Structural characteristics and thermodynamical study

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3.1 INTRODUCTION:

Properties of various materials have been used to describe materials from centuries. Infrared spectrometry is widely used in the identification of polymeric materials for both qualitative and quantitative determination of its composition. It has also been used to identify and determine the concentration of plasticizers, filters, additives, antioxidants, emulsifiers, and residual monomers in the material. Polymers structure studies, such as chain branching, polymer and groups, steric and geometrical isomerism have been performed.

Thermal analysis techniques are used in characterizing the material depending upon types of the materials. Thermal analysis test for characterizing the materials include Melting point (DSC), Glass transition temperature (DSC, DTA, TMA and DMA), Decomposition temperature (DSC, TGA), component quantification etc.

The thermo-gravimetric analysis is widely used method to investigate the thermal decomposition of polymer and to assess their thermal stabilities. Also, considerable attention has been directed recently toward use of thermo-gravimetric data for the determination of kinetic parameters. Many of the methods of kinetics analysis which have been proposed are based on the hypothesis that, from a single thermo-gravimetric
trace, meaningful values may be obtained for parameters such as activation energy, pre-exponential factors and reaction order etc.

Thus, many of these methods make two assumptions, viz, these parameters are useful in characterizing a particular polymer degradation, and that the thermogram for each particular set of these parameter is unique.

3.2 STRUCTURAL CHARACTERIZATION:

3.2.1 Structural Characterization through FTIR:

All forms of polypyrrole reported so far are extremely poor crystalline. The pyrrole blocks were primarily bonded via $\alpha,\alpha'$ carbons, shows that these $\alpha$- positions seems to prevent the polymerization of pyrrole (Salmon et al 1982). In unsubstantiated pyrrole it has been shown by NMR and IR techniques that, in chain bonding the -carbon atom is also involved (Street et al 1982 and Clarke et al 1983). Blocking both the $\beta$-positions with a methyl group eliminates the possibility of other than $\alpha,\alpha'$-bonding. (Street et al 1982). Assuming a completely $\alpha,\alpha'$-bonded polymer, a planer cyclic structure with all the pyrrole nitrogen pointed to the center require 10 pyrrole molecules to complete the ring. Comparison of these spectra with neutral polypyrrole on oxidation shows that the structure of polymer chain is predominantly the same to $\alpha,\alpha'$-bonded planer linear
chain. The FTIR spectra fig.(3.1) were obtained by using Bruker IFS 66 V FTIR spectrometer, using KBr pellet technique at RSIC, IIT Chennai.

3.2.2 Structural Characterization using Thermogravimetry (TG) and Differential Thermal Analysis (DTA):

The usual method of obtaining kinetic data for polymers involves a series of experiments, carried out under isothermal conditions at different temperatures. The study of reaction kinetics was dynamically carried out by differential thermal analysis technique. The methods of analysis for determining the activation energy for solid-state reactions have been proposed by large number of research workers. The method used by Kissinger et al (1956), Augis et al (1978), Matusita et al (1981) utilizes linear relation between peak reaction temperature (Tp) and DTA heating rate, where the main advantage of non-isothermal technique is lost. The other methods (Borchardt et al 1957, Rogers et al 1970, Skvara et al 1970, Marott et al 1966) are based on the evaluation of height ΔT, and/or area, under the single DTA peak.

The DTA/TG was carried out at RSIC, IIT Chennai. The instrument used and experimental conditions are as follows.

Name of instrument : STA 409C

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Reference material: Alumina
Heating Rate: 10°C/min
Heating Range: -30 to 800 °C
Atmosphere: Nitrogen

3.2.3 Structural characterization using XRD:

The X-ray diffraction spectra of polypyrrole thin films is shown in figure (3.11). This analysis was done at National Bureau of Soil Survey and Land Use Planning, Nagpur by Philips Analytical analyzer.

3.3 THEORETICAL ASPECTS:

3.3.1 FTIR:

In the recent year, a number of new experimental techniques and theoretical approaches have been attempted with the view to gain adequate information on the vibrational spectra of vitreous solids and elucidate the nature of vibrational modes. The term infrared spectroscopy normally denotes the study of the absorption and reflectance spectra between the approximate wave number 4000 to 400 cm⁻¹. These studies provide a useful tool for molecular structure determination. In polymers chemical bonding and average spectral distribution of vibrational energies exists; despite of the disorder present in them. Although vibrational spectroscopy does not usually provide direct structural information, it
can be a very useful tool for probing terminal or weakly coupled bridging atoms in terms of short range order. Infrared spectroscopy involves the measurement of absorption of electromagnetic radiation. Miller et al.,(1960) reported a series of investigations, which includes hundreds of organic and inorganic substances and recognized the existence of absorption of characteristics frequencies of specific organic and inorganic molecular structure. The absorption bands, occur in 2 to 16 mm region are due to the fundamental molecular vibration. Two necessary conditions which must met before the absorption of infrared radiation by molecules are ,

a) There must be change in dipole moment of a molecule and this will occur only when the electrical charges on the atoms are unequally distributed. Under these conditions, a stationary alternating electric field is produced, whose magnitude change at the frequency and it is this electric field which interacts with the field of electromagnetic radiation.

b) The molecular vibrational frequency must be identical to that of the electromagnetic radiation. If this condition is not met then, radiation passes through the molecules without the loss of energy.

Consequentially, when infrared radiation of different frequencies is passed through a molecules and the fraction of transmitted energy is
plotted against the frequency or wavelength the result is a series of minima and maxima, which in graphical form refer to as an infrared absorption spectra. The absorption or transmission of this electromagnetic energy is dependent on the number of atoms, their mass, the arrangement of atom and force constant of interatomic bonds. The vibrations between the various atoms in the molecules can be described as stretching vibrations, bending vibration, involving groups of atoms within the molecule and vibrations of molecule as a whole. These vibrations can occur at various frequencies and are characteristics of groups of atoms within the molecules.

3.3.2 Thermo-gravimetry (TG):

Thermo-gravimetry is the another thermal analysis technique used to measure the change in mass of a sample as it is heated, cooled, or held isothermally. One can detect the percentage of moisture and volatile, percentage of filters and additives in multicomponent system, compositional difference in blends, degradation temperature and decomposition kinetics of the sample. The TG curves as shown in fig.(3.2) for different weight percent of pyrrole exhibited a two stage decomposition pattern. The methods of kinetic analysis of thermo-gravimetric data are divided into five categories to facilitate the discussion and comparison. These are (a) Integral method (Coats-Redfern equation) utiliz-
loss versus temperature data directly, (b) Differential method (Freeman-Carroll equation) utilizing the rate of weight loss, (c) Difference differential method (Horowitz-Metzger equation) involving difference in rate, (d) Methods specially applicable to initial rate and (e) Nonlinear or cyclic heating rate method. The polymerization process occurs in polypyrrole as,

$$\text{oxidize} \quad \text{N} \quad \text{H} \quad \rightarrow \quad \text{N} \quad \text{H} \quad \text{A} \quad \text{I}$$

1) **The differential method using Freeman-Carroll equation:**

Differential method based on the rate of weight loss versus temperature data. Freeman et al (1958) have devised a method to calculated the thermal parameters using thermo-gravimetric data.

The Freeman-Carroll equation was used in the form

$$\frac{\Delta \log dw}{dt} = \left( - \frac{\Delta (T^{-1})}{2.303 R} \right) \frac{\Delta log w}{\Delta log w} + n \quad (3.1)$$

where $w_T$ is $w_s - w$

and

- $w_s$ is the mass loss at the completion of the reaction,
- $w$ is the mass loss upto time $t$,
- $T$ is the absolute temperature at time $t$,  

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n is the order of reaction,

R is the gas constant in J°K⁻¹mol⁻¹, and

W is the activation energy in J mol⁻¹.

Of the above term w₁ and T can be directly obtained from the TG traces. The mass - temperature gradient (dw/dt) could be obtained by drawing tangents. The temperature slopes, dw/dT, were covered into time slope, dw/dt, using the relation,

\[
\frac{dw}{dt} = \left( \frac{dw}{dT} \right) \left( \frac{dT}{dt} \right) = \left( \frac{dw}{dT} \right) \Phi \quad (3.2)
\]

where \( \Phi \) is the heating rate. A plot of \( \frac{\Delta (T^{-1})}{\Delta \log w_1} \) versus \( \frac{\Delta (dw/dt)}{\Delta \log w_1} \) was drawn and found to be linear from which the order of reaction and activation energy were obtained. The order of reaction (n) was found unity.

The usual first order rate law expression,

\[
\frac{dx}{dt} = k (a - x) \quad (3.3)
\]

can be put in the following form using the w and \( w_1 \)

\[
\frac{dw}{dt} = k w_1 \quad (3.4)
\]

Combing this with Arrhenius equation, i.e.

\[
k = Z \exp \left( - \frac{W}{RT} \right), \text{ we get}
\]
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\[ \log \left[ \frac{dw}{dt}/w \right] = \frac{-W}{2.303RT} + \log Z \] (3.5)

A plot of the left hand side against \((T^{-1})\) was found to be linear, from the slope of which \(W\) was calculated. \(Z\) was calculated from the intercept and entropy of activation \(\Delta S^*\) was obtain from the equation,

\[ Z = \frac{kT}{h} \exp \left( \frac{\Delta S^*}{R} \right) \] (3.6)

2. **Integral method using Coats-Redfern equation:**

Coats et al (1964) have devised a method to calculate the thermal parameters using thermo-gravimetric data.

Coats-Redfern equation, which is a typical integral method can be represented as

\[ \frac{\alpha}{(1-\alpha)^n} = \frac{Z}{\Phi} \int_0^\tau \frac{\exp (-W)}{RT} \, dt \] (3.7)

The left hand side of equation (3.7) have two different solutions, namely

\[ 1 - \frac{(1-\alpha)^{1-n}}{(1- n)} \quad \text{for } n \neq 1 \] (3.8)

and

\[ - \log (1 - \alpha) \quad \text{for } n = 1 \] (3.9)

Where 'n' is the order of reaction.

In both cases the right hand side of equation (3.7) has the solution
(\frac{ZRT^2}{\Phi W} \left( 1 - \frac{2RT}{W} \right)) \exp\left( \frac{-W}{RT} \right) \quad (3.10)

following equations are obtained after taking the logarithm

\log \left[ 1 - \frac{(1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \left[ \frac{ZR}{\Phi W} \left( 1 - \frac{2RT}{W} \right) \right] - \frac{W}{2.303R} \quad (3.11)

for n \neq 1

and

\log \left[ \frac{-\log(1 - \alpha)}{T^2} \right] = \log \left( \frac{ZR}{\Phi W} \left( 1 - \frac{2RT}{W} \right) \right) - \frac{W}{2.303R} \quad (3.12)

for n = 1

In ordinary thermal decomposition reaction \log \left( \frac{ZR}{\Phi W} \left( 1 - \frac{2RT}{W} \right) \right)

is practically constant and the plot of

\log \left[ 1 - \frac{(1 - \alpha)^{1-n}}{T^2(1-n)} \right] \text{ against } 1/T \text{ for } n \neq 1 \quad (3.13)

and

\log \left[ \frac{-\log(1 - \alpha)}{T^2} \right] \text{ against } 1/T \text{ for } n = 1 \quad (3.14)

respectively results in a straight line having slope of \frac{WR}{2.303} \text{ for the}
correctly chosen value of order of reaction. The reaction order can easily be estimated by observing the lines drawn by using ‘n’ in equation (3.13) and (3.14). Hence the order of reaction can be calculated. The slope and Z can be found out from the intercept.

For the first order process the Coats-Redfern equation may be written in the form

\[ \log \left( \frac{w_{a}}{w_{s}-w} \right) = \log \left( \frac{ZR (1-2RT)}{\Theta W} \right) - \frac{W}{2.303RT} \]  

(3.15)

Since \( \frac{2RT}{W} = 1 \), a plot of left hand side against 1/T was drawn & W was calculated from the slope and Z was found from the intercept.

3. The **Integral method using the Horowitz-Metzger equation**

(Horowitz et al., 1963)

The Horowitz-Metzger method is illustrative of approximation methods. These authors derive the relation

\[ \log \left[ \frac{1-(1-\alpha)^{1-n}}{1-n} \right] = \frac{W\Theta}{2.303RT} \]  

for \( n \neq 1 \)  

(3.16)

When \( n = 1 \) the left hand side of equation (3.16) would be \( \log [-\ln/(1-\alpha)] \). They have also derived a simple relation for obtaining the order of reaction, \( n \) as
where \( C_s = (1-\alpha) \) and \( \alpha \) is fraction decomposed at the DTG peak temperature \( T_s \).

The Horowitz-Metzger equation applicable to the first order kinetic process is in form

\[
\log \left( \log \frac{w_s}{w_f} \right) = \frac{W\Theta RT_s^2}{2.303} - \log(2.303) \tag{3.18}
\]

where \( \Theta \) is \( (T - T_s) \) and the other terms are as described earlier. A plot of \( \log \left[ \log \frac{w_s}{w_f} \right] \) versus \( \Theta \) is to be drawn whose slope is linear. From the slope \( E^* \) can be calculated. The pre-exponential factor \( Z \) is given by

\[
\frac{W}{RT_s^2} = \left( \frac{Z}{\Theta} \right) \exp \left( - \frac{W}{RT_s} \right) \tag{3.19}
\]

The entropy of activation \( \Delta S^* \) was calculated from the equation used earlier for the purpose.

4. **Zsako’s modified Doyle method:**

This method is a modified method proposed by Doyle (1961) and Zsako (1968). This trial and error method of Doyle was modified by Zsako by introducing the standard deviation instead of curve fitting method for the calculations.

The values of \( g(\alpha) \) was calculated for various values of \( n \) in the general equation \( \frac{d\alpha}{dt} = k (1 - \alpha)^n \), where \( n \) can be considered as appar-
If the logarithm of Doyle’s equation is taken,

$$\log(ZW/R \Theta) = \log g(\alpha) - \log P(x) = B$$  \hspace{1cm} (3.20)

where $g(\alpha)$ is a certain function of $\alpha$, where $\alpha$ stands for the fraction of initial compound reacted, $Z$ is frequency factor, $W$ is activation energy, $R$ is gas constant and $\Theta$ is heating rate.

The value of integral

$$P(x) = e^{-s} \int_{x}^{\infty} \frac{e^{-u}}{u} \, du \quad \text{ (where } u = W/RT)$$  \hspace{1cm} (3.21)

$P(x)$ were calculated and tabulated by Doyle for $x$ values covering a range from 10 to 50 and these values were used in calculating $B$.

### 3.4 RESULT AND DISCUSSION:

#### 3.4.1 Fourier Transform Infrared Spectroscopy:

The FTIR spectra of polypyrrole for different weight percent is shown in fig.(3.1). Eleven to seventeen absorption peaks are observed in all polypyrrole samples. The shape of the peaks are sharp, medium and broad. The most impressive characterization is the evolution of absorption bands located at 3464.9, 3437.9, 3427.8, 3427.5, and 3423 cm$^{-1}$ in 1, 5, 8, 10 and 40 Wt.% of polypyrrole thin films corresponds to N-H stretching. The characteristic absorption bands due to hydroxyl (-OH)
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Fig. 3.1 FTIR spectra of 1, 5, 8, 10 and 40 Wt.% of polypyrrole films

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Table 3.1 Wave numbers for different wt. % of polypyrrole films (cm⁻¹)

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>1 Wt.%</th>
<th>5 Wt.%</th>
<th>8 Wt.%</th>
<th>10 Wt.%</th>
<th>40 Wt.%</th>
<th>Bands assigned/remark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3464.9</td>
<td>3437.9</td>
<td>3423</td>
<td>3427.8</td>
<td>3427.5</td>
<td>N-H Stretching</td>
</tr>
<tr>
<td></td>
<td>3281.1</td>
<td>3279.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>O-H Stretching</td>
</tr>
<tr>
<td></td>
<td>3157.8</td>
<td>3152.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C-H Stretching in - CH₃</td>
</tr>
<tr>
<td></td>
<td>2921.7</td>
<td>2922.7</td>
<td>2922</td>
<td>2920.9</td>
<td>2921.4</td>
<td>Pyrrole moist, grafting of Pyrrole on film backbone</td>
</tr>
<tr>
<td></td>
<td>2854.4</td>
<td>2853.8</td>
<td>-</td>
<td>-</td>
<td>2851.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2512</td>
<td>2513.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Weak N-H stretch</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>2061.6</td>
<td>2010</td>
<td>1987</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1703.2</td>
<td>1701</td>
<td>1739</td>
<td>1737</td>
<td>1734.5</td>
<td>C=O Stretching</td>
</tr>
<tr>
<td></td>
<td>1635.2</td>
<td>1635.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C=C Stretching</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>1505.4</td>
<td>1562.9</td>
<td>1564.9</td>
<td></td>
<td>Pyrrole ring stretch</td>
</tr>
<tr>
<td></td>
<td>1456.7</td>
<td>1457.7</td>
<td>-</td>
<td>1432.7</td>
<td>1432.9</td>
<td>C-N Stretching of Pyrrole ring</td>
</tr>
<tr>
<td></td>
<td>1367.8</td>
<td>1360.8</td>
<td>1370.3</td>
<td>1371.4</td>
<td>1372.9</td>
<td>Alifatic C-H deformation peak</td>
</tr>
<tr>
<td></td>
<td>1315.2</td>
<td>1313</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C-H vibration</td>
</tr>
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<td></td>
<td>1257.9</td>
<td>1258.1</td>
<td>1236.5</td>
<td>1234.3</td>
<td>1238.9</td>
<td>C-O vibration in ester</td>
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<tr>
<td></td>
<td>1151.4</td>
<td>1150.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C-C Stretching</td>
</tr>
<tr>
<td></td>
<td>1023</td>
<td>1025.9</td>
<td>1019.6</td>
<td>1019.5</td>
<td>1018.9</td>
<td>Bending vibration of C-H &amp; N-H bond</td>
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<td></td>
<td>933.1</td>
<td>902</td>
<td>932.4</td>
<td>930.2</td>
<td>927.6</td>
<td>Polymerized pyrrole</td>
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<tr>
<td></td>
<td>790.3</td>
<td>-</td>
<td>786.3</td>
<td>790</td>
<td>789.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>661.7</td>
<td>657.1</td>
<td>664.8</td>
<td>668.3</td>
<td></td>
<td>C-H out of plane deformation</td>
</tr>
<tr>
<td></td>
<td>604.4</td>
<td>602</td>
<td>598</td>
<td>600.6</td>
<td>601.1</td>
<td>Fe-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>540.5</td>
<td>525.2</td>
<td>-</td>
<td>531.5</td>
<td>531.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>430.8</td>
<td>-</td>
<td>460.7</td>
<td>466</td>
<td>465</td>
<td>Metal oxide</td>
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<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>424.3</td>
<td></td>
</tr>
</tbody>
</table>

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group of polyvinyl acetate are observed at 3281.1, 3279.1, 2920, 2921.4 and 2922 cm$^{-1}$. Similarly, the characteristic absorption bands due to C-H group of polyvinyl acetate is observed at 3157.8 cm$^{-1}$ and 3152.7 cm$^{-1}$ for 1 and 5 wt.% of polypyrrole thin films. These characteristic absorption bands are not visible in 8, 10 and 40 wt.% of polypyrrole thin films, suggesting that C-H have reacted further (Koji et al, 1996). The characteristic absorption bands at 1703.2, 1701, 1737.3, 1738.5 and 1739 cm$^{-1}$ appears in polypyrrole thin films indicating that polymer containing an approximate amount of C = O group probably due to overoxidation in polypyrrole, results in distruption of structure and loss of conductivity (Chorng et al, 1997). C = C stretching vibration is present in 1 and 5 Wt.% of polypyrrole thin films at 1635.2 cm$^{-1}$ and 1635.2 cm$^{-1}$ and are not present in 8, 10 and 40 wt.% of polypyrrole films suggesting that C= C have reacted further.

The absorption bands at 1257.9, 1258.1, 1236.5, 1238.9 and 1234.3 cm$^{-1}$ are assigned to strong stretching in C - O group in ester for respective weight percent of polypyrrole thin films. The medium absorption bands at 604.4, 602, 600.6, 601.1 and 598 cm$^{-1}$ are due to Fe -Cl stretching, suggested that the - Cl group is linked with polypyrrole in branching. The absorption bands at 1456.7, 1457.7, 1432.7 and 1432.9 cm$^{-1}$ are
assigned to C = C and C - N stretch and deformation of five membered ring which contains C = C - N and C = C - C deformation (Kofranek et al., 1992 and Kostic R et al., 1995). The various peaks positions at corresponding wave number is reported in table (3.1). The bands corresponding to stretching -O-H and -C-H were observed at 3281.1, 3279.1 and at 3157.8, 3279.1 cm⁻¹ for 1 and 5 Wt.% of polypyrrole film respectively. For other samples no such stretching was observed. Presence of IR bands at 2854.4 and 2853.8 cm⁻¹ for 1 and 5 Wt.% of sample shows polyvinylacetate moiety which suggest the grafting of polyvinylacetate on the film backbone (Bhattacharya et al., 1996). The absorption bands at 1504, 1562.9, 1564.9 for 5, 10 and 40 Wt.% representing pyrrole ring stretch and bands at 1456.7, 1457.7, 1432.7 and 1432.9 cm⁻¹ for 1, 5, 10 and 40 Wt.% shows C-N stretching of polypyrrole ring respectively (Mohmud et al., 2005). Absorption bands at 1360.8 to 1372.9 cm⁻¹ in all samples shows alphatic C-H deformation peak (Singh et al., 2001). Presence of C-H vibration in plane was observed at 1315 cm⁻¹. C-C stretch was observed at 1151.4 and 1150.5 cm⁻¹ in 1 and 5 Wt.% samples only. The bending vibrations of C-H and N-H band of polypyrrole ring were observed from 1018.9 to 1025.9 cm⁻¹ in all polypyrrole samples. The bands at 902, 933.1 and 786.3 to 790.3 cm⁻¹ in all samples shows the
presence of polymerized polypyrrole (Vishnuvardhan et al., 2006). The bands at 661.7 to 668.3 cm\(^{-1}\) shows the presence of -C-H band out of plane deformation. The weak bands form at 424.3 to 540.5 cm\(^{-1}\) are indicative of metal oxide (Vishnuvardhan et al., 2006).

### 3.4.2 Thermogravimetry (DTA-TG):

Figure (3.2) shows TGA curves for 1, 2, 5, 8, 10 and 40 Wt.% of polypyrrole thin films in the temperature range 303 to 1073 K. The curves indicate that the composition of films under study are thermally stable up to 567 K. The decomposition of the films occurs in two stages, in the temperature range shown in table (3.2). The weight loss along with the transition temperatures at two different stages of transition is also listed in table (3.2). The thermal decomposition of polypyrrole films as observed from figure (3.2) occurs in two stages for 5, 8 and 40 wt.% of the films. In the first stage of decomposition of samples the mass loss is poor except the film of 40 Wt.% In this film at 588K the mass loss is 2.69 mg and up to temperature 1073 K the complete decomposition occurs as compared to other films and also the residue is only 3.41%. The small loss in mass of 1 to 10 Wt% of the films during first transition was due to the evaporation of residual solvents and moisture. This step reveals that the polypyrrole films retain the solvents and environmental mois-
ture in large amount. But in the film of 40 Wt.% due to large content of pyrrole the porosity reduces, so that it requires comparatively high thermal energy to decompose. Normally in all the samples the rate of decomposition is fast above the temperature of 363K. The percentage of residue after the decomposition is large in 1 to 10 Wt.% (25% to 32.47%) of polypyrrole films, whereas in the film of 40 Wt.%, it is small (3.41%). This less percentage of residue in 40 Wt.% of the film may be due to higher amount of content of pyrrole in the sample.

In studying decomposition kinetics, thermal parameters have been calculated using Freeman-Carroll and Coats-Redfern equation, for which the thermo-gravimetric curves are used for computations of parameters. The various parameters are tabulated in Table (3.3). The Arhenius type plots using Freeman-Carroll equation (3.5) is shown in figures (3.5) and (3.7) for first and second stage of decomposition of the samples respectively. Similarly, The Arhenius type plots using Coats-Redfern equation (3.15) is shown in figures (3.6) and (3.8) for first and second transition stage of decomposition of polypyrrole films respectively. The values of kinetics parameters are well in agreement with the values reported by Vatsala et al (1986).

Figure (3.3) shows the DTA plot for 1, 5, 8, 10 and 40 wt % of polypyrrole films in the temperature range 303 to 1073K. A single stage
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Fig.: 3.2 TG Spectra of 1, 5, 8, 10 and 40 Wt.% of polypyrrole sample

Fig.: 3.3 DTA Spectra of 1, 5, 8, 10 and 40 Wt.% of polypyrrole sample

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weight loss pattern is observed in 1 and 5 Wt % of sample whereas multistage weight loss pattern is observed in 8, 10 and 40 wt. % of polypyrrole films with exothermic decomposition. The multistage decomposition is probably due to heterogenic structure of the films. The slow weight loss around 417 to 431K may have been caused by decomposition of cross-linked Polyvinyl acetate (Battacharya et al, 1996).

Figure (3.4) shows the variation of glass transition temperature (Tg) as observed from DTA plots. It is found that Tg is less for 5 wt % of the sample and is more for 8 and 10 wt % of samples. Again it decreased for 40 wt % of the sample. The decrease in Tg is probably due to the increase in the concentration of pyrrole monomer.

Figure (3.9) shows the variation of entropy ($\Delta S^*$) as calculated from equations (3.6) and (3.15) and tabulated in table (3.3). It is found that entropy increases up to 10 wt.% of polypyrrole film and then decreases for 40 wt % of the film. This decrease in entropy suggested the thermal stability of polypyrrole sample.
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Fig.: 3.5 for 1 Wt. %

Log (I) vs. 1/T graph for 1 Wt. %

Fig.: 3.6 for 5 Wt. %

Log (I) vs. 1/T graph for 5 Wt. %

Fig.: 3.5 for 8 Wt. %

Log (I) vs. 1/T graph for 8 Wt. %

Fig.: 3.6 for 10 Wt. %

Log (I) vs. 1/T graph for 10 Wt. %

Fig.: 3.5 for 40 Wt. %

Log (I) vs. 1/T graph for 40 Wt. %

Fig.: 3.6 for 40 Wt. %

Log (I) vs. 1/T graph for 40 Wt. %

Fig.: 3.5 Arrhenius type plot using to Freeman-Corroll relation for first phase of transition

Fig.: 3.6 Arrhenius type plot using to Coats-Redfern relation for first phase of transition

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Fig.: 3.7 Arrhenius type plot using Freeman-coroll relation for second phase of transition in polypyrrole films

Fig.: 3.8 Arrhenius type plot using Coats-Redfern relation for second phase of transition in polypyrrole films

Fig.: 3.9 Plot of Entropy against Polypyrrole Wt % from TG curve

Fig.: 3.10 Plot of Activation energy against Polypyrrole Wt % from TG curve

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### Table 3.2 Thermal parameters form fig.: 3.2

<table>
<thead>
<tr>
<th>PPY sample Wt %</th>
<th>Weight (mg)</th>
<th>For 1st stage</th>
<th>For 2nd stage</th>
<th>Loss of wt. (%) Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Transition temperature (K)</td>
<td>Temperature range(K)</td>
<td>Transition temperature (K)</td>
</tr>
<tr>
<td>1</td>
<td>10.48</td>
<td>585.5</td>
<td>488-638.5</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>23.97</td>
<td>363.6</td>
<td>308-418</td>
<td>567.5</td>
</tr>
<tr>
<td>8</td>
<td>20.22</td>
<td>386.5</td>
<td>308-418</td>
<td>577.9</td>
</tr>
<tr>
<td>10</td>
<td>16.75</td>
<td>590.5</td>
<td>508-636</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>6.23</td>
<td>588.4</td>
<td>513-640</td>
<td>736.4</td>
</tr>
</tbody>
</table>

### Table 3.3 Kinetic parameters using Freeman-Carroll and Coats-Redfern equations

<table>
<thead>
<tr>
<th>PPY sample Wt %</th>
<th>Thermal Parameters</th>
<th>From Freeman-Carroll equation</th>
<th>From Coats-Redfern equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation energy (W) k J Mole(^{-1})</td>
<td>728.2</td>
<td>472.09</td>
</tr>
<tr>
<td></td>
<td>Entropy (ΔS(^*)) J mole(^{-1}) K(^{-1})</td>
<td>-224.17</td>
<td>-251.41</td>
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<tr>
<td></td>
<td>Frequency factor (Z) s(^{-1})</td>
<td>14.5</td>
<td>42.52</td>
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<tr>
<td>5</td>
<td>Activation energy (W) k J Mole(^{-1})</td>
<td>661.99</td>
<td>681.86</td>
</tr>
<tr>
<td></td>
<td>Entropy (ΔS(^*)) J mole(^{-1}) K(^{-1})</td>
<td>-216.22</td>
<td>-216.69</td>
</tr>
<tr>
<td></td>
<td>Frequency factor (Z) s(^{-1})</td>
<td>38.55</td>
<td>56.9</td>
</tr>
<tr>
<td>8</td>
<td>Activation energy (W) k J Mole(^{-1})</td>
<td>703.4</td>
<td>724.06</td>
</tr>
<tr>
<td></td>
<td>Entropy (ΔS(^*)) J mole(^{-1}) K(^{-1})</td>
<td>-241.93</td>
<td>-215.02</td>
</tr>
<tr>
<td></td>
<td>Frequency factor (Z) s(^{-1})</td>
<td>25.95</td>
<td>70.85</td>
</tr>
<tr>
<td>10</td>
<td>Activation energy (W) k J Mole(^{-1})</td>
<td>282.51</td>
<td>664.65</td>
</tr>
<tr>
<td></td>
<td>Entropy (ΔS(^*)) J mole(^{-1}) K(^{-1})</td>
<td>-215.69</td>
<td>-228.21</td>
</tr>
<tr>
<td></td>
<td>Frequency factor (Z) s(^{-1})</td>
<td>40.58</td>
<td>14.81</td>
</tr>
<tr>
<td>40</td>
<td>Activation energy (W) k J Mole(^{-1})</td>
<td>124.58</td>
<td>745.99</td>
</tr>
<tr>
<td></td>
<td>Entropy (ΔS(^*)) J mole(^{-1}) K(^{-1})</td>
<td>-214.38</td>
<td>-216.02</td>
</tr>
<tr>
<td></td>
<td>Frequency factor (Z) s(^{-1})</td>
<td>77.89</td>
<td>80.02</td>
</tr>
</tbody>
</table>

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The variation of activation energies of 1, 5, 8, 10 and 40 wt% of samples against respective weight percent as tabulated in table (3.3) is shown in figure (3.10). The activation energy of polypyrrole sample increases up to 8 wt% and then decreases for 10 and 40 wt% of the samples.

3.4.3 X-ray diffraction:

The X-ray scattering patterns of polypyrrole film shows a broad peak at $\theta = 23.5^\circ$, which is a characteristics peak of amorphus polypyrrole film (Partch et al, 1991 and Vishvardhan et al, 2006). Also the peak is broad including the formation of crystallinity in the sample (He et al 2003 and Viskey et al 2005). The hkl planes corresponding to different d-spacing have been identified from diffraction data using crystal system, lattice types and lattice parameters (figure 3.11). The crystalline pattern increases in the film. Figure (3.11) shows the hkl planes corresponding to different d-spacing have been calculated from X-ray diffraction data analysis using crystal systems, lattice types and lattice parameters along with the diffraction pattern of pure pyrrole.

The broad peak is due to scattering from polypyrrole chains at the interplaner spacing (Ouyang et al, 1997). The crystalline behavior increases in the film. The reflections at $31^\circ$, $37^\circ$, $44.5^\circ$, $65^\circ$, $75^\circ$ and $78.5^\circ$ indicates the presence of ferrous in polypyrrole films.

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3.5 CONCLUSIONS:

Study of characteristics of polypyrrole has been made by analyzing the films with XRD, FTIR and DTA-TG. From XRD spectra of polypyrrole films, it is observed that the films are partially crystalline. The crystalline peaks observed are due to ferrous ions.
FTIR analysis shows that - N-H stretching, -OH stretching, -C-H stretching, \(-C=\)C stretching, -C-C stretching and Fe-Cl stretching in the structure of polypyrrole. Bending vibration of C-H and N-H are assigned in wave number range of 1099 to 1026 cm\(^{-1}\). The Fe-Cl presence in the film is seen from the XRD spectra.

DTA - TG analysis of polypyrrole films shows that two stages of transition of thermal decomposition. For complete thermal decomposition of the films of 1 to 10\%\text{Wt.\%} a temperature above 1073K is required whereas a film of 40\%\text{Wt.\%} decompose completely at 1073 K. Thermal kinetic parameters like activation energy, entropy and frequency factor using Freeman-Coroll and Coats-Redfern equation have been calculated.
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