Thermal stability of polypyrrole prepared from a ternary eutectic melt

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Abstract

Polypyrrole is prepared electrochemically from a room temperature ternary eutectic melt consisting of acetamide, urea and ammonium nitrate. The temperature effects of conductivity of polypyrrole are analyzed by Arrhenius and Mott equations to understand its conduction mechanism. The thermal degradation of both doped and dedoped samples of the polypyrrole in air and N2 atmosphere has been followed using thermogravimetric (TG) and differential thermal analysis (DTA). The kinetic analysis of the TG data has been carried out to obtain information on the energy of activation for the polymer decomposition.

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1. Introduction

Excellent reviews on polypyrrole and its chemistry are available in literature [1–4]. During the last two decades, investigations have centered mainly on improvement of the physical properties of polypyrrole such as processibility and stability. Serious research on functionalized polypyrroles, blends, composites and on the preparation of soluble dispersions of polypyrrole resulted in many useful publications [5–8]. Polypyrrole has been identified for certain specific applications such as rechargeable batteries, EMI shielding, conducting textiles, electrochmemoehanical devices, electrocatalysis and as membranes for gas and liquid separation processes [3,9].

Solvents have a strong influence on the synthesis and the resulting properties of polypyrrole. In most cases, polypyrrole is prepared from electrolytic solutions based on the aprotic organic solvents, although some work has been done in aqueous solutions [10–12]. High-quality polypyrrole films having conductivities higher than 500 S cm$^{-1}$ have been obtained in aqueous solutions of p-toluenesulfonyl salts [13]. Among organic solvents, acetonitrile has been the most commonly used [14,15]. However, films grown from dry acetonitrile are non-uniform and adhere poorly to the electrode surface. Better physical properties are obtained by increasing the water content of the acetonitrile solution [14,16]. Pickup and Osteryoung [17] synthesized polypyrrole electrochemically in an ambient-temperature molten salt consisting of a mixture of aluminum chloride and 1-methyl-(1,3-ethyl)-imidazolium chloride. The acid–base nature of the melt depended on its composition. Polypyrrole could be prepared only from the neutral melt.

This paper is aimed at presenting a systematic report on the charge transport mechanism and the thermal degradation properties of polypyrrole prepared from a room temperature acetamide–urea–ammonium nitrate ternary eutectic melt. In an earlier report, we discussed the effect of this molten solvent on the stability, structural and redox properties of polypyrrole [18]. The redox activity of the nitrate doped polypyrrole in the melt was higher than that in aqueous solutions. This was attributed to a favourable polymer film morphology facilitating the anion insertion–elimination. Another advantage is that the conductivity of the film prepared from the melt is about 10$^{-3}$ S cm$^{-1}$ suitable for certain applications requiring semiconducting films. The Schottky diodes fabricated with the polypyrrole prepared from this eutectic melt resulted in improved junction properties [19].

Several reports exist on the conductivity versus temperature data for polypyrrole doped with different counter
ions [20–30]. But only very few reports [26,28,31] have analyzed the applicability of Mott model for polypyrrole. The thermal stability of polypyrrole has been reviewed [32]. Despite considerable research [33–36] thermal degradation of polypyrrole is still not clearly understood as the presence of counter anion and their interaction with the polymer affects the degradation process. Recently a number of papers have appeared in literature on the thermal stability of polypyrrole composites [37–40].

2. Experimental

The ternary melt was prepared as follows [18,19]. Fifteen grams vacuum dried acetamide (Merck) was melted at 358 K and 10 g of urea (SD fine) was added to it and stirred. When the mixture became homogeneous, 8.3 g of ammonium nitrate (Merck) was added and stirred till the solution was clear.

Pyrrole (SRL) was purified by vacuum distillation. Polypyrrole was obtained on a platinum (1 cm²) substrate by applying a constant potential of 0.55 V versus Ag, AgCl/Cl⁻ (saturated) from the ternary melt containing 0.5 M pyrrole.

A PAR potentiostat/Galvanostat, Model 263A instrument was used for electrodeposition. The polypyrrole powder sample was pressed into a pellet using a Perkin-Elmer hydraulic press by applying a pressure of 6 tonnes. The resistance of the pellet was measured in the temperature range between 78 and 440 K by two probe method using a digital multimeter (Model 195 A, Keithley Instruments Ltd., USA). A liquid nitrogen bath cryostat (Model DP-422, Scientific Solution, Mumbai, India) was used for low temperature resistivity measurements (78–300 K). The cryostat consisted of a sample chamber surrounded by vacuum isolation chamber. The sample holder was fitted with a platinum temperature sensor (Pt-00) and a 25 Ω heater. GE varnish (which has good thermal conductivity at low temperature) was used for mounting the sample.

A mixture of toluene-ethanol (1:1) was used as the thinner. The electrical connections to the pellet sample were made by conducting silver paint. Temperatures above room temperature were attained by using a specially designed furnace for sample heating (INDFUR, Chennai, India).

The thermograms were recorded for both nitrate doped and dedoped samples in air/N₂ atmosphere at a heating rate of 10 K min⁻¹ using a thermal analyzer (NETZSCH-Geratebau GmbH STA 409 PC). Dedoped sample of the polymer was obtained by treatment with 0.1 M ammonium hydroxide for about 6 h.

3. Results and discussion

3.1. Temperature dependence of conductivity

The room temperature conductivity of the dry polymer sample was measured to be $5.7 \times 10^{-2}$ S cm⁻¹. The increase in conductivity with rise in temperature from 78 to 257 K is typical of semiconductors (Fig. 1a). The conductivity reaches a maximum at 257 K and thereafter there is a gradual decrease in conductivity.

The temperature dependent conductivity data can be fitted to Arrhenius equation of conductivity [3]:

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

where $E_a$ is the activation energy. The $\ln(\sigma)$ versus $T^{-1}$ plot shows (Fig. 1b) two linear segments with slopes of 0.0108 eV (77–150 K) and 0.0195 eV (150–257 K).

The conductivity begins to decrease at 257 K, which is quite lower than the temperature expected for dopant elimination. Such conductivity maxima were attributed to the relaxation processes in the polymer chains [41,42]. Although the mobility of the charge carriers are expected to increase with increasing temperature in the conjugated polymers, the...
The electrical conductivity of polypyrrole-perchlorate in the temperature range between 4 and 350 K for two polypyrrole conduction mechanisms must be predominantly the same in both materials. The hopping distance was 3.98 Å for the high conductivity sample and 5.22 Å for the low conductivity sample. The authors concluded that the Mott conductivity was observed at higher temperature for both types. The $T_0$, $K_0$ and $N(\varepsilon_F)$ were, respectively, $4.6 \times 10^4$ K, 920 S cm$^{-1}$ K$^{-1/2}$ and 1.67 $\times 10^{23}$ eV$^{-1}$ cm$^{-3}$ for the high conductivity sample. In another study by Sato et al. [26], the electrical conduction mechanism of polypyrrole films containing various counterions ($\text{BF}_4^-$, $\text{PF}_6^-$, $\text{ClO}_4^-$, $\text{CF}_3\text{SO}_3^-$, $\text{TsO}^-$) was investigated. Above 100 K the temperature dependence of electrical conductivity obeyed the Mott equation based on variable range hopping. The $T_0$ increased as the size of the counter ion increased while $K_0$ was independent of the size. Inversion of temperature dependence was observed for polypyrrole-hexafluorophosphate film below 20 K suggesting a metallic behaviour.

The analysis of results obtained in the present study shows that the data fitted the Mott equation better than the Arrenhius empirical equation. It is inferred that variable range hopping, rather than nearest neighbour hopping can best explain the conduction mechanism in polypyrrole-nitrate prepared from the ternary melt.

**3.2. Thermal studies**

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) can be used to assess the thermal stability of the polymer. There have been very few reports on the thermogravimetry of polypyrrole. Mohammad et al. showed that polypyrrole doped with $\text{BF}_4^-$ ion lost weight in three indistinct steps in $N_2$ as well as in air [46]. Steps 1 and 2 were identical in $N_2$ as well as in air. Step 1 had a weight loss of 3% in the temperature range of 318–398 K in $N_2$ and similar in air. Step 2 ranged from 398 to 558 K with an additional weight loss of 19.5% in $N_2$ and same in air. Step 3 was monitored up to 973 K and was found to be incomplete with further weight loss of 29% in $N_2$ and 55% in air. Polypyrrole-tosylate exhibited thermal stability under $N_2$ showing a slight plateau (3–4% mass loss) between 408 and 453 K, with a continuing decrease in mass near 10–12% until 663 K. In air it showed an initial 4% loss upon heating followed by small change in mass loss near 423 K and a much larger change at 553 K [37]. The TG and DTA of polypyrrole-perchlorate showed a major decomposition at 523 K [30].

Fig. 2a and b shows the data obtained on the thermal stability of polypyrrole prepared from the ternary eutectic melt, in the doped and dedoped forms, respectively, in air. The TG of dedoped sample shows only one major weight loss step. There is a small weight loss of 10% below 383 K. A gradual weight loss of another 15% occurs between 383 and 673 K. Thereafter there is a rapid change in mass above 673 K, completing the degradation at 933 K. The TG of the doped sample also shows an initial 10% weight loss at temperatures below...
373 K. Above 473 K there is a rapid loss in mass. Twenty-five percent weight loss is completed even at a temperature below 573 K. This stage is inferred to be due to the loss of dopant ion from the polymer. The results show that the polymer is stable in air up to 673 K in the dedoped form and up to 553 K in the doped form. The TG and DTA data obtained in N2 atmosphere (Fig. 2c and d) show the polymer decomposition to occur between 752 and 1025 K. The dopant elimination at 463 K (Fig. 2c) is more distinct in N2 atmosphere than in air.

3.3. Kinetic analysis of TG data

Recently, we have discussed about the importance of kinetic analysis of TG data [47]. Knowledge of kinetic parameters, is one of the keys to determine the reaction mechanisms in solid phases. When changes in the mechanisms are observed, this can lead to a unique thermal behaviour and hence a better knowledge of the materials. Several mathematical methods are available in literature for calculating the kinetic parameters of solid-state reactions [48–51].

In this study, we have used Horowitz and Metzger [51], Coats and Redfern [52] and Chan et al. [53] methods to evaluate the non-isothermal kinetic parameters from the TG data. The Horowitz and Metzger method involves plotting double logarithm of the reciprocal of the weight fraction of the reactant versus temperature (Eq. (5)). A reference temperature \( T_s \) is defined such that \( T = T_s + \theta \) where \( T_s \) is experimental temperature when \( (w/w_0) \) is equal to 0.368 for a first order reaction. Thus, a plot of \( \ln(\ln( (w/w_0) )) \) against \( \theta \) shows a straight line whose slope is \( (E_a/RT_s^2) \), where \( E_a \) is the thermal activation energy:

\[
\ln \left( \ln \left( \frac{w_0}{w} \right) \right) = \frac{E_a \theta}{RT_s^2}
\]

Coats and Redfern derived an expression (Eq. (6)) for determining the energy of activation which contained the order of reaction as an important parameter. A plot of log10(−log10(1−α)/T²) against \( T \) should result in a straight line of slope \( -E_a/2.303R \):

\[
\log_{10} \left[ \frac{\log_{10}(1-\alpha)}{T^2} \right] = \log_{10} \left[ aR \frac{A}{E_a} \right] + \frac{2RT}{E_a} - \frac{E_a}{2.3R}.
\]

Chan et al. followed a much simpler method for evaluating \( E_a \) of polyaniline. They used the Arrhenius plot of log(\( k/w \))

<table>
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<tr>
<th>Table 1</th>
<th>Activation energy (( E_a ) in kJ mol⁻¹) for doped and dedoped polypyrrole in air and N2 atmosphere</th>
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<tr>
<td>Polypyrrole (experimental condition)</td>
<td>Horowitz and Metzger method</td>
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<tr>
<td>Doped (air)</td>
<td>50.2</td>
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<tr>
<td>Doped (air)</td>
<td>50.8</td>
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<tr>
<td>Doped (N2)</td>
<td>55.7</td>
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<td>Doped (N2)</td>
<td>55.6</td>
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versus $T^{-1}$ where $k$ is rate of weight loss (in % (original weight) min$^{-1}$) at temperature $T$, with $w'$ as the corresponding weight (in % (original weight)) of the polymer remaining. The slope is equal to $-\left(E_a / R\right)$.

Fig. 3 shows representative plots obtained from the kinetic analysis of the TG data of the doped polypyrrole in air. The activation energy values derived from the above such plots for the doped and dedoped polypyrrole in air and N$_2$ atmosphere are tabulated (Table 1).

The calculation of different values for the kinetic parameters when applying different methods for processing the same experimental data is one of the controversial kinetic aspects of thermal analysis presented and discussed by Brown in a recent work [54] Budrugeac and Segal [55] made a detailed analysis of the problems concerning the evaluation of the activation energy from non-isothermal data. They suggested that significant differences in the calculated $E_a$ values are due to the way in which the relations that form the basis of the integral methods are derived. These relations are derived considering that the activation parameters do not depend on $\alpha$ (degree of conversion). In the above review, the authors have shown that if $E_a$ depends on $\alpha$, the use of different methods leads to different values of the activation energy.

In the present study, the kinetic analysis using the three methods shows that for each sample under study, a trend is found regarding the magnitude of the $E_a$ values. The $E_a$ values determined from the Coats and Redfern method are always lower while the values obtained by Chan et al. method are higher compared to the results obtained by Horowitz and Metzger method. The differences observed among the $E_a$ values obtained using the three methods can be assigned to the different approximations of the temperature integral. These activation energies may not be the most correct, but give an idea on the range of kinetic parameters. For a serious kinetic study, the standard isothermal technique is still the recommended method. However, the present results can be treated empirically and can perhaps be used for comparative purposes. The activation energy data obtained by a particular method may still serve as a convenient means of comparing the relative thermal stabilities of the various polymers. From a complete analysis by the three methods for the polypyrrole in the present work, the Horowitz and Metzger method is recommended. The $E_a$ values obtained by this method for the polymer decomposition step from the TG data of doped and dedoped polymers in either air or in N$_2$ atmosphere are more consistent with each other than in the other two methods.

4. Conclusions

The Arrhenius and Mott parameters obtained from the analysis of the temperature conductivity data for polypyrrole indicates 3D variable range hopping (VRH) conduction mechanism instead of nearest neighbour hopping. Detailed thermal characterization shows that the polymer is stable in air up to 673 K in the dedoped form and up to 553 K in the doped form. In N$_2$ atmosphere, the polymer is thermally stable up to 750 K. From the kinetic analysis, the thermal activation energy for the decomposition of polypyrrole is estimated to be about 50 and 56 kJ mol$^{-1}$ in air and N$_2$ atmosphere, respectively.

References

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