

# Thermal Stability Characterization of PPy/Cl Conducting Polymer Using Inverse Gas Chromatography Technique

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PPy/Cl was prepared chemically on the surface of reticulated vitreous carbon (RVC) as solid support.  $\text{FeCl}_3$  was used as oxidant for chemical oxidation of pyrrole monomer adsorbed on the surface of RVC particles. Thermal stability of PPy/Cl conducting polymer coated chemically on the surface of RVC as stationary phase and polarity changes with temperature were determined using inverse gas chromatography (IGC) technique.

**Key Words:** Thermal stability, Polypyrrole/chloride, Conducting polymer, Inverse gas chromatography technique.

## INTRODUCTION

Inverse gas chromatography (IGC) has been used as a method of characterization for polymers, fibres and other materials<sup>1,2</sup>. The term inverse indicates that the examined non-volatile material (*e.g.*, a polymer blend or modified silica) to be investigated is placed in a chromatographic column and studied using known test probes, in contrast to the typical use of analytical gas chromatography. Carefully selected test solutes are injected into the flow of an inert carrier gas and transported over the surface of the material. IGC utilizes the same processes as GC.

The properties of the solid phase that is packed inside the column are unknown, but the properties of the carrier gas and injected solutes are known. The retention time ( $t_R$ ) and peak elution profiles of standard solutes is then used to provide information on the molecular interactions occurring. These interfacial forces range from strong covalent or ionic chemical bonds to weak van der Waals interactions. Stronger interactions with the support will tend to move more slowly through the column than those molecules with weaker interactions. It has been reported<sup>3</sup> that polymeric stationary phases using PPy conducting polymers can be synthesized on a wide range of substrates electrochemically. Commercial carbon particles such as graphite or reticulated vitreous carbon (RVC) particles have proved useful due to mechanical stability and chemical inertness.

## EXPERIMENTAL

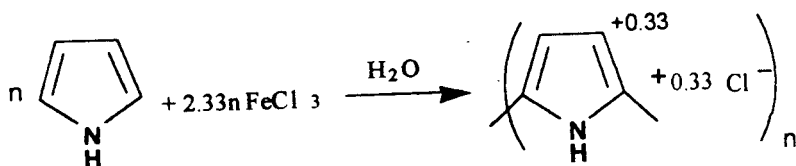
All chemicals were of analytical reagent (AR) grade purity unless stated otherwise. Pyrrole (Sigma) was distilled before use. PPy/Cl on reticulated vitreous carbon (RVC) particles was prepared using chemical polymerization as follows: 1 g of pyrrole was dissolved in 50 mL  $\text{CH}_2\text{Cl}_2$  and mixed with 9 g RVC particles (60–120 mesh). The solvent was evaporated. The particles were then mixed with a solution of 0.5 M  $\text{FeCl}_3$  (used after filtration) in water for 1 h at about  $0^\circ\text{C}$  using an ice bath. The  $\text{FeCl}_3$  to pyrrole molar ratio was chosen 2 : 1. Particles were separated by flotation. The coated RVC particles were washed completely with distilled water, dried, sieved and packed into the gas chromatography (GC) column. Some *n*-alkanes were selected as test probes. The volume of standards (*n*-alkanes) injected was 0.05  $\mu\text{L}$ . Conditioning time for each temperature was 15 h.

The  $\text{N}_2$  gas flow rate was constant at 30 mL/min. Inverse gas chromatography was carried out using a Hewlett Packard Model 419 gas chromatograph with a flame ionization detector (FID).

## RESULTS AND DISCUSSION

Chemical polymerization is a simple and fast process with no need for special instruments. Bulk quantities of polypyrrole (PPy) can be obtained as fine powders using oxidative polymerization of the monomer by chemical oxidants in aqueous or non-aqueous solvents<sup>4–6</sup> or by chemical vapour deposition<sup>7</sup>.

The chemical polymerization of pyrrole appears to be a general and useful tool for the preparation of conductive composites<sup>8,9</sup> and dispersed particles in aqueous media<sup>10,11</sup>.  $\text{FeCl}_3$  has been found to be the best chemical oxidant and water is the best solvent for chemical polymerization with respect to desirable conductivity characteristics. The optimum initial mole ratio of Fe(III)/Pyrrole for polymerization by aqueous iron(III) chloride solution at  $19^\circ\text{C}$  has been reported to be 2.25 or 2.33<sup>12</sup>. The overall stoichiometry resulting from chemical polymerization of PPy with ferric chloride oxidant can be shown<sup>4</sup> as:



During chemical polymerization of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions from the reaction solution. These counterions are usually the anion of the chemical oxidant or reduced product of oxidant. For example, when  $\text{FeCl}_3$  or  $\text{Cl}_2$  are used as oxidants,  $\text{Cl}^-$  ion is incorporated as counterion or when  $\text{I}_2$  is used as oxidant,  $\text{I}_3^-$  ions are incorporated into the polymer matrix. However, the use of chemical polymerization limits the range of conducting polymers that can be produced since only a limited number of counterions can be incorporated. It has been found that factors such as solvent, reaction temperature, time, nature and concentration of the oxidizing agent, affect the

oxidation potential of the solution<sup>4,5</sup> and influence the final conductivity of the chemically synthesized polypyrrole.

### Effect of thermal treatment on polarity changes of PPy/Cl using IGC technique

Surface polarity and thermal stability of conducting polymers can be determined using the polymer as a stationary phase in gas chromatography. The effect of thermal treatment on the polarity of PPy/Cl as determined using this approach was considered (Table-1).

TABLE-1  
EFFECT OF THERMAL TREATMENT ON RETENTION TIME ( $t_R$ ) OF COLUMN USING PPy/Cl AS STATIONARY PHASE

| $T_{con.}$<br>(°C) | $T_{col.}$<br>(°C) | $t_R = (\text{min})$ |        |        |           |
|--------------------|--------------------|----------------------|--------|--------|-----------|
|                    |                    | $nC_6$               | $nC_7$ | $nC_9$ | $nC_{11}$ |
| 110                | 100                | 0.15                 | 0.18   | 0.25   | 0.46      |
| 130                | 100                | 0.13                 | 0.17   | 0.23   | 0.46      |
| 130                | 120                | 0.12                 | 0.15   | 0.18   | 0.29      |
| 150                | 120                | 0.14                 | 0.18   | 0.34   | 1.02      |
| 200                | 120                | 5.70                 | 8.61   | 13.93  | < 20      |

(i)  $T_{con.}$ ,  $T_{col.}$  stand for conditioning and column temperature respectively. The volume of standards injected was 0.05  $\mu\text{L}$ . Conditioning time for each temperature was 15 h. The  $\text{N}_2$  gas flow rate was constant at 30 mL/min. (ii)  $nC_6$ ,  $nC_7$ ,  $nC_9$  and  $nC_{11}$  stand for normal alkanes.

Failure to elute McReynolds polar test probes<sup>2</sup> such as ethanol, acetone and short retention time for  $n$ -alkanes indicate that the polymer is highly polar. Strong interactions such as H-bonding between polymers and alcohols can be a reason for a long  $t_R$  or very broad peak. Thermal treatment of PPy/Cl up to 130°C results in increased polarity since the retention of non-polar test probes decreases. After conditioning the column at temperatures above 130°C the polarity of the polymer decreases. The polymer (PPy/Cl) starts to decompose at 150°C or above.

After conditioning at 200°C the pores of column were filled with the products of degradation and the column failed to elute even simple alkanes. This is most likely due to irreversible oxidation of the polymer and the loss of  $\text{Cl}^-$  (counterions) as volatile HCl, which makes the polymer more non-polar. Increasing capacity factor  $K'$  clearly shows this phenomenon (Table-2).

TABLE-2  
EFFECT OF CONDITIONING TEMPERATURE ON CAPACITY FACTOR OF PPy/Cl (PREPARED CHEMICALLY)

| $T_{con.}$ (°C) | $T_{col.}$ (°C) | $K'^*$ |
|-----------------|-----------------|--------|
| 130             | 120             | 0.46   |
| 150             | 120             | 0.54   |
| 200             | 120             | 22.00  |

Capacity factor ( $K'$ ) as calculated according to  $K' = (t_R - t_M)/t_M$ . The dead time ( $t_M$ ) was measured by injecting methane.

Increase in the retention time or capacity factor of PPy/Cl after treatment at 200°C indicates that the structure of this polymer is not stable at this temperature. Observation of smoky evolving gases which were also acidic (tested by wet pH paper) is a clear indication of thermal decomposition of this polymer at 200°C. It can be concluded that decomposition of polymer which is accompanied by loss of chloride ions (dopant) as HCl gas occurs above 150°C. The results obtained in this investigation are consistent with reported work<sup>13</sup> and have already shown that PPy conducting polymers doped with small inorganic dopants such as Cl<sup>-</sup> suffer from poor thermal stability.

Using TGA and cyclic voltammetry (CV) analyses, it has also been reported that PPy/Cl is not chemically stable at temperatures of 150°C and above<sup>14</sup>. After thermal treatment at 150°C, electroactivity of PPy/Cl was lost completely<sup>14</sup>. The dopant chloride ions are removed as HCl at elevated temperatures. Some other reactions such as chlorination of pyrrole ring may also occur at high temperatures.

## Conclusions

Inverse gas chromatography seems to be a fast and suitable technique to investigate thermal stability of conducting polymers and the effect of thermal treatment on the polarity of the test polymer. Because of insolubility and infusibility of polypyrrole conducting polymers many of the conventional methods of analysis that require solubility cannot be applied to these materials. Therefore, IGC is a versatile technique for investigation of thermal stability of polypyrrole conducting polymers and the effect of thermal treatment.

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