2.55×10^{-5}

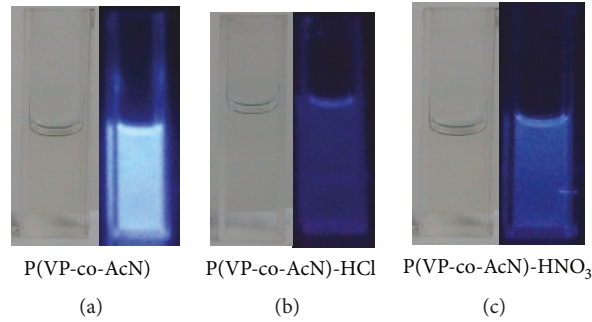
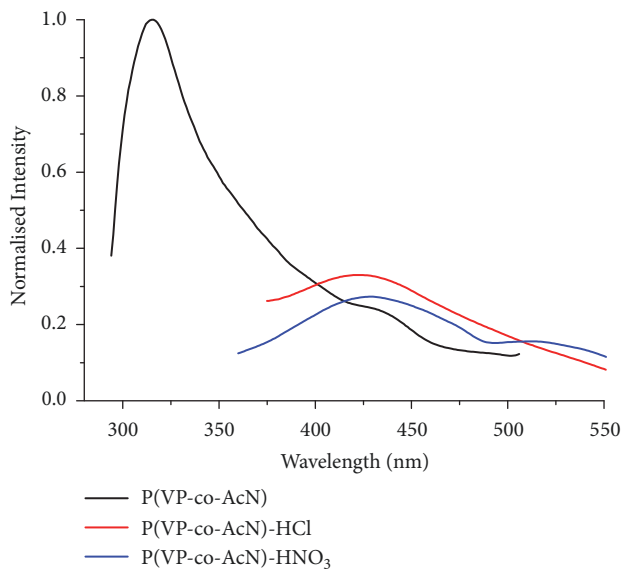
FIGURE 10: Photographic images of P(VP-co-AcN) (a), P(VP-co-AcN)-HCl (b), and P(VP-co-AcN)-HNO₃ (c) under normal light and UV light, respectively.

FIGURE 11: Fluorescence spectra of copolymer and the polyelectrolytes.

pieces. The small polymer films were brought in contact with the acid fumes by keeping at the mouth of test tubes filled with approximately 3 mL of concentrated HCl and HNO₃, respectively. The test tubes were kept undisturbed for 15 minutes, as shown in Figure 12. The films were then slowly removed and the fluorescence spectra were recorded.

The contact of the polymer films with the vapor of the acids resulted in quenching of fluorescence intensity. Thus, the polymer can also be used for detection of acid vapors. The polyelectrolytes, with excellent conductivity, can hence

be formed by contact of the polymer with vapors of acids [37] also. The fluorescence spectra of the copolymer before and after contact with acid vapor are shown in Figure 13.

7. AC Conductivity Measurement

The conductivities of the copolymer and its salts were measured by AC impedance spectroscopy. For each sample, bulk conductivity (σ) values at a certain temperature can be calculated with the help of (2) and (3) [38] by putting the values of capacitance (C) and dielectric loss (D) recorded from the impedance analyzer against applied frequencies (f).

$$\epsilon_0 \epsilon_r = \frac{(C \times l)}{A} \quad (2)$$

$$\sigma = 2\pi \epsilon_0 \epsilon_r f D \quad (3)$$

where ϵ_0 and ϵ_r are the dielectric permittivity and permittivity of air, respectively. A denotes the surface area, and l is the thickness of the samples. The samples were prepared in the form of pellets. The pellets used in this experiment have a constant surface area of 1.1304 cm² and thicknesses of the pellets used were between 0.08 and 0.09 cm. The experiments were carried out at five different temperatures ranging from 30 to 70°C with an interval of 10°C. The values of AC conductivities at 30°C against different frequencies are given in Table 2. It is evident that the conductivity increases with an increase in frequency, probably due to normal dispersion in heteroatomic polymers [39]. Interestingly, the increase in conductivity of the copolymer at 1 MHz is much higher than the expected trend, which may be due to polymeric deformation, leading to electronic as well as ionic conduction.

The complex-impedance plots at 30°C for the copolymer and its salts are shown in Figure 14. In a complex-impedance

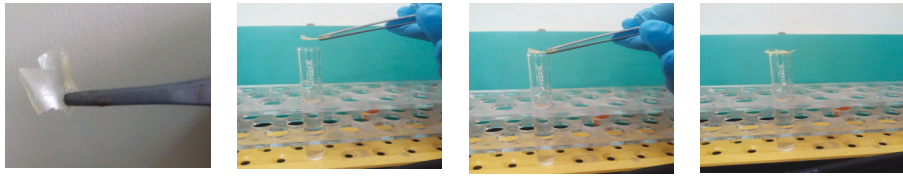


FIGURE 12: Photographic images showing the set-up for the contact of copolymer with acid fumes.

TABLE 3: Temperature versus conductivity data.

Temperature	Conductivities (S cm^{-1}) at different temperature		
	P(VP-co-AcN)	P(VP-co-AcN)-HCl	P(VP-co-AcN)-HNO ₃
30	5.794×10^{-9}	1.294×10^{-6}	1.236×10^{-6}
40	6.353×10^{-9}	1.418×10^{-6}	2.406×10^{-6}
50	6.697×10^{-9}	5.889×10^{-6}	5.014×10^{-6}
60	8.932×10^{-9}	1.271×10^{-5}	1.016×10^{-5}
70	4.411×10^{-8}	2.145×10^{-5}	2.349×10^{-5}

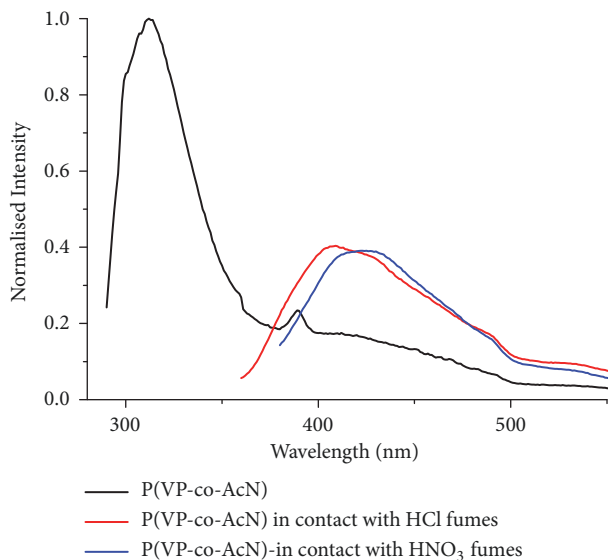


FIGURE 13: Fluorescence spectra of copolymer before and after contact with corresponding acid fumes.

plot, the real part, $Z \cos \theta (Z')$, is plotted against the imaginary part, $Z \sin \theta (Z'')$, where Z is the impedance and θ is the phase angle. The point of intersection of the two semicircles in a complex-impedance plot coincides with the bulk resistance (R_b) of the sample [40]. The small semicircles correspond to the medium-high frequencies, and the large semicircles correspond to the low frequencies. After determining the value of R_b , the values of conductivity at various temperatures are calculated by using

$$\sigma = \frac{l}{(R_b \times A)} \quad (4)$$

The variation of ionic conductivities of the copolymer and its salts with the temperature is shown in Arrhenius plot or $\log(\sigma T)$ versus $1000/T$ plot in Figure 15. The figure shows that with

the formation of salts the ionic conductivity increases. The conductivities of P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃ were found to be higher than that of P(VP-co-AcN) in the whole temperature range. For instance, at 30°C, P(VP-co-AcN) shows an ionic conductivity value of $5.79 \times 10^{-9} \text{ S cm}^{-1}$, whereas P(VP-co-AcN)-HCl gives the ionic conductivity of $1.29 \times 10^{-6} \text{ S cm}^{-1}$ and P(VP-co-AcN)-HNO₃ shows ionic conductivity value of $1.23 \times 10^{-6} \text{ S cm}^{-1}$, respectively. At 70°C, P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃ show ionic conductivity value $2.14 \times 10^{-5} \text{ S cm}^{-1}$ of and $2.349 \times 10^{-5} \text{ S cm}^{-1}$, respectively, which are much higher than that of P(VP-co-AcN) which is $4.41 \times 10^{-8} \text{ S cm}^{-1}$ (shown in Table 3.). There is a 10^2 – 10^3 -fold increase in conductivities in case of the salts than the parent copolymer in the temperature range of 30–70°C. The reason for this may be that the vinyl amide group is more basic than an unsubstituted cyclic amide molecule. Therefore, P(VP-co-AcN) possesses prominent basic character due to the presence of the N-vinyl group in VP and the carbonyl moiety. When an acid is added to P(VP-co-AcN), the N-lone pair of electrons of VP and AcN groups easily forms new N–H and O–H bonds with the protons of the acids and behaves like positive ions. These positive ions then form stable salts with the negative counterparts of the acids, namely, Cl^- and NO_3^- . This results in an increase in the ionic character of the salts and the salts behave as good polyelectrolytes. These salts also can be further applied as inherently conducting polymers (ICP) [41].

Effect of Temperature. The ionic conductivities of the polyelectrolytes were found to get enhanced with rise in temperature. With increasing temperature, expansion of polymer salts takes place to produce free volume which facilitates the enhancement in carrier ions and hence the ionic mobility and polymer segmental mobility, which in turn gives rise to increase in ionic conductivity [42]. When temperature increases, due to the increasing vibration of polymer chain segments, neighbouring atoms create a small amount of space surrounding its own volume in which vibrational motion can occur. Therefore, increasing free volume around the

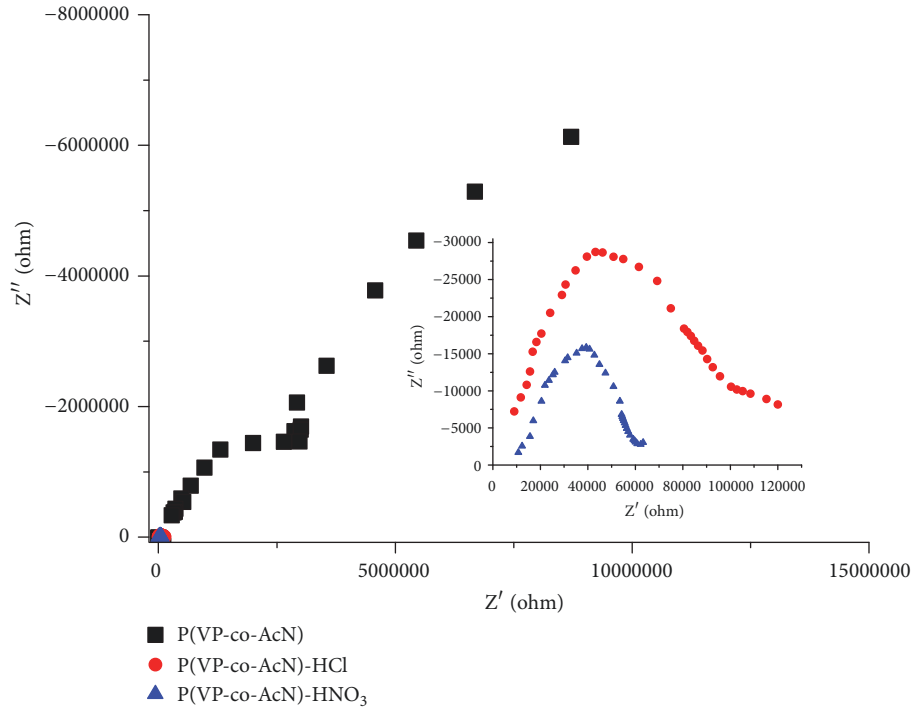


FIGURE 14: Complex-impedance plots at 30° for P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃, respectively.

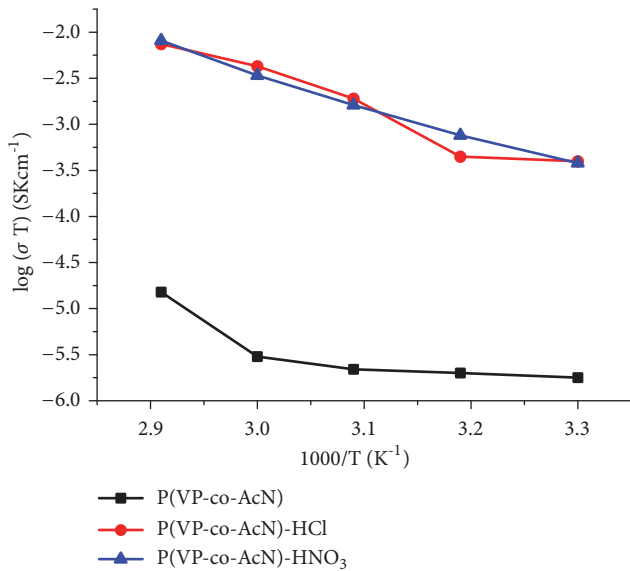


FIGURE 15: log(σ T) versus 1000/T plots for the copolymer and its salts.

polymer chains causes the mobility of the ions to increase. Hence, increasing the temperature causes the conductivity to increase due to the expanded free volume and ionic mobility [43]. In short, ionic conductivity is directly proportional to the temperature. The values of bulk conductivity of the copolymer and its corresponding salts at different temperatures are shown in Table 3. The dependence of ionic conductivity with temperature can be explained by Arrhenius equation, explained in Section 7.1 below.

7.1. *Activation Energy.* The activation energies (E_a) of various reactions can be calculated by using the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

where σ_0 is the preexponential factor, k , is the Boltzmann constant, and T is the absolute temperature. The activation energies were computed from the Arrhenius plots given in Figure 15 and were found to be 0.454, 0.6288, and 0.659 eV, respectively, for the conduction P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃. The higher value of E_a for the salts compared to the copolymer indicates the higher percentage of ionic character because a higher value of E_a is necessary for ionic conduction [44].

8. Transport Number

When a DC voltage is applied through a sample, migration of ions take place until a steady state is reached. The experimental set-up of standard Wagner polarization technique is shown in Figure 16. As the steady state is obtained, the cell gets polarized, and any residual current that flows through the sample is only because of electron migration across the electrode-electrolyte interfaces. Current passing through blocking electrodes falls rapidly with time in the case of ionic samples, because of the polarization of ions [45]. The time versus current plots for all three compounds are shown in Figure 17. From the figure, the transport numbers were calculated. The calculated values of the transport numbers were found to be 0.0278, 0.7596, and 0.7424 for P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃, respectively. The values indicate that P(VP-co-AcN) shows

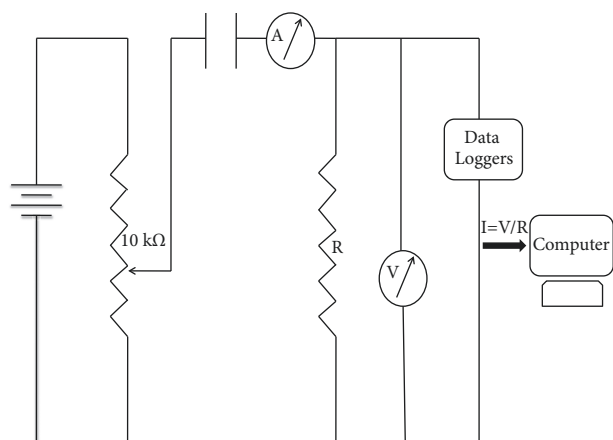


FIGURE 16: Experimental set-up of standard Wagner polarization technique.

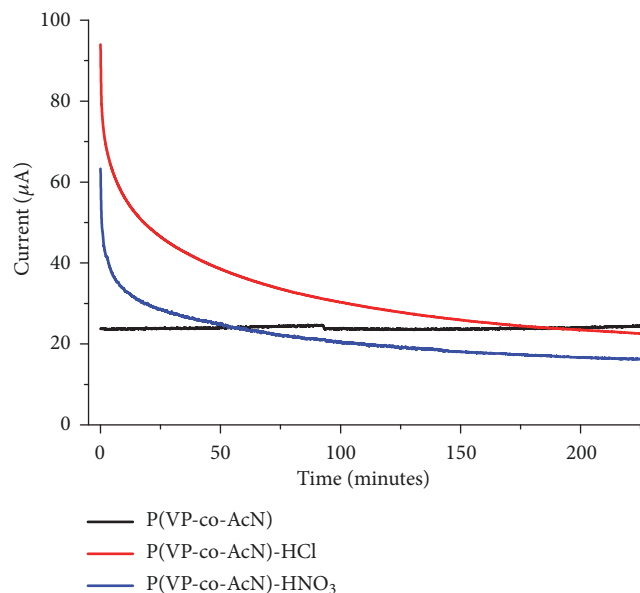


FIGURE 17: Time v/s current plots for the copolymer and the respective polyelectrolytes.

only electronic conduction, whereas P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃ both show good ionic character. The H⁺ mobile ions are responsible for ion transfer in P(VP-co-AcN), which is acquired from the respective acids and they act as counter ions for the amide moiety of the polymer, hence responsible for salt formation [46].

9. Conclusion

We have successfully synthesized and characterized a bright fluorescent polymer, P(VP-co-AcN), and its salts, P(VP-co-AcN)-HCl and P(VP-co-AcN)-HNO₃, and observed that the conducting property of the copolymer was enhanced significantly on the formation of its salts. The copolymer and its salts have some crystalline characteristics. The copolymer is thermally stable up to 110°C, whereas its salts of HCl and

HNO₃ are thermally stable up to 98°C and 109°C, respectively. There is a 10²–10³ fold increase in ionic conductivity in case of the polyelectrolytes compared to the parent copolymer. At 70°C, the values of ionic conductivities of P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃ are 4.411×10⁻⁸, 2.145×10⁻⁵, and 2.349×10⁻⁵ S cm⁻¹, respectively. The transport number values are 0.0278, 0.7596, and 0.7424 for P(VP-co-AcN), P(VP-co-AcN)-HCl, and P(VP-co-AcN)-HNO₃, respectively. This increase in transport number implies that the formation of the salts enhances the ionic conductivities of the parent copolymer. There is also quenching of fluorescence observed in the case of the polysalts. Therefore, the salts prepared from the copolymer can be used as good polyelectrolytes in solid state ionic devices, including dry cells. Moreover, the copolymer can be a suitable applicant for detection of acid by both electrical as well as optical methods.

Data Availability

No data is collected from any published article. The data presented in the manuscript are generated by us and are bonafide work of mine and my students. The manuscript or any part of the manuscript was not published in any other journal.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

Authors are grateful to DST, Government of India, for funding this work. Authors are also thankful to Arun Kumar and Sweetly Biswasi for their support.

References

- [1] T. M. Higgins, S.-H. Park, P. J. King et al., "A commercial conducting polymer as both binder and conductive additive for silicon nanoparticle-based lithium-ion battery negative electrodes," *ACS Nano*, vol. 10, no. 3, pp. 3702–3713, 2016.
- [2] J. Zhang, B. Sun, X. Huang, S. Chen, and G. Wang, "Honeycomb-like porous gel polymer electrolyte membrane for lithium ion batteries with enhanced safety," *Scientific Reports*, vol. 4, article 6007, 2014.
- [3] C. Peng, S. Zhang, D. Jewell, and G. Z. Chen, "Carbon nanotube and conducting polymer composites for supercapacitors," *Progress in Natural Science*, vol. 18, no. 7, pp. 777–788, 2008.
- [4] W. Weppner, "Engineering of solid state ionic devices," *Ionics*, vol. 9, no. 5-6, pp. 444–464, 2003.
- [5] A. Gogoi and N. S. Sarma, "Improvement in ionic conductivities of poly-(2-vinylpyridine) by treatment with crotonic acid and vinyl acetic acid," *Bulletin of Materials Science*, vol. 38, no. 3, pp. 797–803, 2015.
- [6] P. P. Kumar and S. Yashonath, "Ionic conduction in the solid state," *Journal of Chemical Sciences*, vol. 118, no. 1, pp. 135–154, 2006.

- [7] P. V. Wright, "Electrical conductivity in ionic complexes of poly(ethylene oxide)," *Polymer International*, vol. 7, no. 5, pp. 319–327, 1975.
- [8] P. Chetri, N. N. Dass, and N. S. Sarma, "Investigations on pyridinium salts as a solid-state ionics," *Journal of Applied Polymer Science*, vol. 112, no. 3, pp. 1444–1447, 2009.
- [9] H. Sun, H. Zhang, S. Liu et al., "Interfacial polarization and dielectric properties of aligned carbon nanotubes/polymer composites: The role of molecular polarity," *Composites Science and Technology*, vol. 154, pp. 145–153, 2018.
- [10] C. Gao, P. Liu, Y. Ding et al., "Non-contact percolation of unstable graphene networks in poly(styrene-co-acrylonitrile) nanocomposites: Electrical and rheological properties," *Composites Science and Technology*, vol. 155, pp. 41–49, 2018.
- [11] A. Ali, A. A. Ansari, A. Kaushik et al., "Nanostructured zinc oxide film for urea sensor," *Materials Letters*, vol. 63, no. 28, pp. 2473–2475, 2009.
- [12] M. A. Barik and J. C. Dutta, "Fabrication and characterization of junctionless carbon nanotube field effect transistor for cholesterol detection," *Applied Physics Letters*, vol. 105, no. 5, 2014.
- [13] R. D. Bella, S. Karthickprabhu, A. Maheswaran, C. Amibika, G. Hirankumar, and P. Devaraj, "Investigation of the ionic conductivity and dielectric measurements of poly (N-vinyl pyrrolidone)-sulfamic acid polymer complexes," *Physica B: Condensed Matter*, vol. 458, pp. 51–57, 2015.
- [14] P. G. Bruce, *Solid State Electrochemistry*, vol. 5, Cambridge University Press, New York, NY, USA, 1997.
- [15] C. S. Ramya, S. Selvasekarapandian, T. Savitha et al., "Conductivity and thermal behavior of proton conducting polymer electrolyte based on poly (N-vinyl pyrrolidone)," *European Polymer Journal*, vol. 42, no. 10, pp. 2672–2677, 2006.
- [16] C. S. Ramya, S. Selvasekarapandian, G. Hirankumar, T. Savitha, and P. C. Angelo, "Investigation on dielectric relaxations of PVP-NH₄SCN polymer electrolyte," *Journal of Non-Crystalline Solids*, vol. 354, no. 14, pp. 1494–1502, 2008.
- [17] C. S. Ramya and S. Selvasekarapandian, "Spectroscopic studies on ion dynamics of PVP-NH₄SCN polymer electrolytes," *Ionics*, vol. 20, no. 12, pp. 1681–1686, 2014.
- [18] R. A. Aspey and K. J. Brazier, "In situ optical sensing of diesel exhaust particulates using a polychromatic LED source," *Measurement Science and Technology*, vol. 14, no. 6, pp. 751–758, 2003.
- [19] X. Li, S. Kolemen, J. Yoon, and E. U. Akkaya, "Activatable photosensitizers: agents for selective photodynamic therapy," *Advanced Functional Materials*, vol. 27, no. 5, Article ID 1604053, 2017.
- [20] M. Hema, S. Selvasekarapandian, A. Sakunthala, D. Arunkumar, and H. Nithya, "Structural, vibrational and electrical characterization of PVA-NH₄Br polymer electrolyte system," *Physica B: Condensed Matter*, vol. 403, no. 17, pp. 2740–2747, 2008.
- [21] E. A. Rietman, M. L. Kaplan, and R. J. Cava, "Alkali metal ion-poly (ethylene oxide) complexes. II. Effect of cation on conductivity," *Solid State Ionics*, vol. 25, no. 1, pp. 41–44, 1987.
- [22] J. Xi, X. Ma, M. Cui, X. Huang, Z. Zheng, and X. Tang, "Electrochemistry study on PEO-LiClO₄-ZSM5 composite polymer electrolyte," *Chinese Science Bulletin*, vol. 49, no. 8, pp. 785–789, 2004.
- [23] R. Montazami, V. Jain, and J. R. Heflin, "High contrast asymmetric solid state electrochromic devices based on layer-by-layer deposition of polyaniline and poly(aniline sulfonic acid)," *Electrochimica Acta*, vol. 56, no. 2, pp. 990–994, 2010.
- [24] N. Kinomura, T. Toyama, and N. Kumada, "Intercalative polymerization of aniline in VOPO₄·2H₂O," *Solid State Ionics*, vol. 78, no. 3-4, pp. 281–286, 1995.
- [25] P. Hemalatha, M. Veeraiyah, S. Prasannakumar, and K. Anasuya, "Synthesis, characterisation and antibacterial activity of copolymer (N-vinylpyrrolidone-maleic anhydride) with N-diethylethanolamine," *International of Research in Engineering and Technology*, vol. 3, pp. 56–64, 2014.
- [26] S.-I. Lee, K.-H. Yoon, M. Song et al., "Structure and properties of polymer electrolyte membranes containing phosphonic acids for anhydrous fuel cells," *Chemistry of Materials*, vol. 24, no. 1, pp. 115–122, 2011.
- [27] N. S. Sarma and N. N. Dass, "Measurement of ionic conductivity of some electrolytes, polyelectrolytes and complexes in solid state," *Indian Journal of Pure & Applied Physics*, vol. 37, no. 4, pp. 321–324, 1999.
- [28] P. Chetri, N. N. Dass, and N. S. Sarma, "Characterization and ionic conductivity measurement of poly(2-vinyl pyridinium) salt in solid state," *Materials Science and Engineering: B Advanced Functional Solid-State Materials*, vol. 128, no. 1-3, pp. 188–191, 2006.
- [29] V. Y. Kukushkin and A. J. L. Pombeiro, "Metal-mediated and metal-catalyzed hydrolysis of nitriles," *Inorganica Chimica Acta*, vol. 358, no. 1, pp. 1–21, 2005.
- [30] V. K. Kriehle and C. I. Noll, "The hydrolysis of nitriles with acids," *Journal of the American Chemical Society*, vol. 61, no. 3, pp. 560–563, 1939.
- [31] C. P. Wilgus, S. Downing, E. Molitor, S. Bains, R. M. Pagni, and G. W. Kabalka, "The acid-catalyzed and uncatalyzed hydrolysis of nitriles on unactivated alumina," *Tetrahedron Letters*, vol. 36, no. 20, pp. 3469–3472, 1995.
- [32] N. Ghobadi, "Band gap determination using absorption spectrum fitting procedure," *International Nano Letters*, vol. 3, article 2, no. 1, 2013.
- [33] A. P. Alivisatos, "Semiconductor clusters, nanocrystals, and quantum dots," *Science*, vol. 271, no. 5251, pp. 933–937, 1996.
- [34] A. Chakrabarti, R. Filler, and B. K. Mandal, "Borate ester plasticizer for PEO-based solid polymer electrolytes," *Journal of Solid State Electrochemistry*, vol. 12, no. 3, pp. 269–272, 2008.
- [35] K. M. Anilkumar, B. Jinisha, M. Manoj, and S. Jayalekshmi, "Poly(ethylene oxide) (PEO) – Poly(vinyl pyrrolidone) (PVP) blend polymer based solid electrolyte membranes for developing solid state magnesium ion cells," *European Polymer Journal*, vol. 89, pp. 249–262, 2017.
- [36] R. Manjuladevi, M. Thamilselvan, S. Selvasekarapandian, P. Christopher Selvin, R. Mangalam, and S. Monisha, "Preparation and characterization of blend polymer electrolyte film based on poly(vinyl alcohol)-poly(acrylonitrile)/MgCl₂ for energy storage devices," *Ionics*, vol. 24, no. 4, pp. 1083–1095, 2018.
- [37] P. Chetri, N. N. Dass, and N. S. Sarma, "Synthesis, characterization and conductivity measurement of poly (2-vinyl pyridine) complex in nano fine state," *Polymer Bulletin*, vol. 61, no. 1, pp. 11–17, 2008.
- [38] H. Birey, "Dielectric properties of aluminum oxide films," *Journal of Applied Physics*, vol. 49, no. 5, pp. 2898–2904, 1978.
- [39] A. Bozkurt and W. H. Meyer, "Proton conducting blends of poly(4-vinylimidazole) with phosphoric acid," *Solid State Ionics*, vol. 138, no. 3-4, pp. 259–265, 2001.

- [40] A. Gogoi and N. S. Sarma, "Conductivity study of poly(acrylonitrile-co-2-vinylpyridine) complexed with vinyl acetic acid and 4-pentenoic acid," *Ionics*, vol. 22, no. 1, pp. 77–84, 2016.
- [41] S. S. Im and S. W. Byun, "Preparation and properties of transparent and conducting nylon 6-based composite films," *Journal of Applied Polymer Science*, vol. 51, no. 7, pp. 1221–1229, 1994.
- [42] V. Aravindan and P. Vickraman, "A novel gel electrolyte with lithium difluoro(oxalato)borate salt and Sb_2O_3 nanoparticles for lithium ion batteries," *Solid State Sciences*, vol. 9, no. 11, pp. 1069–1073, 2007.
- [43] E. Vargün, M. Sankär, A. Usanma, Y. Kanbur, U. Abacä, and H. Y. Güney, "Preparation and characterization of acrylonitrile-ethyl methacrylate copolymers and the effect of LiClO_4 salt on electrical properties of copolymer films," *Journal of Applied Polymer Science*, vol. 124, no. 1, pp. 840–846, 2012.
- [44] K. K. Maurya, B. Bhattacharya, and S. Chandra, "Hydrogen ion transport studies in PEO: NH_4HSO_4 polymer electrolyte," *Physica Status Solidi (a) – Applications and Materials Science*, vol. 147, no. 2, pp. 347–359, 1995.
- [45] B. Gogoi, P. Dutta, N. Paul, N. N. Dass, and N. S. Sarma, "Polycurcumin acrylate and polycurcumin methacrylate: Novel bio-based polymers for explosive chemical sensor," *Sensors and Actuators B: Chemical*, vol. 181, pp. 144–152, 2013.
- [46] S. A. Hashmi, D. K. Rai, and S. Chandra, "Protonic conduction in $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$: coulometry, transient ionic current, infrared and electrical conductivity studies," *Journal of Materials Science*, vol. 27, no. 1, pp. 175–179, 1992.



Hindawi
Submit your manuscripts at
www.hindawi.com

