Structural, thermal and dc electrical conductivity studies in pristine Polypyrrole samples polymerized at different temperatures

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Abstract

In this work, we report the comparative study of structure, thermal and electronic conductivity properties of pristine polypyrrole (PPy) samples polymerized at different temperatures. The as-prepared samples were characterized using XRD, FTIR, SEM and DSC. The dc electrical conductivity in both PPy samples has been measured using two-probe method between the temperatures 313K and 363K. The temperature dependent dc conductivity in both the samples was found to be a thermally assisted process and is of Arrhenius type. The dc conductivity in the present PPy samples is attributed to the hopping of polarons. The observed variations in terms of structural, thermal and electronic transport studies in both the PPy samples has been ascribed to the different polymerization temperature.

Index Terms- Polypyrrole; Polymerization; dc conductivity; polaron hopping.

1.Introduction

Due to their technologically intriguing electrical and optical features, efforts to build electronically conducting doped polymers have been ongoing. Researchers from all over the world are interested in the synthesis of organic polymers with strong electrical conductivity because of their potential use in a variety of electronic devices, sensors, rechargeable batteries, and corrosion-resistant coatings [1–5]. It is now a common knowledge that extended p-electron organic polymers are efficient electrical conductors. Due to its high electrical conductivity, strong environmental stability, and promise for a wide range of applications in electronics and photonics, polypyrrole (PPy) has received a lot of interest as a conducting polymer [4- 7].

The preparation conditions, synthesis temperature, dopant, and oxidant utilized are all factors that affect the characteristics of conducting polymers made chemically. Polarons and bipolarons are taken into account as the charge carriers in polypyrrole, a non-degenerate ground state polymer [2]. To describe the charge transport mechanism in these systems over a broad temperature range, several models are put forth [8-10]. But as of now, no definite mechanism has been identified to fully explain electronic transport. This can be as a result of the wide range of methods used to prepare and process these conducting polymers.

In the present report pristine we synthesized polypyrrole samples at different temperatures namely, PP1 and PP2, and they have been and subjected to characterization tools viz., XRD, FTIR, DSC, and SEM and, temperature

dependent dc electrical conductivity in both the samples has been studied. The effect of temperature on polymerization is attempted to understand on the structural, thermal and electrical conductivity properties of Polypyrrole.

2. Material and Method of synthesis

The analytical grade (AR) acetone, ammonium persulphate (APS) and pyrrole have been procured from Sigma Aldrich Chemicals in Bangalore, India. Chemical oxidation technique was used to synthesize the polypyrrole. Ammonium per sulphate (APS), an oxidizing agent, is administered at 1:5 ratios. To achieve homogeneity at room temperature, 10 mL of pyrrole is dissolved in 500 mL of distilled water and placed on a magnetic stirrer. The ice tray, which is fixed on a magnetic stirrer, is also placed on top of the beaker containing the 0.3 M pyrrole solution. With the use of a burette, 0.06 M ammonium persulfate solution was continually added drop by drop to the 0.3 M pyrrole solution above. The reaction was kept at 273K for 6 hours while being stirred continuously. The precipitated polypyrrole was filtered, dried in a muffle furnace at 100°C, and then dried in a hot air oven. In terms of weight percent, the yield of the polypyrrole was 3.2 gm [11]. The produced polypyrrole was labelled as PP1.Similarly, at 283K, using the same chemicals and procedure another batch of polypyrrole was prepared and labelled as PP2. The yield for PP2 was about 2.25 gm. To get rid of impurities, if any, both PP1 and PP2 powder samples were once again filtered out under vacuum and repeatedly washed with double-distilled water. At room temperature, the Polypyrrole samples were dried for two days.

2.1. Preparation of pellets

In an agate motor, the powder of Pristine Polypyrrole samples PP1 & PP2 were crushed and thoroughly mixed for two hours in presence of acetone medium. The powdered sample is put through an 80 MPa hydraulic press to produce pellets, which are then placed in a furnace for an hour. The pellets had a flat surface and were about 2mm thick and 10mm in diameter. To establish the electrode leads, silver paste was applied on two major surfaces of the samples.

3.Characterization

The structural investigations of Pristine PP1 and PP2 have been examined using powder X-ray diffraction (X-ray diffractometer – Make: Zeiss, Germany). The XRD patterns were captured using Cu-kα radiation with wavelength 1.5418 A^0 and in the 2θ range of 10° to 80° [12,13].

Transition mode FTIR spectra were captured for both PP1 and PP2 samples [14,15]. For this, a FTIR-8400S (Make: Shimadzu Tokyo, Japan), 32-bit high performance FTIR software, paired with the IR solution was used. At room temperature, FTIR spectra for both PP1 and PP2 with wave numbers ranging from 4000 cm^{-1} to 400 cm^{-1} were captured in KBr medium.

DSC studies were carried out using DSC Standard Cell FC DSC Q20 V24.10 Build 122. Initial scan was taken from 50°C to 100°C to remove the thermal history effects, and then cooled to 50°C under nitrogen atmosphere. The samples were heated with a heating rate of 10°C/min, in the temperature range from 300 ºC to 400 ºC [16].

The DC conductivity studies of samples were done using Two Probe Method using TPX-200 (Make: SES instruments, Roorkee-Uttarakhand,India) as a function of Temperature in the range 313K to 363K.

4.Results and Discussion

4.1 X-Ray diffraction

The powder form of PP1 and PP2 is taken to study X-ray diffraction using Cu kα radiation of wavelength λ = 1.5418 A° and in the range from 10° to 80°. The XRD spectrum (Fig.4.1) has exhibited a broad hump [17,18] at around 15.14° and 30.99° for PP1 and similar broad hump from 16.34° to 30.67° is observed for PP2. No sharp peaks have been observed in both PP1 and PP2. This shows that the sample is non-crystalline in nature [17]. However, the observed broad hump is attributed to the low angle scattering and also confirms that the sample is of amorphous nature.

Average chain separation(S)

The broad hump is characteristic of amorphous nature of PP1 and PP2. The average chain separation for both PP1 and PP2 is calculated from the following relation [18-22].

$$S = \frac{5\lambda}{8 \, Sin\theta} \qquad (4.1)$$

Where S is the polymer chain separation, λ is the X-ray wavelength and θ is the diffraction angle at the maximum intensity. The polymer separation for PP1 is 4.4 A° and for PP2 is 4.5 A °. The average chain separation (R) was found to be 4.45 A° for PP.

The average crystal size (D)

The average crystallite size from a peak at 24.45˚ for PPy is estimated by using the Scherrer's formula [23].

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad (4.2)$$

Where D is the crystallite size, K is the shape factor, which can be assigned a value of 0.89 or 0.9 if the shape is unknown, θ is the diffraction angle at maximum peak intensity, and β is the full width at half maximum of diffraction angle in radians. Using the above equation (4.2) the average crystallite size of PP1 and PP2 has been estimated to be 51.37 nm and 46.23 nm, respectively. This indicates that both PP1 and PP2 samples have different crystalline sizes.
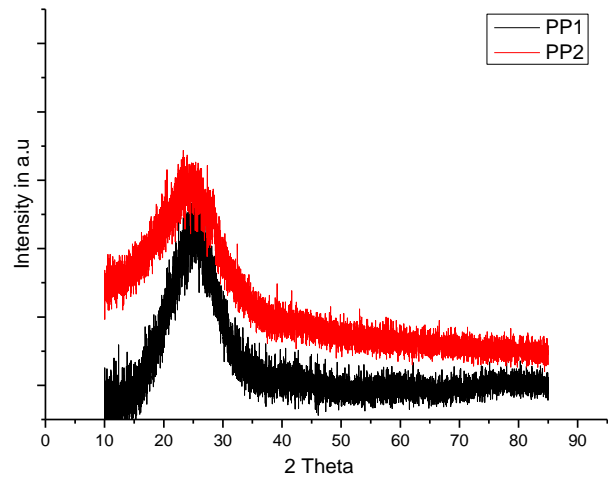

Fig.4.1 X-Ray Diffraction Patterns of PP1 and PP2

Dislocation density (δ)

Dislocation density is the length of dislocation lines per unit volume of the crystal is determined by the following (4.3) equation [24],

$$\delta = \frac{1}{D^2} \qquad (4.3)$$

The dislocation density of PP1 and PP2 is found to be $0.3 \times 10^{-3} (nm)^{-2}$ and $0.46 \times 10^{-3} (nm)^{-2}$

Inter-planar spacing(d)

The interplanar spacing for both PP1 and PP2 has been calculated using the Bragg's law [24,25],

$$2d \, sin\theta = n \, \lambda \qquad (3.1)$$

Where n is an integer, λ is the wavelength of the incident X-radiation, which is taken as 1.54 Å in the present study, d is the distance between atomic planes, 2θ is the diffraction

angle in degree.The inter-planar spacing for the PP1 and PP2 is 35nm and 36.19 nm .

Degree crystallinity (X_c%)

The degree crystallinity (X_c%)of the Polypyrrole were studied by using X-ray diffraction (XRD) θ–2θ scans. The studies for XRD is done from 10°–85°, broad peak found in the sample and measured for PP1 and PP2. The full width half maximum (FWHM) values were measured by fitting a Gaussian function to the peaks using Origin8.5 software. Using Eq.(4.4) the percentage of crystallinity is determined [25].

$$X_C = \frac{A_C}{A_C + A_A} \times 100 \qquad (4.4)$$

The Crystallinity of the PP1and PP2 is measured by taking total area of amorphous and area of the peak. The degree of crystallinity is drawn in Table 4.1.

As comparative study of PP1 and PP2 is done and observed that there is no much variation in the inter planar spacing (d), inter chain separation and degree of crystallinity of Polypyrrole.

4.2 FTIR characteristic

The FTIR spectra for PP1 and PP2 is depicted in Figs 4.2a and 4.2b, respectively

From, Fig.4.2a, the characteristic peaks for pristine PP1 can be observed at 3387cm^{-1},1597cm^{-1}, 1409 cm^{-1}, 1330 cm^{-1}, 945 cm^{-1},842 cm^{-1} and 468 cm^{-1}. Similarly, the spectra in Fig.4.2b shows the characteristic peaks for PP2 at 3199 cm^{-1}, 2225 cm^{-1},1592 cm^{-1} , 1293 cm^{-1} and 605 cm^{-1}. The peak of PP1 at 3387 cm^{-1} and 3199 cm^{-1} are assigned to the N-H stretching vibrations in pyrrole ring. The peak at 1597cm^{-1} in Fig.4.2a, and 1592 cm^{-1} in Fig.4.2b, are respectively attributed to the fundamental vibrations of polypyrrole ring of PP1 and PP2. This is in conformity with the

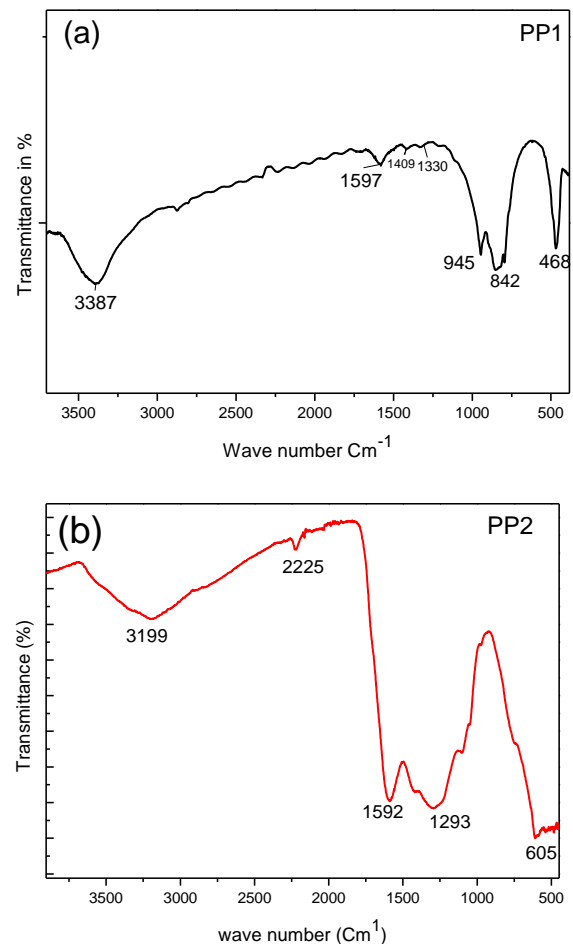number of reports published in literature [26-29].

Fig.4.2 FTIR spectra of (a) PP1 and (b) PP2

Sample	2θ(A°)	d(nm)	S (A°)	Degree of Crystallinity($X_{c)}$)
PPy 1	25.3	35	4.4	20.38
PPy 2	24.69	36.19	4.5	19.47

Table 4.1.Values of the degree of crystallinity (X_c), angular peak position (2θ), interplanar spacing (d) and inter-chain separation (S) of PP1 and PP2 .

4.3 Scanning electron microscope

The polypyrrole showing the grains grown one on another forming a chain like structure.

The grains showing nearly spherical shapes. The figs 4.3a and 4.3b respectively shows the SEM photographs for PP1 and PP2. Both the figures describe that the monomers are chained to form polymer structure. The observed individual

grains are nearly spherical in nature and have a close packing [30,31]. A granular morphology of the PP1 and PP2 polypyrrole particle structures is measured from SEM

and found to be of the order of 200 nm and 220nm. However, the PP2 seems to be little more orderly arranged compared to PP1 and PP2 and has a cauliflower like structure.
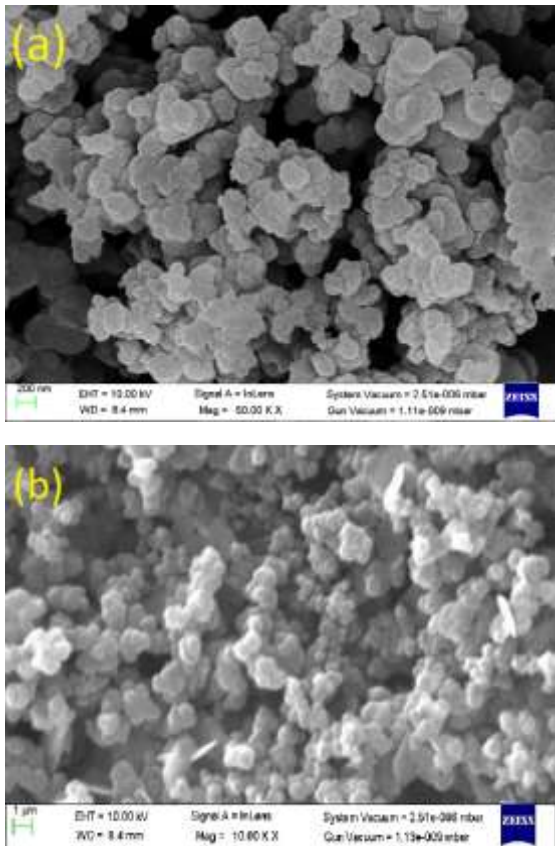

Fig.4.3 Scanning Electron Micrographs for (a) PP1 and (b) PP2

4.4 Differential scanning calorimeter

Figs 4.5a and 4.5b exhibit the DSC thermographs of PP1 and PP2

respectively. In both the thermographs, a steep endothermic dip, indicating the glass transition temperature, T_g, is observed respectively at 90.1^0C and 98.9^0C for PP1 and PP2. This is comparable with the T_g values reported for pristine PPy [32,33]. However, different glass transition temperatures for undoped PPy have been reported in literature depending on the polymerization conditions used [34,35]. Figs 4.5a and 4.5b exhibit endothermic peak at 300^0C for both PP1 and PP2, which may be attributed to the melting of PPy chain and to the loss of moisture [36-39]. The endothermic peak observed around 410^oC for PP1 and 380^oC for PP2 is related to crystallization temperature (T_c) [40].
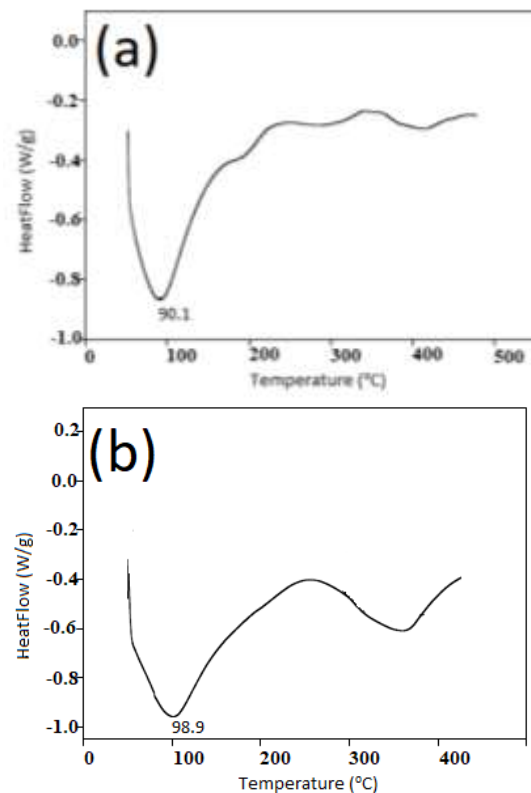

Fig 4.4 DSC thermographs for (a) PP1 and (b) PP2

4.5 DC conductivity

The temperature dependence of electrical conductivity was studied in the temperature range of 313K–363 K. The variation of dc conductivity as a function of temperature is shown in Fig. 4.5 for sample PP1 and PP2. In both the samples, the dc conductivity was found to increase with increase in the temperature indicating that the conductivity is a thermally assisted phenomenon. Within the studied range of temperature, the dc conductivity for both PP1 and PP2 was found to vary from 1×10^{-7} Ohm^{-1}m^{-1} to 8×10^{-7} Ohm^{-1}m^{-1}.
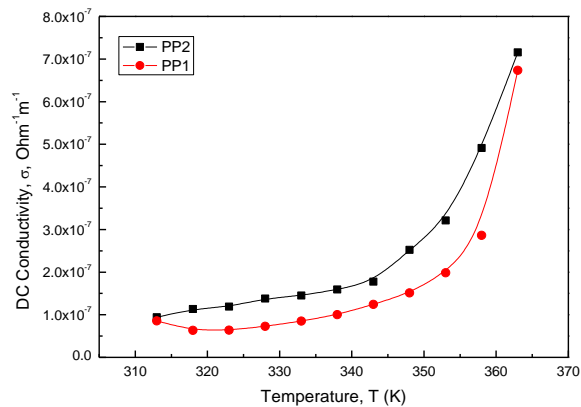

Fig.4.5 Dc conductivity, σ, of PP1 and PP2 samples as a function of Temperature, T. Lines are drawn as a guide to the eye.

The measured dc conductivity was subjected to Arrhenius equation in order to understand the conduction mechanism in the present polypyrrole samples. According to Arrhenius equation, the temperature dependent conductivity can be expressed as [40,41],

$$\sigma(T) = \sigma_o \, exp^{\left(-E_a/k_B T\right)} \qquad (4.5)$$

Where σ is the conductivity of the composites, σ_o is the pre-exponential factor and is constant, E_a is the activation energy, k_B is the Boltzmann's Constant, T is the absolute temperature. A graph of lnσ versus 1000/T

was plotted. The curves were found to be linear in high temperature regime. The general behaviour of the curves is similar to that of the reported for similar polymer systems [42,43]. As per equation (4.5), the least square linear fittings were made to the plots in the high temperature region. The best fits to the $ln(\sigma T)$ versus $(1/T)$ plots gave the $r^2 = 0.991$ to 0.998 (r= correlation coefficient). The slope of linear fits is determined from the plots and activation energies, E_a, were calculated. The activation energies, E_a, were estimated to be 1.95eV for PP1 and 1.63eV for PP2.

The variation of temperature dependent dc conductivity in the present samples is ascribed to presence of conjugated single and double bonds along the polymeric chain [44]. Both single and double bonds include a localized σ bond, which forms a strong chemical bond. In addition to this, each double bond also consists of a weak localized π-bond.
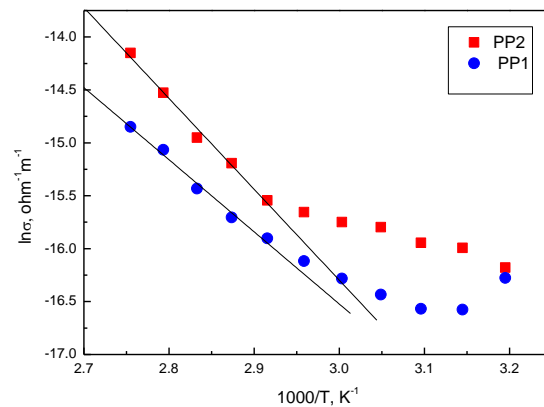

Fig. 4.6 Plots of lnσ vs 1000/T for PP1 and PP2 samples. Lines are least square fits to the curves.

The transport properties of the conducting polymers depend on their synthetic routes and can have different ranges of conductivities which is ascertained due to the hopping of polarons [45]. In the present PP1 and PP2 samples, the observed dc electrical conductivity is attributed to the hopping of

delocalized electrons and also is a thermally activated process [44-48].

4.6 Conclusion

Pristine polypyrrole samples polymerized at different temperatures labelled as PP1 and PP2 have been synthesized using chemical oxidation method. The samples were subjected to various characterization tools and the dc electrical conductivity has been measured as a function of temperature between 313K and 363K. The results PP1 have been compared with that of PP2. The estimated values of average chain separation, average crystal size, dislocation density, interplanar spacing and degree of crystallinity for both PP1 and PP2 were comparable. The FTIR and SEM results for both the samples were comparable. The measured dc conductivity was found to be slightly higher for PP2 compared to that of PP1. The measured dc conductivity was found to be a thermally assisted one. The temperature dependence of dc electronic conductivity in both the samples was explained using Arrhenius equation. The variation in the physical properties of both PP1 and PP2 has been attributed to the synthesis of these samples being at different temperature.

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