Effect of Thermal Treatment on Electrical Conductivities of Polypyrrole Conducting Polymers*

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Received 14 May 2003; accepted 21 October 2003

ABSTRACT

Some polypyrrole free standing films or membranes doped with different electrolytes (aromatic sulphonated) were prepared from aqueous monomer solutions in order to investigate the effect of thermal treatment on their electrical conductivity. It was found that the nature of counterion has the most important effect on determining the electrical conductivity and stability of conductivity when the polymer is exposed to high temperatures. However, mild heating can improve conductivity of polypyrrole conducting polymers. In order to carry out thermal effect studies on conductivity and measure the thermal stability of the PPy film, a variety of anions were examined. It was found that when polypyrrole is being doped with aromatic sulphonates (mainly benzene or naphthalene sulphonates) as counterions, it produces flexible and smooth films that can be readily detached from working electrode as membrane and they have good mechanical properties. Other counterions such as inorganics (e.g., Cl−, SO42−), aliphatic surfactants (e.g., DS), and polymeric (PVS) produce films that are either impossible to remove from working electrode, or give brittle, and rough films.

INTRODUCTION

Electroactive, conductive polymer films can be generated on electrode surfaces by the oxidation of aromatic compounds such as benzene, and heterocycles. Because of the lower oxidation potential for pyrrole compared with other heterocyclic monomers, PPy is readily synthesized from a range of aqueous and non-aqueous solvents [1-2]. Polypyrrole conducting polymers usually find applications either as deposits on electrodes, free standing films and powdered form [3-8]. Some of these applications may

Key Words:

polypyrrole; membranes; counterions; electrical conductivity; thermal treatment.

(*) Part of this paper was introduced in ISPST, Tehran, 12-15 May (2003).
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demand high thermal stability [8]. Free-standing polypyrrole films or membranes incorporating a large variety of anions or counterions as dopants can be prepared from aqueous electrolytes [9]. Good films are typically not produced when the anion is a halide, because halides are fairly nucleophilic and they are easily oxidized. The highly nucleophilic anions such as cyanide, acetate and benzoate do not produce good quality films either and instead produce soluble products, which colour the reaction solution. The nucleophilic species react with the electrochemically generated radical cations of pyrrole. It has been reported [10] that the use of sulphonated aromatic counterions during synthesis produces materials with good mechanical properties, which can then be removed from the electrode.

EXPERIMENTAL

All the chemicals used were Analytical Reagent (AR) grades and were used as purchased except pyrrole (Sigma), which was used after distillation. All polymerization solutions were prepared in Milli Q- deionized water. A Princeton Applied Research (PAR) Potentiostat / Galvanostat (Model 363) was employed for electropolymerizations. Scanning electron microscopy (SEM) photographs were obtained using a Hitachi S 450 and a Leica S 440 instruments.

The counter ions selected to prepare free standing films were the para substituted forms of the sodium salts of benzenesulphonate. A polymeric anion (PVS) was also used in this investigation. The chemical structures of the anions (sodium salt) used in this work are given in Scheme I.

(BS)=Benzenesulphonate, (TS) = toluenesulphonate, (SB) = Sulphobenzoic acid, (PVS) = polyvinylsulphonate, (DBS) = Dodecylbenzenesulphonate, (HBS) = hydroxybenzenesulphonate, (ABS) = aminobenzene-sulphonate, (NDS) = 1,5-naphthalenedisulphonate, (ADS) = 2,6-anthraquinonedisulphonate.

Electropolymerization was carried out galvanostatically using a current density of 2mA/cm². Polymerization solutions were prepared from 0.2 M pyrrole as monomer in 0.05M aqueous solutions of the counterions listed in Scheme I.

A single compartment electrochemical cell was used for electropolymerization. This cell consisted of a stainless steel plate working electrode, RVC (5 × 10 × 0.5cm) auxiliary electrode and an Ag/AgCl (3M NaCl) reference electrode. An electrochemical cell was used for preparing polypyrrole membranes and it is shown in Figure 1.

The cell solutions were deoxygenated using high purity nitrogen before electropolymerization. The thickness of the films (4-5 µm) was controlled by checking the total charge passed during electropolymerization (Q = It) or duration of electropolymerization. The polymerization time was 12 min. After polymerization, the polymer films were peeled off the working electrode, washed thoroughly with Milli-Q
water and finally dried at room temperature before characterization and thermal treatment.

The minimum thickness necessary to prepare PPy as free-standing films or membranes with adequate mechanical properties was found to be 4 µm. Increasing the thickness had the effect of decreasing the conductivity of the films. Dry state conductivity (dc) of the polymers was determined using a four-point probe technique. In this work, a four-point probe (standard design) was used for measuring the dry state conductivity.

The determination of the film thickness (X) is very important and it is the major source of error in the technique. So a very accurate digital multimeter was used to measure the potentials. The film thickness was measured using a digital micrometer (Mitutoyo) with a resolution of 1 µm. Thermal treatment of samples was carried out using a special home-made tubular furnace equipped with a temperature programmer and a nitrogen flow through the system was used for thermal treatment of polymer samples in dry air or nitrogen atmosphere (Figure 2).

RESULTS AND DISCUSSION

Conductivity measurements of the samples before and after thermal treatment were carried out at room temperature under atmospheric conditions using a standard four-point probe. This method can be applied to all materials that exhibit volume resistivity in the range of 1-107 Ω-cm [11]. In this method, a current is forced to flow between the pair of outer contacts as shown in Figure 3. This generates a potential difference between the two inner contacts, proportional to the current and the resistivity of the material. The current should be applied carefully, with regard to the resistivity of the sample. Applying a high current to a resistive polymer may damage the polymer. In the case of PPy films, which have good conductivity (20-100 S/cm); a current between 0.5 to 1 mA is suitable. In the case of resistive materials, the current should be sufficiently low (e.g., 0.1mA or less) to ensure that the heat evolved is small as this may damage or destroy the polymer.

Where, A and B present current electrodes and C and D are potential measuring electrodes, embedded in an electrical insulating material such as epoxy resin (A, B, C, D electrodes were prepared from copper). E is the strip of specimen. The equation (second) used for calculation of the electrical conductivity of samples can be drawn from Ohm’s law and it is shown below:

\[
\sigma_v = \frac{1}{R_v} = \frac{Z_i}{X \times Y \times E}
\]

\(R_v = \) Volume resistivity (S.cm), \(\sigma_v = \) volume con-
ductivity (S/cm), $Z$ = distance between inner points or potential electrodes (cm), $i$ = DC current applied between outer electrodes (mA), $X$ = thickness of the conducting polymer film (cm), $Y$ = width of the conducting polymer film (cm), $E$ = potential difference over inner electrodes (mV).

In this investigation, the samples used for 4-point probe analysis had $Y = 0.5$ cm, $X = 5$ and $L = 6$ cm dimensions and the current used was $1mA$.

**Preparation of PPy as Free-standing Films or Membranes**

Among the counterions used for preparation of PPy membranes only $p$-toluene sulphonate (PTS), $p$-hydroxybenzenesulphonate (HBS), $p$-dodecylbenzenesulphonate (DBS) and naphthalene disulphonate (NDS) anions produced polymers of adequate mechanical strength to allow them to be peeled from the electrode substrate.

Aromaticity in the structure of counterions seems to be important for preparation of PPy as free-standing films or membranes with good mechanical properties. For example, we found that the DBS (aromatic structure) anion unlike DS or PVS (aliphatic structure) can produce free standing films of PPy with good mechanical properties.

Using $p$-aminobenzene sulphonate (ABS) no polymerization occurred. This was probably due to the nucleophilic nature of the electrolyte, which reacts with radical monomer cations formed during monomer oxidation [12].

Benzenesulphonate (BS) and $p$-sulphobenzoate (SB) anions produced films with poorer mechanical properties than PPy/PTS films. However, it was observed that the conductivity and mechanical properties of PPy/SB improved considerably when gold foil was used as working electrode instead of stainless steel. The nature of working electrode is a critical consideration for preparation free-standing films of PPy. Since the films are produced by an oxidative process, it is important that the electrodes should not be oxidized concurrently with the monomer. Therefore, the mechanical properties of the PPy films prepared as free-standing films are strongly dependent on the nature of working electrode (WE), counterion, substitutions, and the position of the substituents. The substituents in arylsulphonates and their positions affect hydrophobicity or hydrophilicity and the symmetry of the counterion, respectively. The nature of substituent in arylsulphonates (counterion) affect the mechanical properties of the PPy membranes.

Anthraquinone disulphonic acid (ADS) electrolyte produced very brittle films that could not be peeled from the electrode as a membrane. Also, monomer solution immediately changed colour when a constant current was applied to initiate electropolymerization. On the other hand, ADS electrolyte was not electrochemically stable, so it was not a suitable dopant for PPy.

**Effect of Thermal Treatment on Conductivity of PPy Films**

It was found that thermal treatment affects the electrical conductivity of polypyrrole films. As the results show (Table 1), the change in conductivity through thermal treatment is greatly dependent on the nature of the counterion incorporated during synthesis.

The conductivity of PPy/DBS after treatment at 150°C under N$_2$ increased by about 60%. The same treatment resulted in a 36% increase for PPy/PTS. By contrast, decay in conductivity of about 50% was obtained for the PPy/PVS film.

Thermal treatment of PPy/PTS membranes from room temperature to 200°C produced a 30-40% improvement in film conductivity. However, at temperatures above 200°C a reversal of this trend was resulted. For example, after heating at 250°C for 1 h the con-

<table>
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<th>Anion</th>
<th>As grown</th>
<th>$\sigma$ (S/cm)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>BS</td>
<td>45</td>
<td>49</td>
</tr>
<tr>
<td>PTS</td>
<td>80</td>
<td>96</td>
</tr>
<tr>
<td>HBS</td>
<td>110</td>
<td>115</td>
</tr>
<tr>
<td>SB</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>NDS</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
<td>DBS</td>
<td>25</td>
<td>32</td>
</tr>
<tr>
<td>PVS</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

(i) Conductivity measurements were carried out after heat treatment under nitrogen, at room temperature. (ii) Mechanical properties after thermal treatment were not adequate to allow conductivity of the films to be measured.
ductivity of PPy/PTS dropped to 55 S/cm and after thermal treatment at 300°C it decreased further to 20 S/cm. As these results indicate, the conductivity of PPy/BS film is not stable at temperatures at or above 200°C. There are differences in the thermal stability of conductivity of PPy films doped with different aryl-sulphonates due to the differences in the properties of the counterions (e.g., size, geometry, charge and electronic structure).

The conductivity of PPy/HBS was almost unchanged when the polymer was treated up to 200°C under N₂. However, after 250°C, its conductivity was reduced by about 26%. The major loss in conductivity was observed when the polymer was treated at 300°C as a drop of 80% was measured. The TGA results indicated that the decay in conductivity at T ≥ 250°C is mainly due to the thermal decomposition of the polymer [13].

The conductivity of PPy/PVS was not very stable at relatively low temperatures. The conductivity decreased by about 45-50% when the polymer was treated at 150°C for 1 h under N₂. The degradation in conductivity may not be always due to the degradation of the polymer. The poor thermal stability of conductivity in PPy/PVS may be due to the thermal degradation of the dopant.

The improvement in electrical conductivity in polypyrrole films by thermal treatment is assumed to be due to annealing effects, which improve the local ordering within the film [14]. Annealing is a phase transition with recrystallization that has the effect of decreasing the number of defect sites. Also, with thermal treatment, volatile-trapped fragments (low MW polymers or oligomers) or solvent, which act as insulator gaps in the polymer matrix are removed. This produces a more homogeneous and compact polymer surface.

Some structural or morphology changes resulting from the interactions of counterion with polymer at elevated temperatures may also occur [15-16]. The effect of thermal treatment on conductivity of PPy films in air atmosphere was then considered (Table 2).

As shown in Table 2, PPy/PTS showed higher thermal stability than PPy/NDS or PPy/PVS films in the air atmosphere but it had poorer stability than PPy/HBS films. However, the thermal stability of all polymers examined was poor after exposure to elevated temperature in the oxidative atmosphere (air). For example, the conductivity of PPy/PTS was stable up to 200°C in nitrogen. By contrast, the conductivity loss was about 75% after 1 h treatment at 200°C in air (not shown in Table).

The degradation of film conductivity at elevated temperatures in air atmosphere has also been found to be extremely time dependent. For example, it was found that the conductivity of PPy/PTS was 37% lower after 1 h and 75% lower after 2 h of thermal treatment at 150°C in the air atmosphere.

It has been suggested [17] that decreases in conductivity in air follow a first-order reaction involving the formation of a carbonyl group (as shown in Scheme II), which can act as an electron trap, leading to a decrease in electrical conductivity. This mechanism may be more effective for those polymers, which have larger surface areas, e.g. chemically synthesized polypyrroles.

It may be concluded that the chemical reaction of the polymer with oxygen in air is the main reason for conductivity loss in PPy films in air environments. As the results show, the dopant type plays an important role in the degradation of electrical conductivity and thermal stability. The importance of the counterion in

<table>
<thead>
<tr>
<th>T (°C)*</th>
<th>PTS</th>
<th>HBS</th>
<th>NDS</th>
<th>PVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ₁ (S/cm)</td>
<td>80</td>
<td>100</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>σ₂ (S/cm)</td>
<td>90</td>
<td>100</td>
<td>21</td>
<td>8.5</td>
</tr>
<tr>
<td>σ₃ (S/cm)</td>
<td>52</td>
<td>77</td>
<td>13</td>
<td>5</td>
</tr>
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</table>

σ₁ = Conductivity before thermal treatment; σ₂ = Conductivity after thermal treatment at 105°C for 1 h; σ₃ = Conductivity after thermal treatment at 150°C for 1 h.

Scheme 2. A suggested mechanism for oxidative degradation of conductivity in PPy.

![Scheme 2](image-url)
Figure 4. SEM Photographs of PPy (a) PPy/PTS before heat treatment, (b) PPy/PTS after heat treatment, (c) PPy/DBS before heat treatment, (d) PPy/DBS after heat treatment (e) PPy/NDS before heat treatment, (f) PPy/NDS after heat treatment. Heat treatment was carried out at 150°C for 1 h under N₂.
determining the thermal stability of PPy films has also been reported by other investigators [15]. It has been reported that any process that changes or hinders the chain hopping conduction mechanism can cause degradation of the film's conductivity.

Reaction of the main polymer chain with oxygen, water, or damaging radiation (e.g., UV) can lead to an irreversible loss of conjugation and, therefore, conductivity.

**SEM Analysis**

Scanning electron microscopy results show that the surface morphology of PPy and the structures of the PPy films are not affected significantly by the thermal treatment in nitrogen up to 150°C (Figure 4). This is in good agreement with our previous data, which indicated no decrease in film conductivity up to this point. It may be, however difficult to detect minor morphological changes after thermal treatment using this technique or low magnifications.

No significant morphological changes were observed for PPy/PTS films thermally treated with temperatures of less than 300°C in nitrogen. However, thermal treatment at 300°C resulted in a less ordered structure accompanied by deterioration of mechanical properties due to the chemical decomposition of the polymer [13]. We have already shown from TGA studies that thermal degradation of conductivity did not necessarily occur at the decomposition temperature of the dopant or the counter ion [13]. More conductive PPy films have been found thermally and environmentally, more stable. Environmental stability is a key factor for successful applications of conducting polymers, so PPy conducting polymers such as PPy/PTS or PPy/HBS seem to be good candidates for application in future technology.

It has also been reported [18] that, mechanical properties, electrical conductivity and thermal stability of PPy conducting polymers are also dependent on some other important factors such as: the solvent used for electropolymerization, temperature of synthesis and chemical post-treatments.

**CONCLUSION**

Many factors affect conductivity of PPy films. Among them, the counterion incorporated into the polymer during preparation has the greatest effect on determining the conductivity and thermal stability of the PPy conducting polymers. In fact the counterions (dopant anion) employed during electropolymerization governs general properties of PPy films.

Aromatic sulphonates (mainly benzene-sulphonates) produce polymer films with higher thermal stability than those containing other counterions (e.g., aliphatic, polymeric, and inorganic anions). The more thermally, chemically and electrochemically stable counterions produce more thermally stable polymers too. More thermally stable PPy films were also found to be more environmentally stable.

Any chemical and electrochemical interaction between dopant and polymer will result in poor conductivity stability at elevated temperatures. The easily oxidizable organic or inorganic counterions were found to be not suitable for preparation of PPy as free standing films. In addition, the electrolyte should not have corrosive effect on the working electrode. Electropolymerization of polypyrrole CEP’s is also limited to using high nucleophilic anions or substituents such as -NH₂.

The rate of thermal degradation of film conductivity is also very much dependent on temperature, atmosphere and duration of heat exposure. The decay of PPy polymer conductivity occurs much faster in oxidative atmospheres, such as air, compared to the decay observed in inert atmospheres such as nitrogen.

The thermal treatment of polypyrrole conducting polymer films in the inert atmosphere can produce some improvements in the electrical conductivity.

The increase in conductivity may be related to annealing effects, which improve the local ordering within the film and also facilitate the removal of non-polymeric impurities, which become trapped in the polymer matrix during growth. However, the amount of conductivity change is greatly dependent on the nature of the dopant anion that is incorporated during growth.

**REFERENCES**