CHAPTER 8

THERMOGRAVIMETRY, DIFFERENTIAL THERMAL ANALYSIS
AND X-RAY STUDIES IN SOME POLYPYRROLE SAMPLES
8.1 Introduction

Thermal analysis embraces all methods in which measurements are made up of a property that changes as the temperature changes. The equipment used ideally consists of a measurement cell in which the specimen is placed, the measuring apparatus, and the means to change the temperature of the specimen in a controlled manner, preferably according to a pre-set programme.

In thermogravimetric analysis, weight losses of the sample with the rise in temperature are monitored. Weight losses occur as a result of driving off volatiles and at higher temperatures, degradation products. Thus this technique can be used both to examine the state of the material (i.e., the presence and quantity of volatiles, often water) and to investigate the process of degradation [1].

Differential thermal analysis (DTA) can also be used to investigate the thermal behaviour of materials. In
differential thermal analysis (DTA) the temperature of the sample and a thermally inert reference material are measured as a function of temperature. Any transition which the sample undergoes will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A monitoring of the whole process will lead to an understanding of the temperature of transition and whether the transition is exothermic or endothermic [2]. X-ray diffraction is the traditional method of crystallographic structure determination, and standard techniques and analysing procedures can be used in the study of crystallinity in polymers [3].

8.2 Experimental

Thermal analysis of polypyrrole samples prepared by electrochemical and chemical methods were carried out. The thermogravimetric plot was obtained using a delta series TGA 7 at a scanning rate 20°C per minute and differential thermal analysis plot was obtained using a delta series DTA 7 at a scanning rate 20°C per minute. The X-ray diffraction patterns of films and powders of polypyrrole were recorded using a Shimadzu model 610 X-ray diffractometer using CuKα radiation.
Figure 8.1.
TGA of conducting polypyrrole film prepared by electrochemical method.

Figure 8.2.
DTA of conducting polypyrrole film prepared by electrochemical method.
Figure 8.3.
TGA of polypyrrole film prepared by chemical method.

Figure 8.4.
DTA of polypyrrole film prepared by chemical method.
Figure 8.5.
TGA of polypyrrole powder prepared by chemical method.

Figure 8.6.
DTA of polypyrrole powder prepared by chemical method.
Figure 8.7. X-ray diffraction pattern of the polypyrrole film prepared by electrochemical methods.
Figure 8.8. X-ray diffraction pattern of the polypyrrole film prepared by chemical methods.
Figure 8.9. X-ray diffraction pattern of the polypyrrole powder prepared by chemical methods.
8.3 Results and discussion

The TGA and DTA curves of conducting polypyrrole prepared by electrochemical method (Section A of Chapter 3) are shown in figure 8.1 and 8.2. It is seen that the polypyrrole sample starts decomposition at 220°C and that slow decomposition continues up to 450°C during which there is about 14% of mass loss. This indicates that the polypyrrole sample is stable up to a temperature of about 220°C. But in the case of polypyrrole prepared chemically (Section D of Chapter 3) it is seen from figure 8.3 and 8.4 that the polypyrrole sample starts degradation at 150°C. The material undergoes the decomposition from 150 to 550°C during which there is a mass loss about 17 to 20%. In the case of a third sample of polypyrrole prepared chemically (Section E of Chapter 3) the degradation is found to start at 120°C (Figure 8.5 and 8.6) and these slow degradation causing a mass loss of about 20% extents up to 180°C. Thus it is seen that polypyrrole films prepared by electrochemical method are much superior in terms of thermal stability compared to those prepared by chemical methods.

The X-ray diffraction pattern of polypyrrole samples prepared by electrochemical and chemical methods are shown in figure 8.7 and 8.9. It is seen from these figure that
the polypyrrole samples prepared by electrochemical methods described in section A (Figure 8.7) and section B (Figure 8.8) of chapter 3 are poorly crystalline than that prepared by chemical method described in section E (Figure 8.9) of chapter 3. Since the mechanism of conduction in conducting polymers is different from that in crystalline materials, the lack of crystallinity in polypyrroles is to be considered as a factor enhancing conductivity. This reasoning actually supports the observation (reported in chapter 3 of this thesis) that the conductivity of electrochemically prepared polypyrrole is much lower than that of samples prepared by chemical methods.

From the thermal and X-ray studies of conducting polypyrroles it is concluded that polypyrrole samples prepared by electrochemical methods are superior in terms of thermal stability and that they have more amorphous structure than chemically prepared polypyrrole samples. These observations combined with the observations reported in chapter 3 of this thesis shows that the DC conductivity of polypyrrole samples prepared by electrochemical methods is much larger than that of polypyrrole prepared by chemical methods may be considered to be an indication that the structure of polypyrrole samples prepared by electrochemical methods are more properly oriented and less contaminated.
Conclusion

Thermal and X-ray diffraction studies of polypyrrole prepared by electrochemical and chemical methods had been carried out. It was found that polypyrrole sample prepared by electrochemical methods are thermally more stable and structurally more amorphous than those prepared by chemical methods.
References

