Polypyrrole has drawn a lot of interest due to its high thermal and environmental stability in addition to high electrical conductivity. The present work highlights the enhanced crystallinity of polypyrrole films prepared from the redoped sample solution. Initially hydrochloric acid (HCl) doped polypyrrole was prepared by chemical oxidative polymerization of pyrrole using ammonium peroxidisulphate (APS) as oxidant. The doped polypyrrole was dedoped using ammonia solution and then redoped with camphor sulphonic acid (CSA). Films were coated on ultrasonically cleaned glass substrates from the redoped sample solution in meta-cresol. The enhanced crystallinity of the polypyrrole films has been established from X-ray diffraction studies. The results of Raman spectroscopy and Differential scanning calorimetry (DSC) studies, and Thermo gravimetric analysis (TGA) of the samples support the enhancement in crystallinity. Percentage crystallinity of the samples has also been estimated from XRD and DSC data. The present work is significant, since crystallinity of films is an important parameter for selecting polymers for specific applications.
7.1 Introduction

Conducting polymers have attracted a great deal of attention in the last few decades because of their unusual and tunable electrical and optical properties. The electrically conducting polymers are capable of electrical charge transfer to the same extent as an electrical conductor or a semiconductor. Due to their fascinating electrical and optical properties, conducting polymers have played indispensable roles in specialized industrial applications in spite of their short history. However, the major aspects useful for most applications are not the metal or semiconductor like electrical properties alone, but the combination of electrical conductivity and polymeric properties such as flexibility, low density and ease of structural modification that suffice for many commercial applications. The possibility of synthesizing materials capable of simultaneously presenting the properties of organic polymers and those of crystalline semiconductors has attracted the interest and efforts of both academic and industrial researchers.

Of all known conducting polymers, polypyrrole (PPy) is one of the most extensively studied polymers, since monomer pyrrole can be easily oxidized for polymerization, is commercially available and possesses good redox properties. Polypyrrole is frequently used in commercial applications, due to the long-term stability of its electrical conductivity and the possibility of forming copolymers or composites with optimal mechanical properties. In the last few years, investigations have centered mainly on the improvement of the physical properties of polypyrrole, such as processability, stability or mechanical integrity. Several techniques including blend or composite formation are being optimized
in order to prepare processable materials which can be used and processed like common polymers. The possibilities of improving the physical properties of PPy as well as its good intrinsic properties make this material a serious candidate for use in specific technological applications such as batteries, super capacitors, electrochemical (bio) sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference shielding devices, anti-static coatings and drug delivery systems [1,2]. Polypyrrole coatings have excellent thermal stability and are good for use in carbon composites [3] Chemical and electrochemical polymerization techniques are the two widely used methods to synthesize polypyrrole. In the chemical polymerization process, monomer pyrrole is oxidized by oxidizing agents or catalysts in the presence of suitable dopants, to produce the conducting form of the polymer. The advantage of chemical synthesis is that it offers mass production at reasonable costs. This is often difficult to achieve with electrochemical methods. On the other hand, electrochemical methods offer the possibilities of synthesizing polymers with better conducting properties. Recent years have witnessed the development of improved synthesis and processing routes for the preparation of more ordered and homogeneous polypyrrole samples, both in bulk and thin film forms [4-6].

7.2 Semi crystalline polymers

Polymer crystallinity is one of the important properties of all polymers since crystallinity influences many of the polymer characteristics, including mechanical strength, opacity and thermal properties. Crystallinity measurement provides valuable information for both materials research and quality control in material processing [7-12].
Polymers exist both in crystalline and amorphous forms. The polymer chains are not aligned with each other over their whole length, and the alignment is limited only to small crystallite regions [13]. Such polymers are the so-called semi-crystalline polymers having both crystalline and amorphous regions. Semi-crystalline polymers are interesting because they combine the strength of crystalline polymers with the flexibility of amorphous ones. They are generally strong with the ability to bend without breaking. As the polymer crystallinity increases, its level of secondary bonding also increases. This in turn increases the stiffness (elastic modulus) and strength of the polymer. On the other hand, ductility declines as crystallinity increases. Factors affecting crystallinity are

- Linearity of the polymer chain
- Presence of more than one monomer type
- Arrangement of side groups on the backbone
- Processing conditions

Crystallinity in polymers is a measure of the extent of the crystalline regions with respect to amorphous ones. The percentage crystallinity is an important parameter, which influences the optical, thermal, and mechanical properties of a polymer. DSC is an advantageous technique, which provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer. XRD technique is also used to establish the nature of the polymer and estimate the extent of crystallinity present in the polymer.
This chapter deals with a detailed study of the crystallinity in polypyrrole film samples, prepared from the redoped PPy solution in meta-cresol. A quantitative assessment of the crystallinity in these films has been carried out using DSC and XRD analysis. The Raman spectroscopic analysis supports the conclusions drawn from DSC and XRD studies.

7.3 Synthesis of PPy samples

Polypyrrole was prepared by oxidative polymerization of pyrrole using ammonium peroxidisulphate as oxidant. Freshly distilled pyrrole was dissolved in the dopant acid (HCl) solution. Ammonium peroxidisulphate (APS) dissolved in water was added drop by drop to it with continuous stirring for 4-5 hours. The polymerization was carried out at 0°C temperature with an oxidant /monomer molar ratio of 1:1. The black precipitate obtained was filtered, washed and dried under vacuum for 12 hours. The HCl doped polypyrrole powder was reduced by ammonia solution and the resulting precipitate was filtered, washed and dried to obtain the dedoped polypyrrole powder. The dedoped PPy powder was mixed with CSA in a mortar for redoping. This redoped sample dissolved in meta-cresol (m-cresol) was used to prepare films on glass substrates by solution casting.

7.4 Characterization of PPy samples
7.4.1 XRD analysis

The X-ray diffraction (XRD) studies of the samples were done on a Rigaku X-ray Diffractometer with Cu – Ka (1.5418 Å) radiation operating at 30 kV and 20 mA. Scanning was carried out in the 20 range
from 0 to 60° at a scan speed of 2° per minute. The XRD patterns of the PPy samples are shown in figure 7.1. The CSA redoped PPy film shows exceptionally higher crystallinity compared to the HCl doped and dedoped samples. The peaks in HCl doped PPy and dedoped PPy (Figure 7.1 (a) and (b)) are mostly of amorphous nature. However, the peaks appear with excellent sharpness in the XRD pattern of CSA redoped polypyrrole film as shown in figure 7.1(c).

Figure 7.1: XRD patterns of (a) HCl doped PPy (b) Dedoped PPy and (c) CSA redoped PPy film prepared from meta-cresol solution.

In figure 7.1(c), the prominent peaks observed at about 10.5°, 21° and 32° correspond to the d spacing values 8.377, 4.208 and 2.809 Å respectively. These d values correspond to the interlayer distance from
pyrrole to pyrrole ring, from pyrrole ring to the camphor sulphonate dopant, and the face-to-face stacking distance, respectively [14, 15]. The d-value of 16.7 Å corresponding to the peak at 5.34° is an indication of the order closely associated with the dopant ions between the polymer chains. The peaks are indexed by calculating hkl indices as in the case of crystalline samples. The hkl indices suggest a simple cubic structure, and the dimension of the fundamental repeating unit is found to be 1.67 nm (Table 7.1).

<table>
<thead>
<tr>
<th>hkl planes</th>
<th>d(nm)</th>
<th>a(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.67341</td>
<td>1.67341</td>
</tr>
<tr>
<td>110</td>
<td>1.17775</td>
<td>1.6656</td>
</tr>
<tr>
<td>200</td>
<td>0.83767</td>
<td>1.67534</td>
</tr>
<tr>
<td>320</td>
<td>0.46509</td>
<td>1.6769</td>
</tr>
<tr>
<td>400</td>
<td>0.42082</td>
<td>1.6832</td>
</tr>
<tr>
<td>531</td>
<td>0.28096</td>
<td>1.66218</td>
</tr>
</tbody>
</table>

The XRD pattern of CSA redoped polypyrrole film exhibits extraordinarily high crystallinity, which has not been reported earlier. One of the reasons for the excellent crystallinity of the CSA redoped film can be the secondary doping effect of the solvent meta-cresol. Other reasons for the enhanced crystallinity can be (a) the effect of controlled doping (redoping using one molar CSA) by which more crystallite regions are formed and (b) ultrasonication. The enhanced crystallinity in turn improves the electrical conductivity of the sample also [16].
Majority of polymers diffracts X-rays like any crystalline substance, but behaves like amorphous materials giving very broad and diffuse XRD patterns. Unlike simple inorganic compounds, polymers do not have a perfectly ordered crystal lattice formation and are not fully crystalline. In fact, they contain both crystalline and amorphous regions, and consequently the X-ray diffraction spectra are found to be a mixture of sharp as well as diffused patterns. The sharp peaks correspond to crystalline and ordered regions and the diffuse and broad ones refer to amorphous regions. Crystallinity of a polymer is expressed in terms of the crystalline fraction of the sample [17]. The crystallinity is calculated by separating intensities due to amorphous and crystalline phases of the diffracted graphs. The total area of the diffracted pattern is divided into crystalline ($A_c$) and amorphous ($A_a$) components. Percentage crystallinity ($X_c \%$) is estimated as the ratio of crystalline area to total area [13].

$$X_c \% = \frac{A_c}{(A_c + A_a)} . 100 \%$$  \hspace{1cm} (7.1)

The percentage crystallinity values obtained for the PPy samples are given in table 7.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_c$</th>
<th>$A_a$</th>
<th>$X_c %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl doped PPy (bulk)</td>
<td>2092.35</td>
<td>3136.67</td>
<td>40</td>
</tr>
<tr>
<td>Dedoped PPy (bulk)</td>
<td>1548.65</td>
<td>4197.35</td>
<td>27</td>
</tr>
<tr>
<td>CSA redoped PPy film</td>
<td>2766.7</td>
<td>1555.8</td>
<td>64</td>
</tr>
</tbody>
</table>

Numerous X-ray diffraction studies have been conducted on PPy films to characterize the degree of molecular order. It has been reported that the degree of alignment increases as the applied potential and
temperature of polymerization decreases in electrochemical polymerization of pyrrole [18]. The mechanical properties of PPy films have been observed to improve under such conditions. Thus, there may be some correlation between molecular order and the mechanical properties of PPy films. A greater degree of order has been observed when the films are mechanically stretched [19, 20]. The stretching is believed to orient the molecular chains in the direction of the applied stress. In the present work, about 64% crystallinity has been observed in chemically synthesized, CSA redoped films of PPy from m-cresol, without being mechanically stretched or subjected to any other types of strain.

7.4.2 Atomic force microscopy (AFM) studies

The AFM images of the CSA redoped PPy films were obtained with Park XE-100 Atomic Force Microscope. The AFM image is shown in figure 7.2. Some extent of ordering of polymer chains in PPy film is seen in the AFM picture.

![AFM picture of polypyrrole film](image)

Figure 7.2: AFM picture of polypyrrole film
7.4.3 FT-IR analysis

Fourier transform infrared (FT-IR) spectra of the samples were obtained with AVTAR 370 DTGS FT-IR spectrophotometer in the wave number range 500 – 4000 cm⁻¹. FT-IR investigations have been carried out to confirm the polymerization of the monomer and redoping of CSA during the synthesis process.

The FT-IR spectrum of HCl doped PPy, shown in Figure 7.3(a), indicates the typical characteristics of PPy, which are consistent with the reported data [21-23]. The bands at 1555 and 1474 cm⁻¹ correspond to the stretching vibrations of C=C and C-N of PPy respectively. The band at 1198 cm⁻¹ corresponds to the breathing vibration of the pyrrole ring. The band of C-H in-plane deformation vibration is located around 1043 cm⁻¹ while the band of C-H out-of-plane deformation vibration is found at 921 cm⁻¹. The strong absorption at 3400 cm⁻¹ is due to N-H stretching and the characteristic absorption band of PPy at 1126 cm⁻¹ is due to C-C stretching. [24-27]

![Figure 7.3: FT IR spectra of (a) HCl doped PPy and (b) CSA redoped PPy](image-url)
Figure 7.3(b) shows the FT-IR spectrum of CSA redoped PPy sample. The bands in the range 500-700 cm\(^{-1}\) correspond to S-O and C-S stretching modes, which indicate the presence of sulfonic acid groups in the polymer backbone [27]. The absorption bands at about 1040 and 1740 cm\(^{-1}\) are due to the SO\(_3\) group and C=O stretching vibrations respectively, in the camphor sulfonate [28]. Most of the absorption bands of CSA are overlapped by those of PPy, but the CSA absorption at 1640 cm\(^{-1}\) is clearly seen (Figure 2 (b) [24]. The bands at 1560 and 1472 cm\(^{-1}\) correspond to the stretching vibrations of C=C and C-N of PPy respectively. From the FT-IR spectra, it is clear that polymerization as well as CSA doping have taken place during the synthesis process.

### 7.4.4 Raman spectral studies

Raman spectroscopic study is one of the important tools to obtain structural information on polymers. In most cases, Raman scattering is sensitive to the degree of crystallinity in a sample. Typically, a crystalline material yields a spectrum with very sharp and intense Raman peaks, while an amorphous material shows broader and less intense Raman peaks.

The Raman spectra of CSA redoped PPy film and HCl doped PPy are shown in figure 7.4. Many researchers have studied Raman spectra of polypyrrole [29-31]. The most important peak shown in figure 7.4 (a) is the one at about 1580 cm\(^{-1}\), which can be attributed to the C=C backbone stretching of PPy. The peak at about 1052 cm\(^{-1}\) is assigned to the C–H in plane deformation. Another peak at 1370 cm\(^{-1}\) is attributed to the ring-stretching mode of PPy. The bands located at about 940 and 990
cm$^{-1}$ are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively [32-34].

Two broad bands centered around 1370 and 1590 cm$^{-1}$ are observed in the Raman spectrum of PPy bulk sample (Figure 7.4(b)), whereas narrow and sharp peaks are found in the spectrum of CSA redoped PPy film (Figure 7.4(a)). Most of the peaks observed in the spectrum of the PPy film are very sharp compared to those reported in literature [35-37]. The sharpness of the Raman lines observed in the spectrum of PPy film is a consequence of the enhanced crystallinity of the film. In other words, Raman spectroscopy studies support the enhancement in crystallinity of the PPy films, established through the XRD analysis.

![Figure 7.4: Raman spectra of (a) CSA redoped PPy film and (b) HCl doped PPy](image)

Figure 7.4: Raman spectra of (a) CSA redoped PPy film and (b) HCl doped PPy
7.4.5 Thermal studies

7.4.5 (a) Differential scanning calorimetry (DSC)

The measurement of a polymer’s crystalline content (given as percentage crystallinity) by DSC is a straightforward and easy-to-perform test. This simply involves taking a small quantity of the polymer (generally 10 mg) and heating it at a steady rate (10°C/minute). The DSC curve of CSA redoped sample in m-cresol is shown in figure 7.5. DSC evaluation can be used to estimate the extent of crystallinity in the sample by two methods [38].

**Method 1**: Let the heat of crystallization be $H_C$, and the total heat given off during melting be $H_T$,

$$H = (H_T - H_C) \text{ Joules}, \quad \text{----------------------------------------(7.2)}$$

where $H$ is the heat given off by that part of polymer, which is already in crystalline state. By dividing $H$ by $Hc_1$ (specific heat of melting), where $Hc_1$ is the amount of heat given off when 1 gram of polymer is melted, the total amount of polymer that is crystalline below $T_C$, the crystallization temperature, is obtained.

$$\frac{H}{Hc_1} = \frac{\text{Joules}}{\text{Joules per gram}} = \text{Mc grams} \quad \text{---------(7.3)}$$

The percentage of crystallinity in the polymer sample is

$$\left(\frac{M_C}{M_t}\right) \times 100 = \% \text{ crystallinity in the sample} \quad \text{---------(7.4)}$$

where, $M_t$ is the total mass of sample taken.

The percentage crystallinity of the sample estimated from DSC data as per equation (7.4) is about 61%. The values of the glass
transition temperature $T_g$ and of the melting point $T_m$ are respectively 120 $^\circ$C and 314 $^\circ$C for the PPy films (Figure 7.5(b)). The increase in the value of $T_g$ (from 100 to 120$^\circ$C) of the redoped PPy film from that of the HCl doped sample also supports the enhancement in crystallinity of the former.

![DSC curves](image)

**Figure 7.5: DSC curves of (a) HCl doped PPy and (b) CSA redoped film sample**

**Method 2:** The percentage crystallinity can also be estimated from the heat of melting. The experimental heat of melting ($H_m$) is evaluated by integrating the area under the melting peak and then comparing to a reference value ($H_m^\circ$), which represents the heat of melting of the theoretically 100% crystalline sample

$$\% \text{ crystallinity} = \frac{H_m}{H_m^\circ} \times 100 \% \quad \text{(7.5)}$$

The percentage crystallinity of the sample calculated, following method 2 is about 63%.

**7.4.5 (b) Thermo gravimetric analysis (TGA)**

Thermo gravimetric analysis determines the weight changes of a sample as a function of temperature or time. The TGA curves (Figure 7.6)
show the enhancement in thermal stability of the redoped film sample compared to the doped powder sample. The increase in crystallinity of the CSA redoped film sample is evident from the more or less sharp weight loss of this sample (Figure 7.6 (b). The thermal stability of HCl doped PPy (Figure 7.6 (a) is less than that of the CSA redoped PPy (Figure 7.6 (b) film sample in m-cresol. The increase in thermal stability of the redoped film sample is attributed to the enhanced crystallinity of the sample, brought about by controlled doping.

![Figure 7.6: TGA curves of (a) HCl doped PPy and (b) CSA redoped PPy film](image)

7.4.6 Electrical Conductivity studies

The four-point probe technique is the most common method for measuring the resistivity/conductivity of samples with appreciable conductivity. The room temperature DC electrical conductivity of HCl doped PPy sample in the form of pressed pellet (diameter-13 mm) and CSA redoped PPy film has been measured using a standard four-probe setup. The conductivity of the redoped polypyrrole film is 8.5 S/cm,
which is found to be about 30 times higher than that of the HCl doped PPy, which is around 0.27 S/cm.

The observed increase in the electrical conductivity of the CSA redoped film samples can be attributed to the secondary doping effect of the solvent, m-cresol and the effects of controlled CSA doping (redoping using one molar CSA), by which more crystallite regions are formed. This in turn improves the mobility of charge carriers and hence increases the conductivity of the sample [16].

7.5 Conclusions

Highly crystalline polypyrrole films have been prepared from CSA redoped sample solution in m-cresol. Crystalline peaks have been identified in the XRD pattern of the CSA redoped film samples, which correspond to the distance between pyrrole rings, the distance from the pyrrole ring to the camphor sulphonate dopant and the face-to-face stacking distance. The extent of crystalinity has been assessed using the DSC and XRD data. The sharp peaks in the Raman spectrum of the PPy film also support the observed increase in crystallinity of the film samples. The thermal analysis establishes the higher stability of the CSA redoped PPy film compared to the HCl doped sample. The d.c. electrical conductivity of the redoped polypyrrole film is about 30 times higher than that of the HCl doped pellet sample. The secondary doping effect of the solvent, m-cresol and the controlled doping using CSA facilitate the enhancements in crystallinity and conductivity. The observation of extra ordinarily high extent of crystallinity in the CSA redoped PPy film is the highlight of this chapter. Semi-crystallinity is desirable for most polymers because semi crystalline polymers combine the strength of
crystalline polymers and the flexibility of amorphous ones. Crystallinity influences many of the polymer properties, and hence it plays an important role while selecting polymers for specific applications. The present work is quite significant from this point of view.

References


Novel polypyrrole films with excellent crystallinity and good thermal stability


.....SOQR.....