

Effect of Dodecyl Benzene Sulphonic Acid on the Electrical Conductivity Behaviour of Poly(2-chloroaniline) and Poly(2-chloroaniline)/Silk Blends

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Abstract The poly(2-chloroaniline) and poly(2-chloroaniline)-DBSA/Silk and P2ClAn/Silk were prepared by *in situ* chemical oxidative polymerization technique using ammonium per sulphate (oxidant), HCl and dodecyl benzene sulphonic acid (DBSA) as the dopant and sodium lauryl sulphate as the surfactant. The formation of polymers and blends were confirmed by FTIR, UV-visible and NMR spectroscopy. The degree of crystallinity is reduced in the blends as revealed by X-Ray diffraction studies. The polymer blends have lesser thermal stability than the polymer. The presence of DBSA reduces the thermal stability of the blend. The polymer and the blends are semiconducting and the polymer has higher conductivity than the blends. The presence of DBSA enhances the conductivity of the blend. The temperature dependent DC conductivity obeys the Arrhenius equation and the activation energy was found to be around 0.1eV for the polymer and the blends. The increase in conductivity with increase in the temperature suggested the electron hopping mechanism. The P2ClAn-DBSA/Silk has higher dielectric constant than the P2ClAn-DBSA and can find applications in the energy storage devices.

Keywords Poly(2-chloroaniline), Polypropyleneglycol, Dodecyl benzene sulphonic acid, Electricalconductivity, Blends

1. Introduction

Typical conducting polymers include polyacetylene, polyaniline, polypyrrole, polythiophene, poly (para phenylene), poly (phenylenevinylene), polyfuran etc. [1]. Among the whole conducting polymers, polyaniline has a specific situation because of its simple synthesis, environmental stability and doping with protonic acids [2, 3]. The applications of polyaniline in various important fields include active electrode [4], electromagnetic shielding materials [5], microelectronic materials and electrochromic device [5], metal anti-corrosive coating [6, 7], anti-static coating [8], rechargeable batteries [9, 10], energy storage and transfer, redox micro-template [11], indicators and sensors [12, 13]. The conducting polyanilinemicroparticles can be electrostatically accelerated to hypervelocities, indicating their suitability as mimics of solar system dusts for the calibration of impact ionization detectors for spacecraft [14]. Polyaniline also shows very high gas-separation ability with the highest ideal oxygen/nitrogen separation factor of up to 30 [15].

In spite of various advantages, polyaniline has certain

limitations when it comes to its applications as it is neither soluble nor fusible in organic solvents as well as water [16]. In order to overcome such disadvantages, attempts have been made by the use of molecular design, modification of monomer structure, use of functionalized acid dopant, formation of blends/composites and copolymerization [17, 18]. The synthesis of different homopolymers and copolymers derived from anilines with electron withdrawing groups has been reported [19-22]. Colloidal particles have the potential to be finely dispersed in a polymer medium due to their small size. Therefore when colloidal particles of an intrinsically conducting polymer are used to form polymer blends, fine conductive path may generate and high conductivity levels may be realized [23]. Silk, a natural polymer is a well known conductor but there are no reports on the study of substituted polyaniline blend with silk. An attempt has been made to synthesize the poly(2-chloroaniline) blends with the natural polymer silk and study the effect of DBSA on the rate of polymerization.

In the present investigation poly(2-chloroaniline) (P2ClAn-DBSA) and poly(2-chloroaniline)/Silk in the presence/absence of DBSA (P2ClAn-DBSA/Silk & P2ClAn/Silk) were prepared by *insitu* chemical oxidative polymerization method using hydrochloric acid and dodecyl benzene sulphonic acid as dopants, ammonium per sulphate as an oxidant and sodium lauryl sulphate as surfactant at 0-5 °C. This pathway was selected because one expects that

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the presence of dodecyl benzene sulphonic acid in the polymer blends enhances the solubility, stability, conductivity in organic solvents and hence the processibility as reported in our previous work with clay composites [24]. The resulting polymer and polymer blends were characterized by FT-IR, UV, $^1\text{H-NMR}$ and XRD studies. The thermal stability was studied by TGA and DTA analysis and the electrical conductivity was measured by four point probe method.

2. Experimental

2.1. Preparation of Poly(2-chloroaniline)

2-chloroaniline, ammonium per sulphate, sodium lauryl sulphate (SDS) and dodecyl benzene sulphonic acid (DBSA) were purchased from LOBA Chemic, Qualigens and Avra Synthesis Pvt. Ltd respectively and used as received.

The poly(2-chloroaniline) (P2ClAn-DBSA) was synthesized by *in situ* chemical oxidative polymerization method [25] using ammonium per sulphate as the oxidizing agent, HCl and dodecyl benzene sulphonic acid as the dopants and sodium lauryl sulphate as the surfactant. The monomer and oxidant were taken in 1:2 mole ratio. 2-chloroaniline was suspended in 100 ml of 1 M HCl solution and placed in the freezing mixture. The oxidant, dopant and surfactant were added drop wise to the monomer with constant stirring. The polymerization was allowed to take place for 6 hours and placed at 0°C overnight. The green coloured product was filtered, washed and dried and obtained in high yield.

Adopting the same method, the poly(2-chloroaniline)-DBSA/Silk was prepared. Silk was dissolved in 1 M HCl solution and the monomer was dispersed in the water. The monomer and silk solutions were mixed and stirred for an hour for uniform dispersion and adopting the same procedure as described above, the poly(2-chloroaniline)-DBSA/Silk was prepared. The resulting product was dark green in colour.

The poly(2-chloroaniline)/Silk was also prepared by the same technique in the absence of DBSA. The resulting product was blue in colour and the yield was high. The P2ClAn/Silk was partially soluble in DMSO, DMF and partially soluble in other organic solvents like methanol, acetone, etc. The P2ClAn-DBSA and P2ClAn-DBSA/Silk were soluble in DMSO, DMF and partially soluble in other organic solvents like methanol, acetone, etc.

2.2. Experimental Methods

The FT-IR spectra of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk blend in KBr were recorded by Thermo Nicolet, Avatar 370 spectrophotometer from 500 cm^{-1} to 4000 cm^{-1} . The UV-Visible spectra were recorded from 200-800 nm using Systronics double beam spectrophotometer 2201. XRD analysis of polymer and polymer blends were performed on a Bruker AXS D8

advance X-ray diffractometer using $\text{Cu-K}\alpha$, wavelength 1.5406 \AA . Thermo gravimetric analyses were carried out with a Perkin Elmer STA 6000 at the heating rate of $10^\circ\text{C} / \text{min}$ from 40°C to 750°C under inert gas atmosphere. The complex impedance measurements were carried out on pelleted specimens of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk using a Hewlett Packard model HP4284A precision LCR meter in the frequency range 20 HZ - 3 MHz and in the temperature range 295-373 K. Accordingly, the synthesized solid polymers and its blend were ground into fine powders and disc shaped pellets of 10 mm diameter and the required thickness were prepared by pressing the powder samples in an IR sample press under a pelletizing pressure of 7 ton/cm^2 to form circular pellets. The thickness of the pellet was measured using a screw gauge.

3. Results and Discussion

3.1. IR spectroscopy

The IR spectra of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk blends are shown in **Figure 1.1**, **Figure 1.2** and **Figure 1.3** respectively.

The IR characteristic peaks of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk are tabulated in **Table 1**.

Table 1. The IR peaks of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk

Peak assignment	P2ClAn-DBSA (cm^{-1})	P2ClAn-DBSA/Silk (cm^{-1})	P2ClAn/Silk (cm^{-1})
-NH stretching	3452	3286	3290
-CH stretching	2917 & 2850	2924 & 2858	2924 & 2858
Quinonoid	1588	1579	1641
Benzenoid	1495	1508	1514
-CN stretching	1294	1298	1298
B- N ⁺ H- B / Q=N ⁺ H- B	1156	1155	-
C-Cl	745	678	678
1,2,4 tri substitution	815	817	812
Amide band of silk	-	1627	1641
Helical Structure of silk	-	1035	1045

The -NH stretching peaks of polymer and blends are appearing around 3300 cm^{-1} . The asymmetric and symmetric stretching frequency of -CH present in dodecyl benzene sulphonic acid (DBSA) are observed around 2900 cm^{-1} and 2800 cm^{-1} . The characteristic peaks due to quinonoid and benzenoid rings of poly(2-chloroaniline) occur around 1600 cm^{-1} and 1500 cm^{-1} [26, 27]. The peak around 1300 cm^{-1} is due to aromatic C-N stretching vibration. The peak at 1156 cm^{-1} is due to charged species (B-N⁺H-B/Q=N⁺H-B) present in the emeraldine salt structure [26]. The bands at 900 cm^{-1}

and 810 cm^{-1} are due to $-\text{CH}$ out of plane bending vibration of 1, 2, 4 tri substituted aromatic rings. The peak at 700 cm^{-1} corresponds to the chlorine atom attached to the phenyl ring. All the above peaks confirm the formation of

poly(2-chloroaniline). The ratio of the area of benzenoid and quinonoid peak is 1:3 which indicates the formation of emeraldine salt structure.

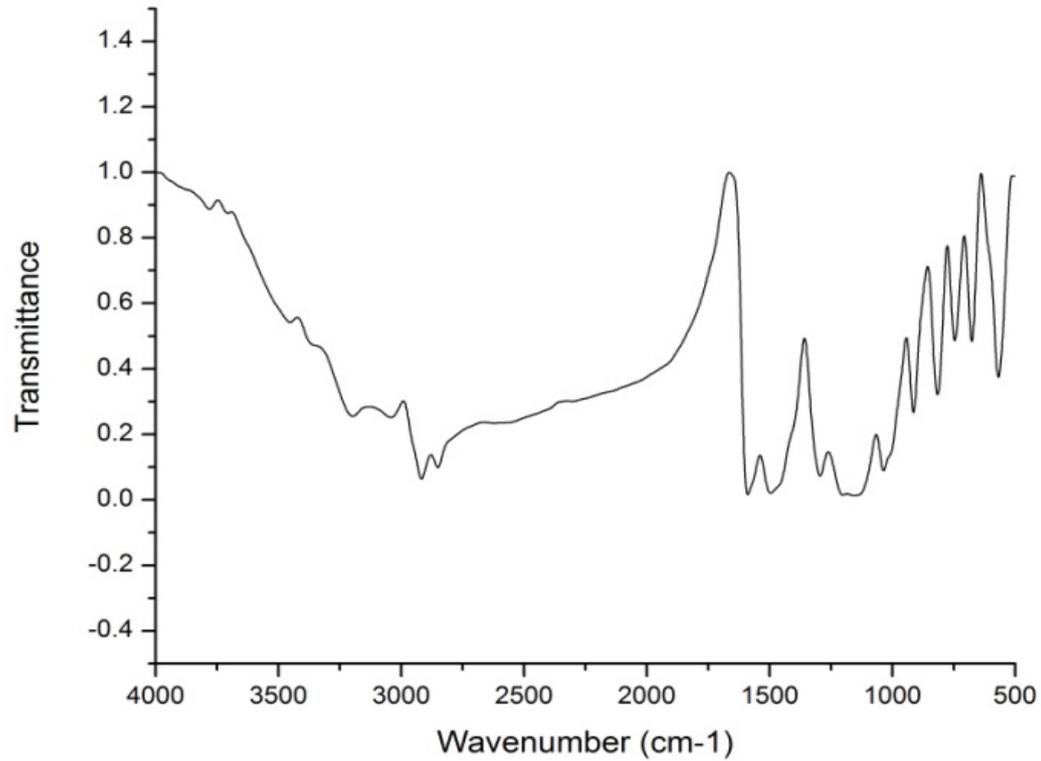


Figure 1.1. IR spectrum of P2ClAn-DBSA

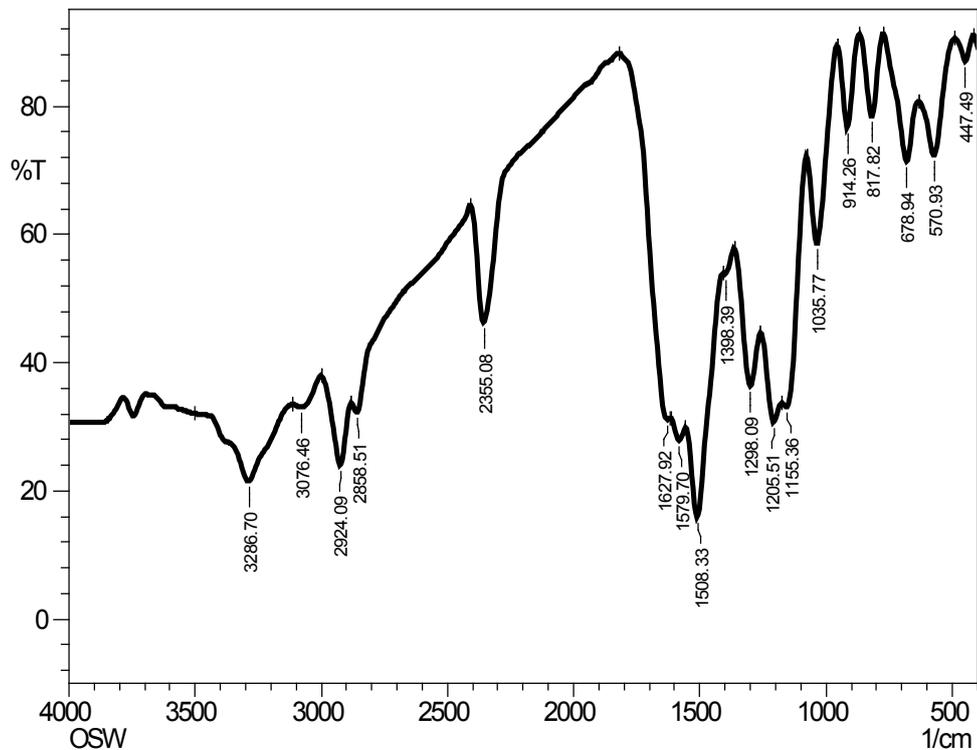


Figure 1.2. IR spectrum of P2ClAn-DBSA/Silk

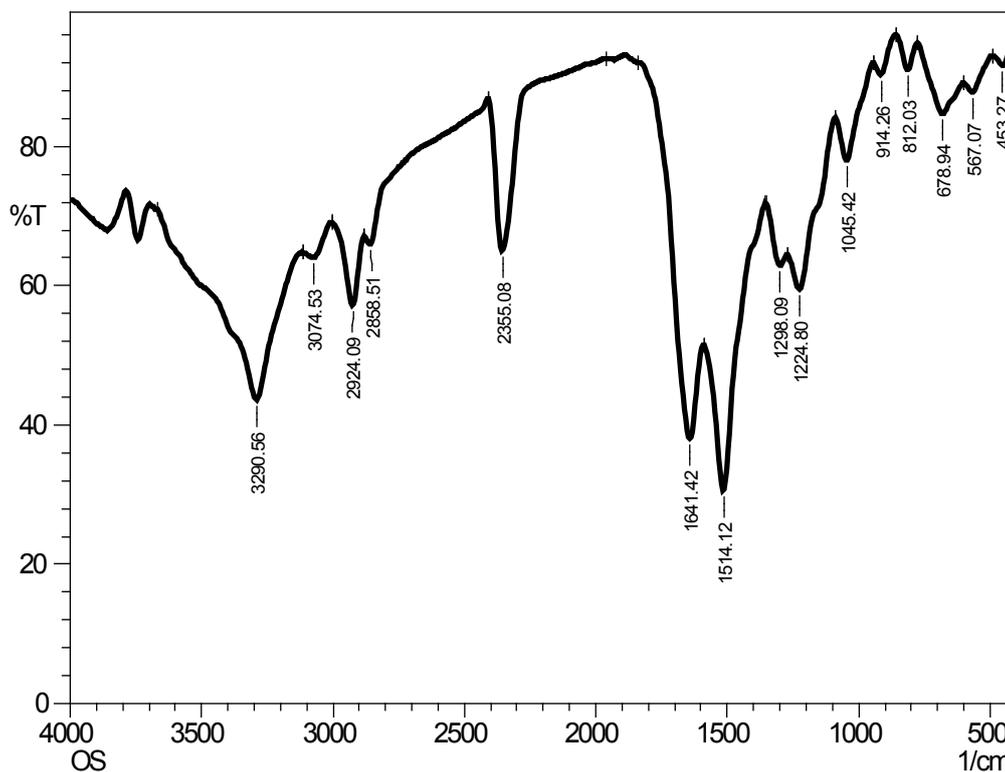


Figure 1.3. IR spectrum of P2ClAn/Silk

In addition to these peaks, the band due to the helical structure of the silk is found at 1035 cm^{-1} in P2ClAn-DBSA/Silk and at 1043 cm^{-1} in P2ClAn/Silk [28]. This band is not found in the pure polymer but present in the blends which confirms the incorporation of silk. The -NH band is shifted from 3452 cm^{-1} in the pure polymer to 3286 cm^{-1} in P2ClAn-DBSA/Silk and 3290 cm^{-1} in P2ClAn/Silk blends. The peak at 1155 cm^{-1} is due to charged species ($\text{B-N}^+\text{H-B/Q=N}^+\text{H-B}$) present in the emeraldine salt structure of P2ClAn-DBSA/Silk. The peak due to charged species is not present in the P2ClAn/Silk. Hence the P2ClAn/Silk is formed in the emeraldine base form. The bands due to -NH, benzenoid, quinonoid, amide band of silk, helical structure band of silk are all shifted to lower wavelength in the blend prepared in the presence of DBSA. The presence of DBSA favours more interaction between the polymer and the silk moiety.

3.2. UV-Visible Spectroscopy

The UV-Visible spectra of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk are shown in Figure 2.

The polymer and blends show three absorption bands. The absorption bands around 260 nm are due to the $\pi\text{-}\pi^*$ transition of benzenoid ring and the bands around 350 nm are due to the $n\text{-}\pi^*$ transition of quinonoid ring. The bands around 650 nm is due to the electron transition between the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied orbital of the quinonoid ring. In case of polymer blends the absorption bands due to the $\pi\text{-}\pi^*$ and

$n\text{-}\pi^*$ transitions are shifted to the lower wavelength than the P2ClAn-DBSA. The formation of blends reduces the π electron delocalization hence there is the shift in the absorption bands. UV-Visible spectroscopy also confirms the formation of blends.

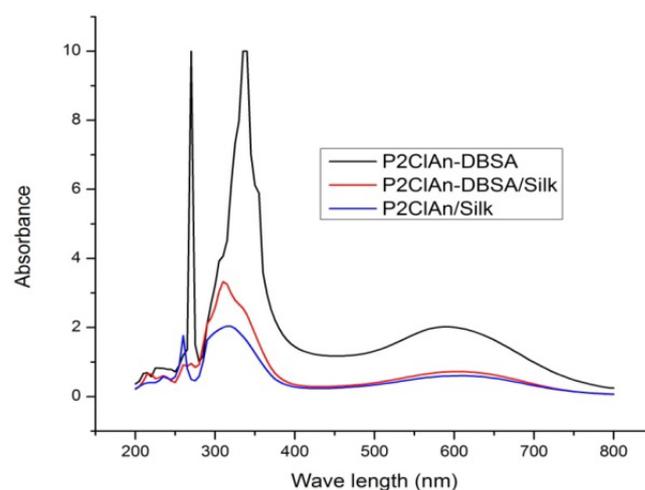


Figure 2. UV-Visible spectra of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk

When compared to the polymer and blends the absorbance intensity is high in the polymer. The presence of silk reduces the absorbance intensity.

3.3. ^1H NMR Spectroscopy

The proton NMR spectra of P2ClAn-DBSA and P2ClAn-DBSA/Silk blends are shown in Figure 3.1 and

Figure 3.2 respectively.

The peak at 2.5 ppm is due to the methyl proton present in the DMSO solvent. The singlet at around 4 ppm is due to the N-H proton. The aromatic protons of benzenoid and quinonoid can be ascribed to the peaks at 7.2 to 7.6 ppm. The multiplet at 1 ppm is due to the methyl protons present in the dodecyl benzene sulphonic acid. The NMR spectrum of P2ClAn-DBSA/Silk shows the intense N-H proton peaks around 4 ppm and intense aliphatic proton peaks around 1

ppm clearly indicating the presence of silk which increases the intensity in the blends. NMR spectrum also confirms the presence of dodecyl benzene sulphonate ion acting as a dopant.

3.4. X-Ray Diffraction Studies

The XRD pattern of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk are shown in **Figure 4**.

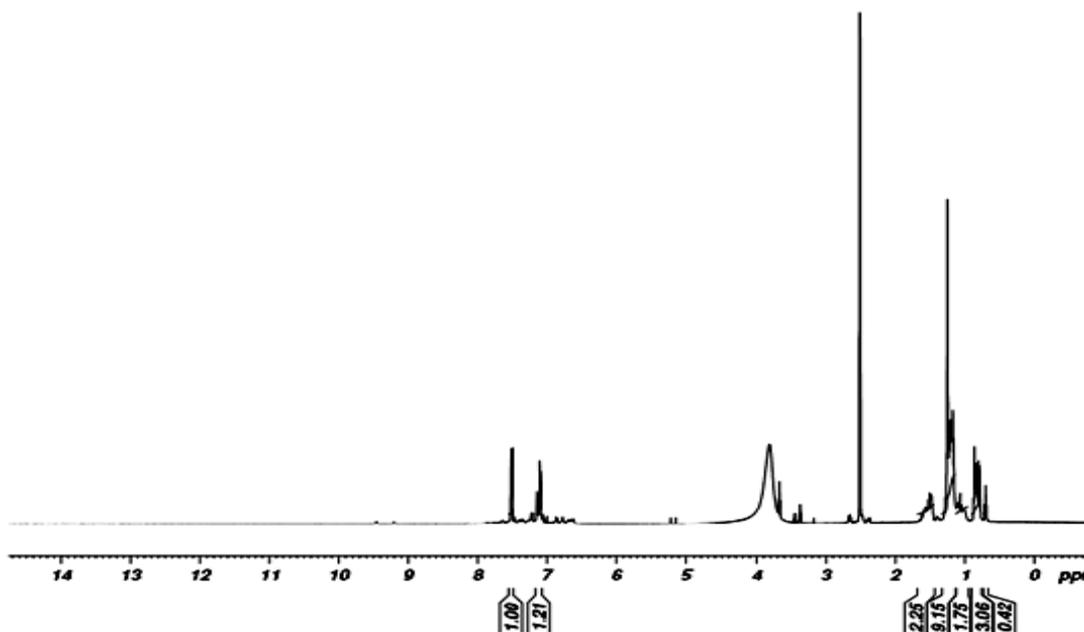


Figure 3.1. ^1H NMR spectrum of P2ClAn-DBSA

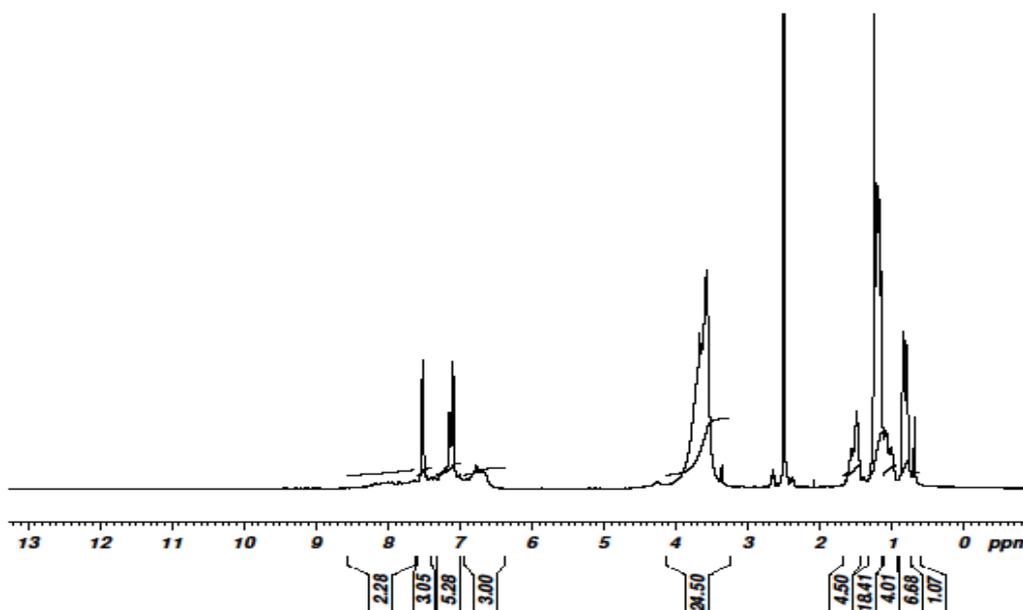


Figure 3.2. ^1H NMR spectrum of P2ClAn-DBSA/Silk

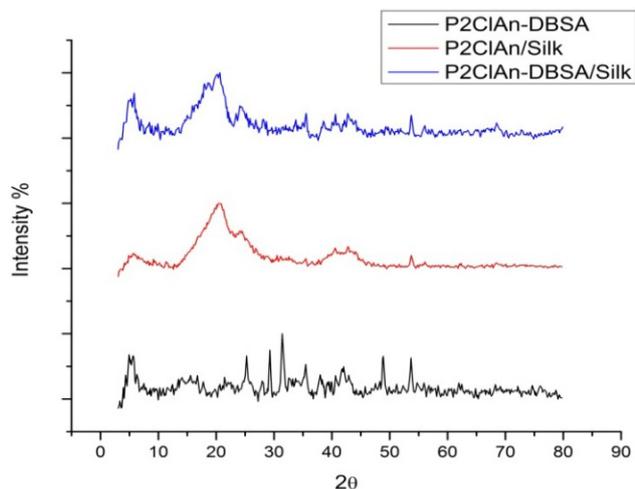


Figure 4. XRD pattern of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk

The diffraction peaks of P2ClAn-DBSA at $2\theta=26^\circ$ indicates the crystalline structure of poly(2-chloroaniline). The peak at $2\theta=26^\circ$ represents the (110) reflections of emeraldine salt [29]. Other reflections are due to DBSA which also acts as a dopant. These peaks were observed at various values of 2θ because the DBSA molecules were oriented in various directions in the polymer matrix. In case of the P2ClAn-DBSA-Silk and P2ClAn/Silk the crystalline structure of the polymer chain was influenced by the presence of silk. The resulting polymer blends shows the broad halo indicating the reduction in the crystallinity due to the formation of blend with the silk moieties.

3.5. Thermo Gravimetric Analysis

The TGA of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk are shown in **Figure 5**.

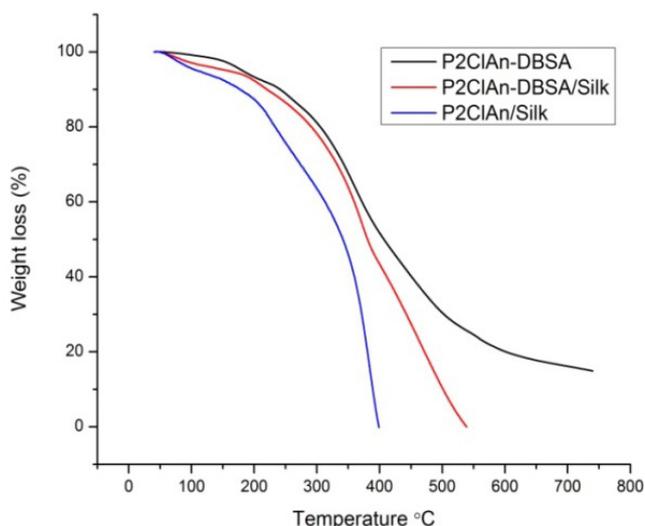


Figure 5. TGA of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk

The P2ClAn-DBSA undergoes four step weight losses. The first weight loss is due to loss of moisture, second is due to loss of HCl, third is due to loss of DBSA, fourth is due to loss of SDS and the polymer is decomposed

exothermically around 550°C . It is also noted that even after 700°C , complete decomposition has not taken place. The presence of chlorine atom has prevented the complete decomposition of the pure polymer.

When compared to the P2ClAn-DBSA the polymer blends are thermally less stable. The P2ClAn-DBSA/Silk completely decomposed around 400°C and the P2ClAn/Silk decomposed around 550°C . While comparing both the P2ClAn-DBSA/Silk and P2ClAn/Silk, the polymer blend in the absence of DBSA shows higher thermal stability, because the bulky DBSA moiety present in the polymer blend reduces the thermal stability.

3.6. Impedance Analysis

The complex impedance plots for P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk measured at various temperatures ranging from room temperature to 383K in the frequency region 50 Hz to 35 MHz are shown in **Figure 6.1**, **Figure 6.2** and **Figure 6.3** respectively.

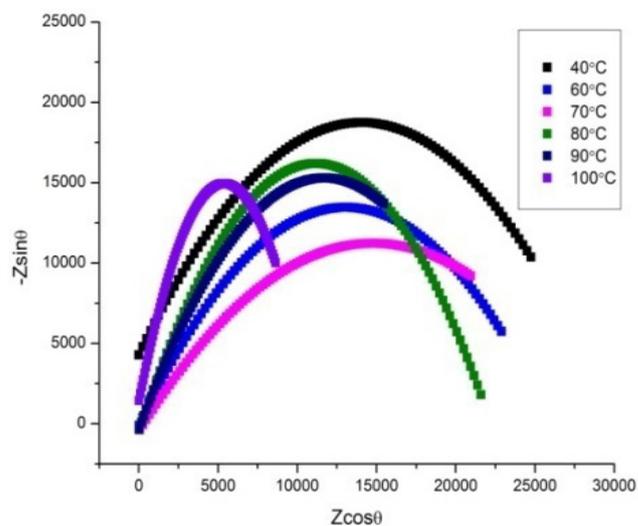


Figure 6.1. Complex impedance plot of P2ClAn-DBSA at various temperatures

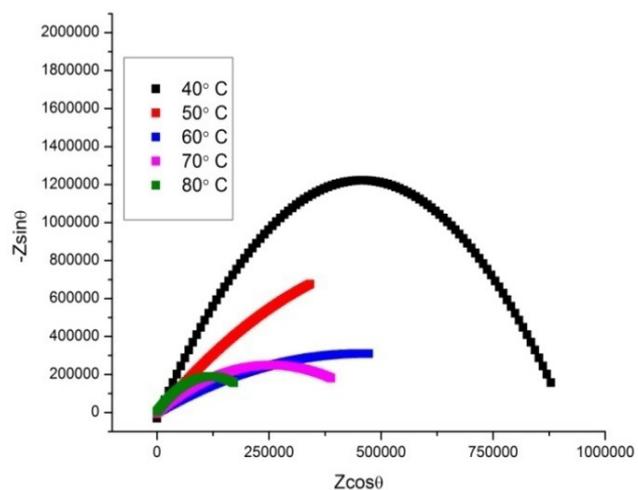


Figure 6.2. Complex impedance plot of P2ClAn-DBSA/Silk at various temperatures

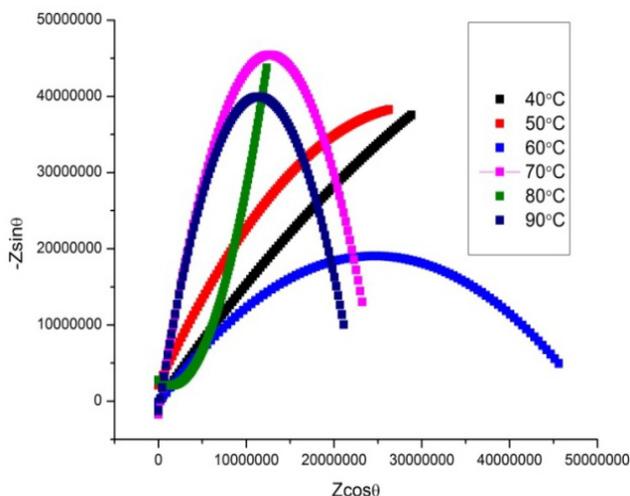


Figure 6.3. Complex impedance plot of P2ClAn/Silk at various temperatures

The point of intersection of the impedance plot on the real axis gives the bulk resistance of the polymer. The conductivity is calculated from the bulk resistance (R_b) value using the following equation.

$$\sigma = \frac{A}{Rbt}$$

where ‘A’ is the area of the pellet and ‘t’ is the thickness of the pellet.

It can be seen from the figure that as the temperature is increased, the point of intersection on the x-axis in the Cole-Cole plot is shifted towards the origin. Hence, it is evident that the bulk resistance of the polymer decreases with the increase in temperature, resulting in the enhancement of electrical conductivity at higher temperatures. The temperature dependent conductivity values for P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk reveal that the conductivity increases with temperature. The conductivity value of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk at various temperatures are tabulated in **Table 2**.

Table 2. The Electrical conductivity of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk at various temperature

Temperature	P2ClAn-DBSA (S/cm)	P2ClAn-DBSA/Silk (S/cm)	P2ClAn/Silk (S/cm)
313K	3.10×10^{-6}	1.02×10^{-7}	3.15×10^{-9}
323K	3.22×10^{-6}	1.12×10^{-7}	3.41×10^{-9}
333K	3.54×10^{-6}	1.35×10^{-7}	3.79×10^{-9}
343K	3.64×10^{-6}	1.85×10^{-7}	3.92×10^{-9}
353K	3.96×10^{-6}	3.90×10^{-7}	4.25×10^{-9}
363K	4.28×10^{-6}	-	-
373K	7.35×10^{-6}	-	-

When compared to the conductivity of polymer and blends, the P2ClAn-DBSA has higher conductivity than the

P2ClAn-DBSA/Silk and P2ClAn/Silk. The formation of blends decreases the conductivity of the polymer. While comparing the blends in the presence and absence of DBSA, the polymer blend in the presence of DBSA has higher conductivity than the blend formed in the absence of DBSA. The presence of DBSA increases the conductivity. The IR spectrum of P2ClAn-DBSA/Silk shows a peak at 1155 cm^{-1} which is due to charged species ($B-N^+H-B/Q=N^+H-B$) present in the emeraldine salt structure. The blend prepared in the presence of DBSA has the emeraldine salt form of backbone with relatively longer conjugation length due to the formation of head-to-tail junctions. This emeraldine salt structure contributes to the electrical conductivity to the blend. The peak due to charged species is not present in the P2ClAn/Silk. The product formed was also blue in colour which indicates that it polymerized in the emeraldine base form. The base form has lower conductivity than the salt form. Colloidal particles have the potential to be finely dispersed in a polymer medium due to their small size. Therefore, when colloidal particles of an intrinsically conducting polymer are used to form, fine conductive paths may generate and high conductivity levels may be realized [23]. The DBSA acts as both emulsifier and dopant, and helps the reaction occurs in the large number of loci dispersed in a continuous phase providing a larger surface area [29]. The conductivity of the P2ClAn-DBSA/Silk blend is higher than the P2ClAn/Silk due to the formation of long conjugated chains [30].

3.7. Temperature Dependent Conductivity

The variation of conductivity as the function of inverse temperature for the P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk are in the **Figure 7**. In the form of plots of $\log \sigma$ versus $1000/T$ where σ denotes the conductivity and T the absolute temperature.

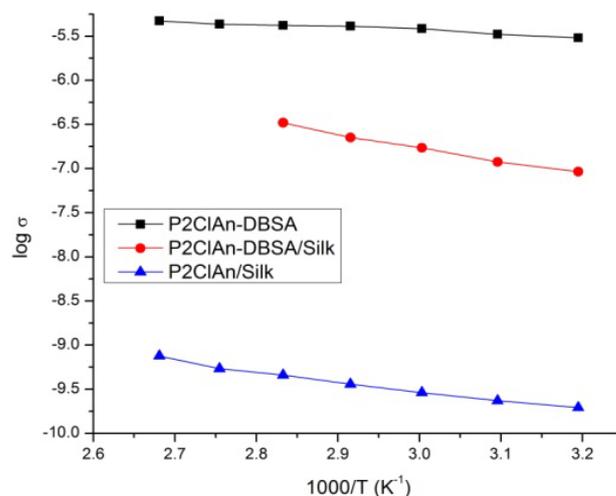


Figure 7. Arrhenius plot of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk

The straight line indicates that the conductivity increases with increasing the temperature. The temperature dependent

dc conductivity obeys the Arrhenius relation.

$$\sigma = \sigma_0 \exp\left(\frac{-Ea}{kT}\right)$$

where σ_0 is the pre-exponential factor, Ea is the activation energy and k is the Boltzmann constant. The increase in conductivity with increase in temperature suggested the electron hopping mechanism. As the temperature increases the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn favors hopping inter-chain and intra-chain ion movements and accordingly the conductivity of the polymer becomes high [31]. The activation energy was calculated from the slope of the observed linear plot drawn by the least square method and was found to be around 0.1 eV for the polymer and the blends.

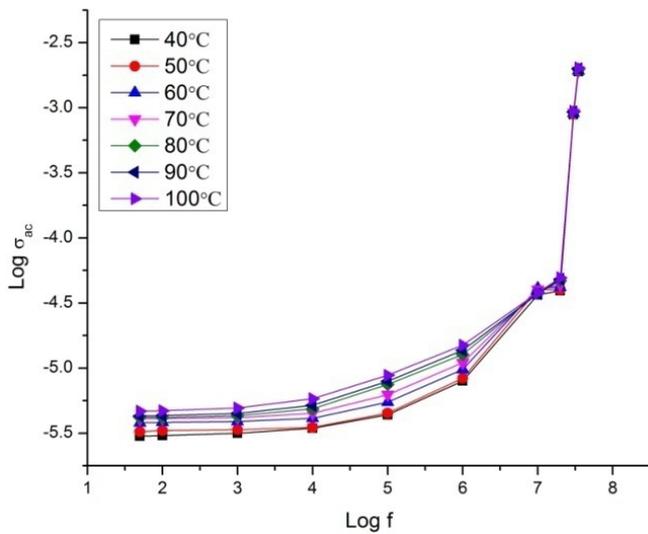


Figure 8.1. Conductance spectrum of P2ClAn-DBSA at various temperatures

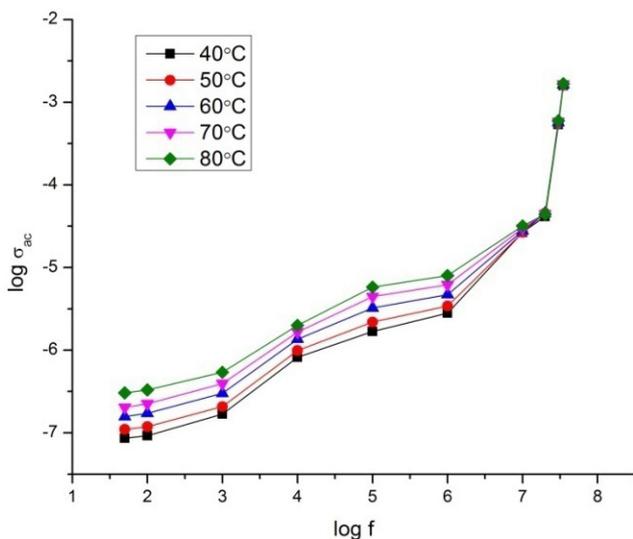


Figure 8.2. Conductance spectrum of P2ClAn-DBSA/Silk at various temperatures

3.8. Conductance Spectra

The conductance spectra show the relation between the

conductivity and the frequency. The frequency dependent AC conductivity of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk at various temperatures are shown in Figure 8.1, Figure 8.2 and Figure 8.3.

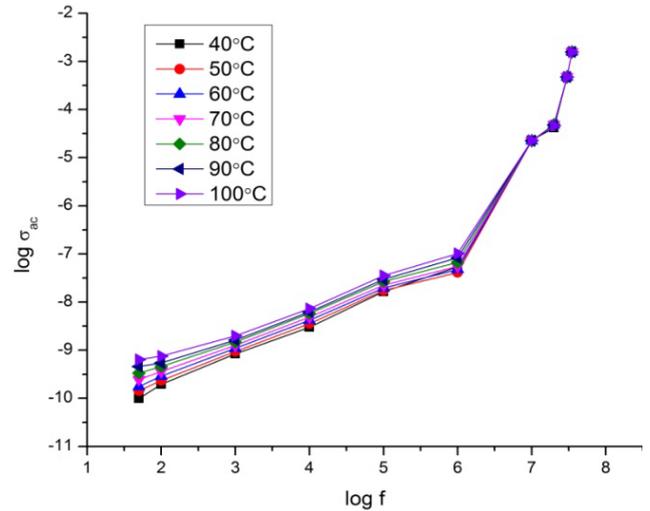


Figure 8.3. Conductance spectrum of P2ClAn/Silk at various temperatures

As the frequency decreases, more and more charge accumulation occurs at the electrode electrolyte interface, which leads to decrease in number of mobile ions and eventually to a drop in conductivity at lower frequency. In the high frequency region, the mobility of charge carriers is high and hence the conductivity increase with frequency [32].

3.9. Dielectric Properties

The dielectric properties of conducting polymers are one of the main focus points of research because of their novel technological applications. It is well established that the polymers, as dielectric materials, are excellent host matrices and also provide environmental and chemical stability [33]. The dielectric constant (ϵ') has been calculated from the measured values of capacitance using the following formula

$$\epsilon' = \frac{Cd}{\epsilon_0 A}$$

where C is the measured capacitance of the sample, d is the thickness of the sample, A is the area of the pellet, and ϵ_0 is the permittivity of free space.

Figure 9.1, Figure 9.2 and Figure 9.3 indicate the variation of dielectric constant of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk with respect to the frequency with various temperature ranges.

The dielectric constant values of P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk decreases moderately with frequency. As the frequency increases, the charge carriers migrating through the dielectric get trapped against a defect site and induce an opposite charge in its vicinity, as a result of which they slow down and the value of dielectric constant decreases moderately [34]. The dielectric constant value is higher in the case of P2ClAn-DBSA/Silk than the P2ClAn-DBSA, due to the increase in charge due to the

presence of silk. The blend prepared in the absence of DBSA shows lower dielectric constant than the blend prepared in the presence of DBSA.

3.10. Proposed Structure of the Polymer Blend

The formation of blend between the polymer and silk was confirmed by the spectroscopic techniques. Silk in its raw state consists of two main proteins, sericin and fibroin. The maximum part of the silk contains the amide group which is present in the aminoacids. The interaction may be due to the hydrogen bonding between the hydrogen present in the polymer and the oxygen present in the amide group of the silk. Figure 10 designates the schematic representation of the proposed structure.

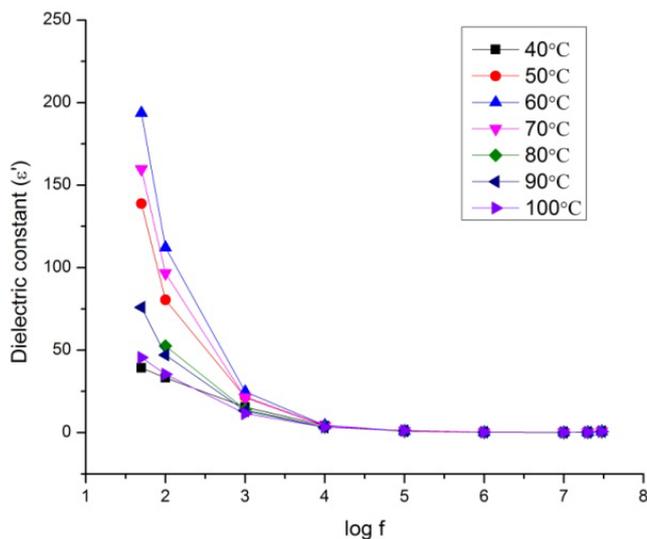


Figure 9.1. Variation of dielectric constant as a function of frequency for P2ClAn-DBSA at different temperatures

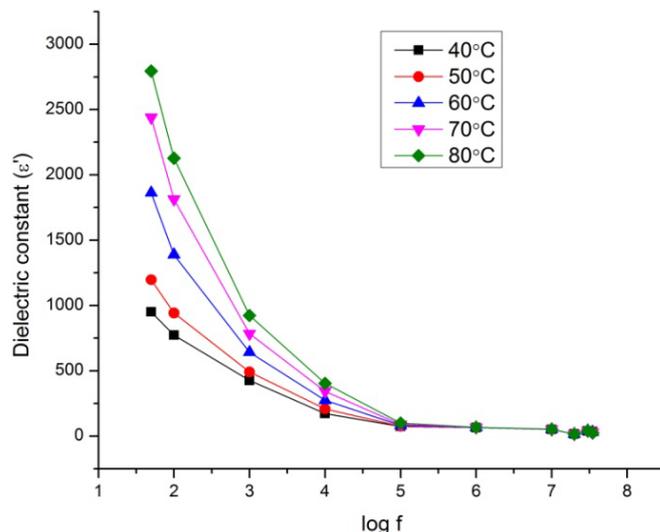


Figure 9.2. Variation of dielectric constant as a function of frequency for P2ClAn-DBSA/Silk at different temperatures

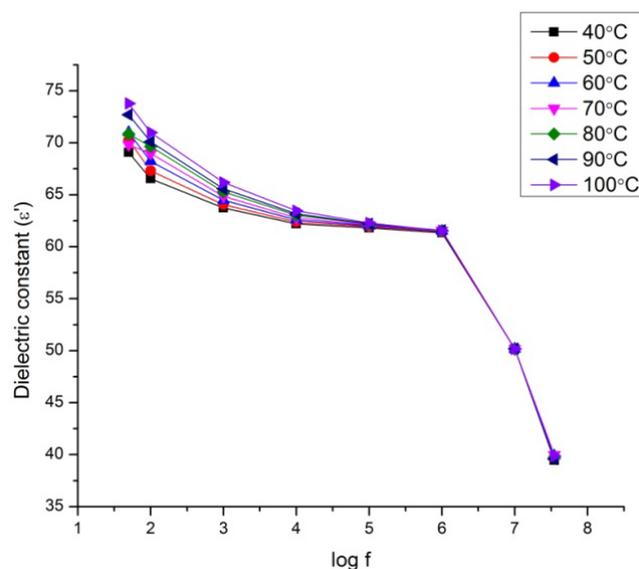


Figure 9.3. Variation of dielectric constant as a function of frequency for P2ClAn/Silk at different temperatures

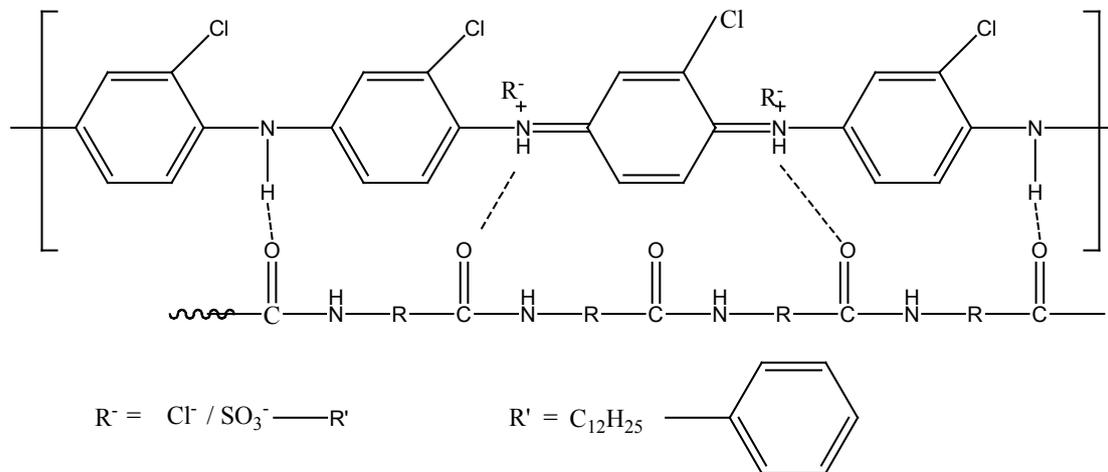


Figure 10. Schematic representation of the proposed structure

4. Conclusions

The P2ClAn-DBSA, P2ClAn-DBSA/Silk and P2ClAn/Silk were successfully synthesized by *insitu* chemical oxidative polymerization method. The synthesized polymer and its blends were characterized using IR, UV, $^1\text{H-NMR}$ and XRD. The presence of benzenoid and quinonoid rings indicates the formation of polymer and the blends. The ratio of the area of benzenoid and the quinonoid rings suggest the emeraldine salt structure. The crystallinity of the polymer is reduced by the formation of blends. The P2ClAn-DBSA shows higher conductivity than the polymer. While comparing the conductivity of the silk blends, the enhanced conductivity is observed in the presence of DBSA due to formation of emeraldine salt structure. Whereas in the absence of DBSA, the emeraldine base structure is formed and hence a low conductivity is observed. The temperature dependent DC conductivity has been obeying the Arrhenius equation. The activation energy of the polymer and blends are found to be 0.1 eV. The P2ClAn-DBSA/Silk has higher dielectric constant than P2ClAn-DBSA and P2ClAn/Silk, hence it can be used in the energy storage devices.

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