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The Synthesis, Characterization and DC Electrical Conductivity of Polypyrrole-Zirconium Complex

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Polypyrrole-zirconium complex has been synthesized by reacting 2-amino-3,4-dicyano-5-mercaptopyrrole with zirconium nitrate in absolute ethanol under reflux for 24 h. The product has been characterized by elemental analyses, FTIR spectroscopy, in addition to thermal analysis (TGA and DSC) and its solubility has been investigated. The DC electrical conductivity variation of polypyrrole-zirconium complex has been studied in the temperature range 300–500 K after annealing for 24 h at 100°C and doping with I_2, $FeCl_3$ and $CuCl_2 \cdot H_2O$ for comparison. An attempt has been made to interpret the DC electrical conductivity behavior and thermal properties to chain length, dopant used, polymer structure and attached groups.

Keywords polypyrrole-zirconium complex, DC electrical conductivity, doping, thermal analysis and activation energies

Introduction

The successful commercial applications of electrically conducting polymers attracted the attention of researchers quite a while ago and has triggered intensive research (1–4).

Polypyrrole (5) is among the most promising electrically conducting polymers. Many polymer metal conducting polymers have been synthesized and also studied (6, 7). The conductivity of the zirconium polymers has been studied in two cases: conjugated and less conjugated polymer. The conductivity of the zirconium polymer with the conjugated benzidine derivative is slightly higher than the zirconium polymers with less conjugated structures (8). This study aims at studying a combination of pyrrole moiety linked with a zirconium ion forming a polypyrrole-zirconium complex.

This study is designed to investigate the action of zirconium on the electrical conductivity of polypyrrole-zirconium complex with zirconium as the connecting ions between the pyrrole units. Both the nitrogen of the cyano group and sulfur of the mercapto group play (8, 9) the same role as donors of electrons for coordination and improve the environmental and thermal stability of the polymer chains when present in the conjugated backbone (10).

It is well known that the introduction of cyano groups in the polymer main chain could improve the electron affinity of material (11, 12). On the other hand, the polymers

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substituted with a cyano group on the vinyl position will exhibit a lower energy level of LUMO (13, 14).

In this study, we report the syntheses, characterization, thermal analysis and DC electrical conductivity of polypyrrole-zirconium complex. The action of zirconium on thermal behavior, DC electrical conductivity and structure-property relationship of the polypyrrole-zirconium complex is studied.

The objective of this study is: 1) to synthesize and characterize (polypyrrole-zirconium complex), 2) present a comparative study of the DC electrical conductivity of the polymer complex and its change with temperature at 300–500 K, in the intrinsic and doped states, 3) to study the influence of the zirconium ion in the system, 4) to investigate the action of the different dopants in the DC electrical conductivity of the polymer complexes, and 5) to investigate the thermal properties of the polymer metal complex using TGA and DSC.

Experimental

Chemicals

The chemicals, synthesized or purchased (Aldrich Chemicals), were recrystallized twice before use. The solvents are reagent grade: dry absolute ethanol, DMF (BDH, Analar), and methanol (Fluka) are used as received.

Synthesis of Polypyrrole-Zirconium Complex

3,4-Dicyano-2,5-diaminothiophene (15) was used to synthesized 2-amino-3,4-dicyano-2-mercaptopyrrole (16) according to literature procedures.

The polymer-metal complex was synthesized by mixing equimolar quantities of the zirconium nitrate and 2-amino-3,4-dicyano-2-mercaptopyrrole (3 mmol) in the minimum amount of ethanol (20 ml) and refluxed for 24 h. The precipitated polymer is filtered, washed twice with ethanol and then dried in air for 24 h.

Instrumentation

The melting point was measured on an electro-thermal melting point apparatus. FTIR spectra were recorded using the KBr disc technique on a JASCO 410 FTIR Spectrophotometer. The elemental (CHN) analysis was performed using an Exeter CE-440 Elemental Analyzer. The zirconium content was determined by X-Ray Florescence (XRF) using Fe55 PCD 109 AM 241 as a radioisotope primary source. The thermal analyses (TGA and DSC) were carried out on STA 625 at 25 to 625°C under 30 ml nitrogen per minute and a heating rate of 10°C per min. The electrical conduction measurements and annealing were performed as described previously (17, 18).

Doping of the Polypyrrole-Zirconium Complex

Doping was done in two ways. The first method, doping by mixing, was performed according to the following procedure. The technique ensures homogeneity down to the scale of the individual grain of the material.

A 5wt/wt% of the dopants (I_2, $FeCl_3$ and $CuSO_4 \cdot 5H_2O$) were added to 1 ml of acetone. A specified amount (200 mg) of the polypyrrole-zirconium was immersed in the dopant solution and mixed thoroughly. The acetone was allowed to evaporate completely at room temperature. The specimen of the doped polypyrrole-zirconium was then pressed into compact discs for the DC electrical conductivity measurements.

The second method, chemical doping, was performed by dissolving the dopants (I_2, $FeCl_3$ and $CuCl_2 \cdot 2H_2O$) in the minimum amount of ethanol followed by the addition of an equivalent weight of polymer-zirconium complex. The mixture was refluxed for 20 min, filtered, dried in air for 24 h and then annealed in a vacuum oven for 24 h at 100°C, and compressed into pellets for electrical conductivity measurement.

Results and Discussion

Synthesis and Characterization

The polypyrrole-zirconium complex (Scheme 1) is prepared by the reaction of 2-amino-3,4-dicyano-2-mercaptopyrrole with zirconium nitrate in absolute ethanol under reflux for 24 h.

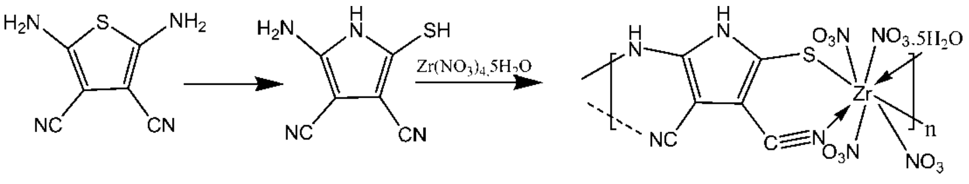
The color of the produced polypyrrole-zirconium complex ($C_6H_{12}N_8O_{17}SZr$) (mol wt) (calculated: 591.49) was very dark brown and the yield was 79%. The elemental analysis was consistent with the suggested structure: C, 12.2% calculated (12.5% found); H, 2.0% (2.3%); N, 18.9% (18.5%). The zirconium content was determined by X-ray Florescence (XRF) Calculated (Found) 15.4% (15.0%). The melting point was above 350°C. It was sparingly soluble only in DMF and in DMSO after heating.

FTIR Spectra

Figure 1 shows the IR spectra of the starting material (2-amino-3,4-dicyano-2-mercaptopyrrole) and polypyrrole-zirconium complex. The main IR bands are summarized in Table 1. The assigned absorption bands are consistent with the suggested structures for both compounds.

The main absorptions of 2-amino-3,4-dicyano-5-mercaptopyrrole are NH_2 and -NH- of the hetero-ring (19) (3442, 3340, 3242, 3179 cm^{-1}). The aromatic C=C and C=N vibrations are noted at 1636, 1598, 1530 and 1478 cm^{-1}. The C-N single bond is shown at 1094 cm^{-1}. The -CN triple bond is shown at 2225, 2212 cm^{-1}. The -SH is evident at 2520 cm^{-1}. The C-S single bond stretch appeared at 696, 657 cm^{-1}.

The IR spectra bands of polypyrrole-zirconium complex include the amino group and the -NH- single bond of the pyrrole ring, which are buried under the broad water absorption (3690–2600 cm^{-1}). The aromatic C=C and C=N vibrations are noted at 1638, 1541 cm^{-1}. The -CN triple bond is seen as a small absorption at 2235 cm^{-1}. The nitrate NO_3 group display an asymmetrical stretching appeared at 1654 cm^{-1}, while the



Scheme 1. The synthesis of the polypyrrole-zirconium complex.

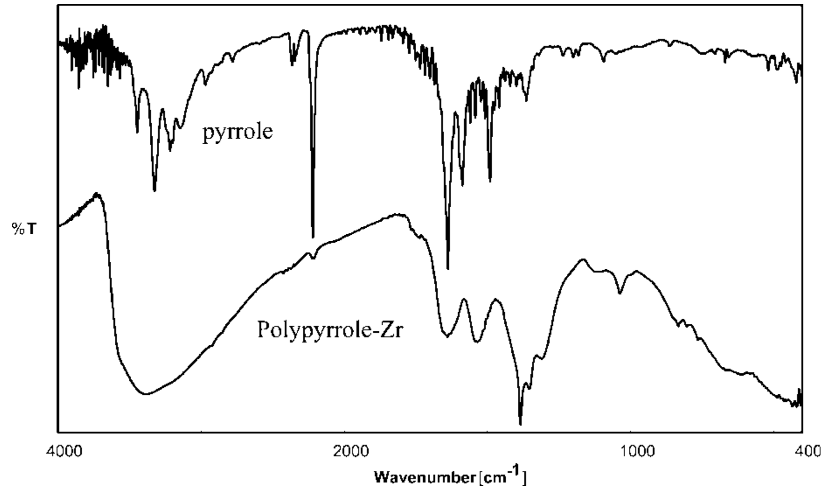


Figure 1. The FTIR spectra of the polypyrrole-zirconium complex.

symmetrical stretching appeared at 1384, 1305 cm^{-1}. The N-O stretch single bond is shown at 802 while the bending is shown at 764 cm^{-1}.

DC Electrical Conductivity

Figure 2 displays the DC electrical conductivity vs. 1/T for the annealed and non-annealed polypyrrole-zirconium complex together with the non-annealed polypyrrole-zirconium complex doped by mixing with three different dopants, namely I_2, $FeCl_3$ and $CuSO_4.5H_2O$. The highest DC electrical conductivity at ambient and higher temperatures was noticed for $FeCl_3$ doped material. Non-annealed polypyrrole-zirconium complex gave the lowest DC electrical conductivity at higher temperature. The second highest DC electrical conductivity was caused by the presence of $CuSO_4 \cdot 5H_2O$ at ambient and high temperature. The third highest DC electrical conductivity was noticed for I_2 doped polypyrrole-zirconium.

The non-annealed polypyrrole-zirconium complex and the non-annealed polypyrrole-zirconium complex doped with the three different dopants contain adsorbed water which was noted in the range 82–125°C by a negative slope.

Figure 3 shows The DC electrical conductivity vs. 1/T for the annealed and non-annealed polypyrrole-zirconium complex together with the annealed polypyrrole-zirconium complex chemically doped with three different dopants, namely I_2, $FeCl_3$ and $CuCl_2 \cdot 2H_2O$. The chemical doping of polypyrrole-zirconium complex did not show a great enhancement of DC electrical conductivity. This is attributed to the non-formation for any charge transfer complexes (20); the three dopants I_2, $FeCl_3$ and $CuCl_2 \cdot 2H_2O$ are similar in action and gave similar enhancement of electrical conductivity that did not respond to heat at high temperatures.

Table 2 summarizes the increase in electrical conductivity by heat between 300 and 500 K for the polypyrrole-zirconium complex in itsdoped and annealed states, for easy comparison. All the compounds start the DC electrical conductivity around 10^{-11} Scm^{-1} at ambient temperatures except the doped polypyrrole-zirconium complex by $FeCl_3$ 5% with mixing method, it is only the only one that gave 7×10^{-9} Scm^{-1}.

Table 1
The main IR bands of the polypyrrole-zirconium and start material

	C═C a, C═N	NH2+ NH − ring	C-N	C-S	S-H	N-O	N═O as.	N═O sy.	-CN	H_2O
Pyrrole	1636, 1598, 1530, 1478	3442, 3340, 3242, 3179	1094	696, 657	2520	—	—	—	2225, 2212	—
Polypyrrole-Zr	1638, 1541	Under water	1037	622	—	802, 764	1654	1384, 1305	2235b	3690, 2600 b

a = aromatic ring stretch, b = broad, as. = asymmetric stretch, sy. = symmetric stretch.

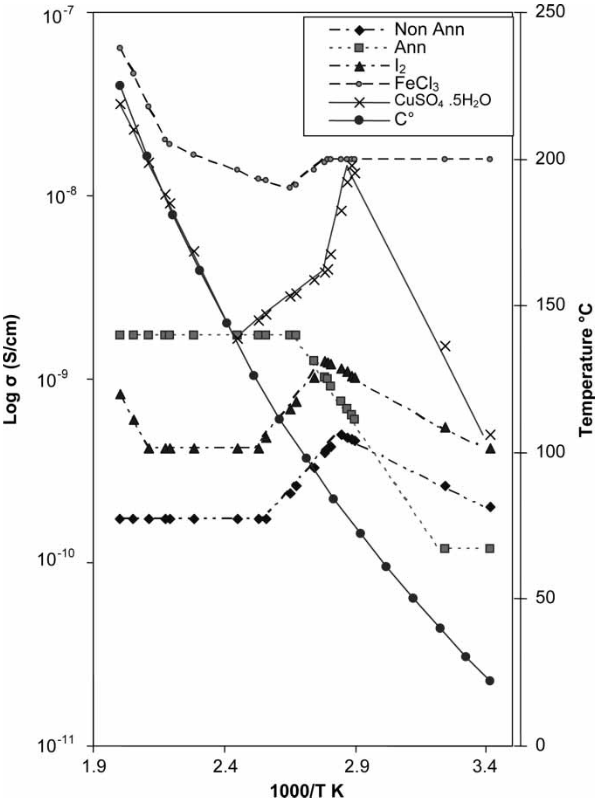


Figure 2. The DC electrical conductivity vs. 1/T for the annealed and non-annealed polypyrrole-zirconium complex together with the non-annealed polypyrrole-zirconium complex doped by mixing with three different dopants, namely I_2, $FeCl_3$ and $CuSO_4 \cdot 5H_2O$.

From Figure 4, the DC electrical conductivity vs. 1/T of doped polypyrrole-zirconium chemically and by mixing with I_2 together with the annealed polypyrrole-zirconium complex. The activation energy of the annealed polypyrrole-zirconium complex showed three segments with values of 0.00 eV (22–38°C), 0.41 eV (38–103°C) and 0.00 eV (103–225°C). The chemically doped annealed complex was heated at 100°C for 24 h; hence the presence of water was eliminated. The doped polypyrrole-zirconium by mixing showed four segments: 0.15 eV (22–87°C), (87–124°C), 0.0 eV (124–199°C) and 0.56 eV (199–225°C). After it eliminates the adsorbed or coordinated water in the second segment (87–124°C) the polypyrrole-zirconium became temperature independent 0.00 eV at 124–199°C, then the activation energy increased to 0.56 eV at 199–225°C.

From Figure 5, the chemically doped polypyrrole-zirconium with $CuCl_2 \cdot 2H_2O$ and annealed polypyrrole-zirconium showed three segments: 0.00 eV (22–74°C), 0.15 eV (74–137°C) and 0.0 eV (137–225°C). However, doping by mixing showed four segments: 0.56 eV (22–75°C),-eV (75–86°C),-eV (86–137°C) and 0.56 eV (137–225°C). Here again the loss of water was in the same range and showed a negative activation energy slope.

Figure 6 displayed the chemically doped polypyrrole-zirconium with $FeCl_3$ and annealed polypyrrole-zirconium. The doped polypyrrole-zirconium showed four

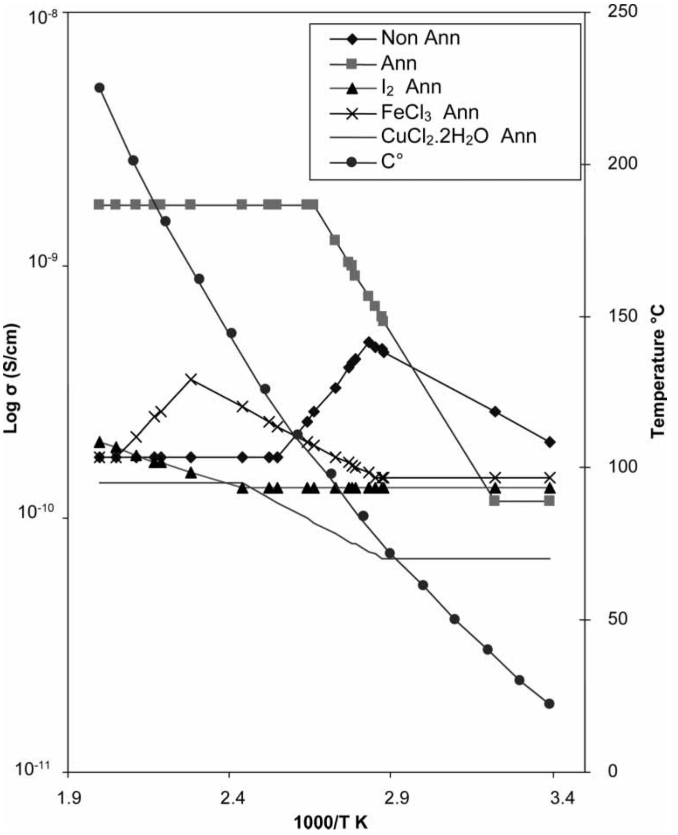


Figure 3. The DC electrical conductivity vs. 1/T for the annealed and non-annealed polypyrrole-zirconium complex together with the annealed polypyrrole-zirconium complex chemically doped with three different dopants, namely I_2, $FeCl_3$ and $CuCl_2 \cdot 2H_2O$.

segments: 0.00 eV (22–78°C), 0.12 eV (78–165°C),-eV (165–215°C) and 0.00 eV (165–225°C). The polypyrrole-zirconium when doped by mixing also showed four segments: 0.00 eV (22–85°C),- eV (85–105°C),- eV (105–186°C) and 0.56 eV (186–225°C).

The negative (−) activation energy of the segment of the doped polypyrrole-zirconium is caused by the loss of water. Annealing eliminates the presence of adsorbed or coordinated water in the polypyrrole-zirconium. The polypyrrole-zirconium doped by mixing was not annealed. Hence, water, adsorbed or coordinated to the complex, was evolved. The presence of water was confirmed in FTIR by a broad absorption. Similarly, its presence is confirmed in the TGA and DSC of the complex.

Activation Energies

The carriers available for the DC electrical conductivity are electrons and holes. Table 3 summarizes the activation energies for all the segments of the curves of the annealed

Table 2
The DC electrical conductivity of the annealed and non-annealed polypyrrole-zirconium with different doping

	Chemically doped/annealed $S\ cm^{-1}$		Doped by mixing/non-annealed $S\ cm^{-1}$	
	300 K	500 K	300 K	500 K
Polymer complex	4.0×10^{-11}	1.2×10^{-9}	1.2×10^{-10}	1.2×10^{-10}
I_2	6.0×10^{-11}	1.5×10^{-10}	3.1×10^{-10}	4.6×10^{-10}
$FeCl_3$	8.0×10^{-11}	1.2×10^{-10}	7.0×10^{-9}	4.2×10^{-8}
$CuSO_4 \cdot 5H_2O$	—	—	3.5×10^{-10}	2.5×10^{-8}
$CuCl_2 \cdot 2H_2O$	4.2×10^{-11}	7×10^{-11}	—	—

non-annealed and doped complex. To explain the curves of Figures 4 to 6, let us introduce Figure 7, which represents an energy schematic model based on the band theory for the annealed, non-annealed and doped polypyrrole-zirconium complex. It covers the whole temperature variation for the DC electrical conductivity.

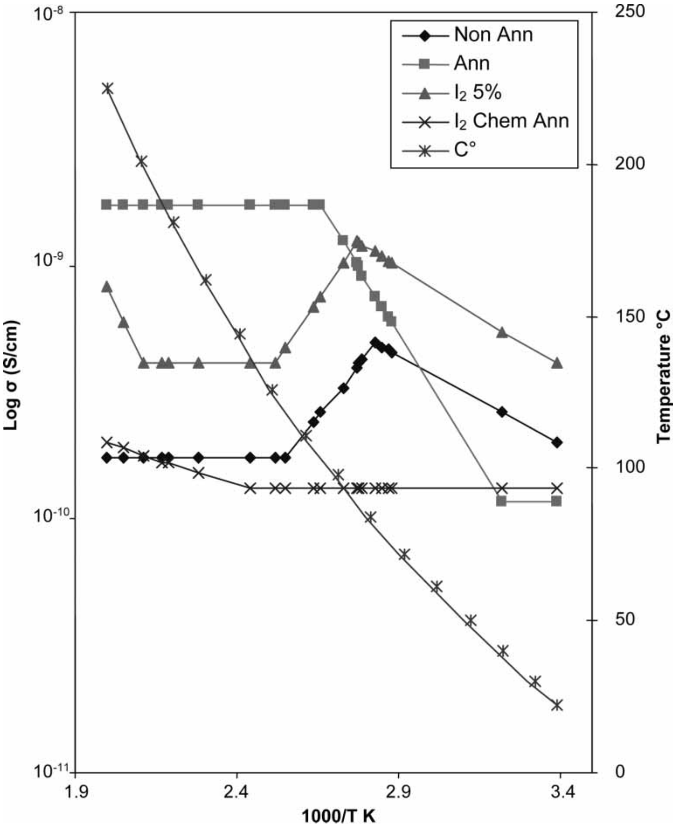


Figure 4. The DC electrical conductivity vs. $1/T$ of doped polypyrrole-zirconium chemically and by mixing with I_2 together with the annealed polypyrrole-zirconium complex.

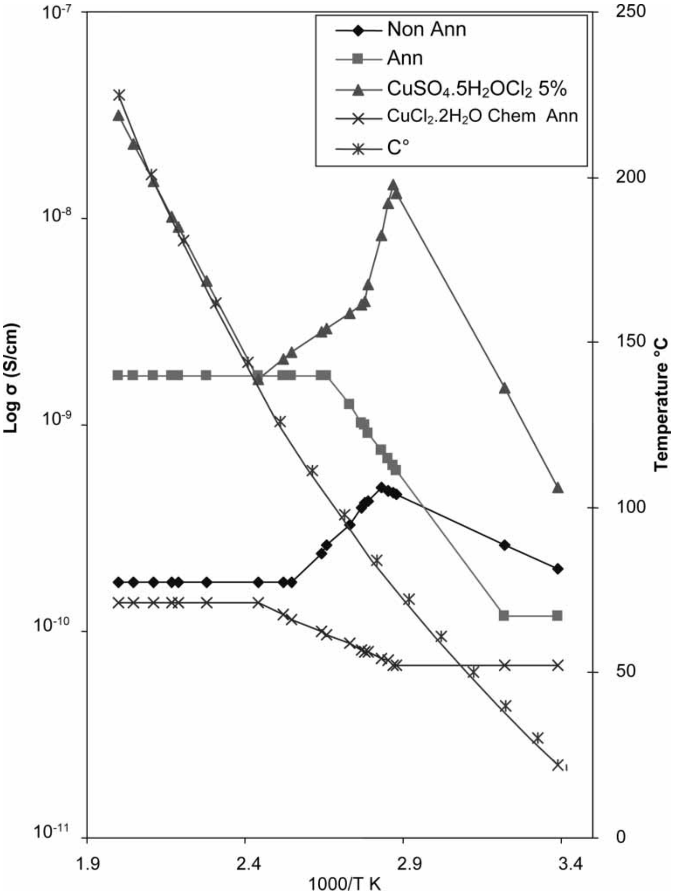


Figure 5. The DC electrical conductivity vs. 1/T of doped polypyrrole-zirconium chemically doped with $CuCl_2 . 2H_2O$ and doped by mixing with $CuSO_4 . 5H_2O$ together with the annealed polypyrrole-zirconium complex.

In the segments where the creation and combination of carriers are equal, by using Arrhenius equation, one gets a temperature independent zone with *Ea* equals 0.00 eV, this is seen in 10 states at different stages and all segments and is explained by recombination:

$$\sigma = \sigma^\circ \exp -(E_1 - E_2/kT)$$

The segments with Ea of 0.56 eV are the result of the excitation of carriers from the bulk valence band to the bulk conduction band. This is the intrinsic conductivity of the polypyrrole-zirconium complex seen in the first and last segments only in the doping by mixing states.

Activation energy of 0.15 eV is seen in four states only in the first or second segments, i.e., at fairly low temperatures. This is attributed to a loss of a positive polaron. There is a sudden rise in conductivity attributed to excitation from a negative polaron (P−) seen only once giving activation energy of 0.41 eV. This is the valence band minus a positive polaron, i.e., 0.56 – 0.15 = 0.41 eV.

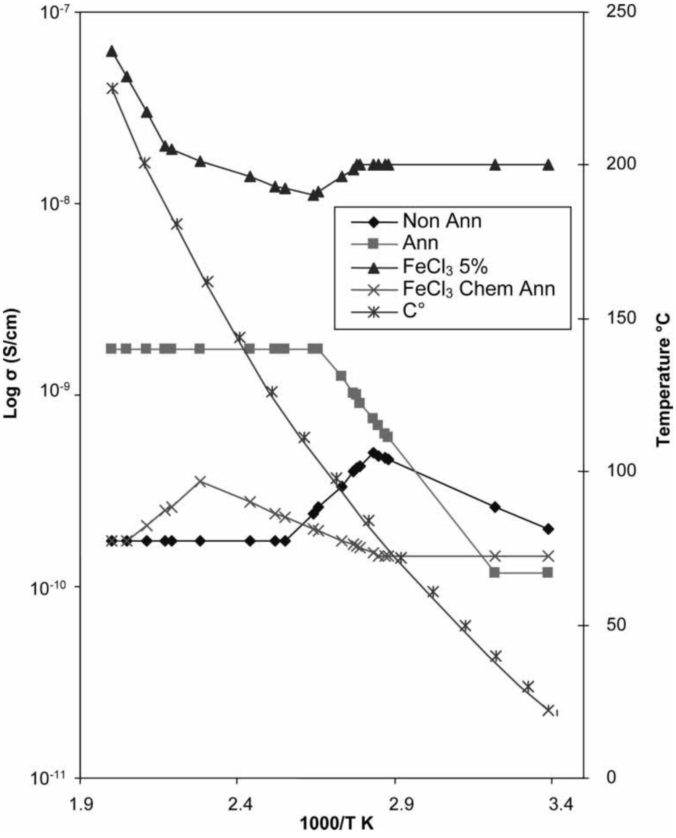


Figure 6. The DC electrical conductivity vs. 1/T of doped polypyrrole-zirconium chemically and mixing with $FeCl_3$ together with the annealed polypyrrole-zirconium complex.

The only left point to discuss is the negative activation energy noted in the case of non-annealed polypyrrole-zirconium either doped or not doped. The annealing of materials at 100°C for 24 h eliminates the adsorbed, coordinated and crystallization water. In non-annealed polypyrrole-zirconium, water remains. By heating under vacuum this water is lost causing, in this case, a negative activation energy. This has been noted before in these laboratories (21). The water release is confirmed in the DSC and TGA measurements (22, 23).

Thermal Properties

The material under study was subjected to temperature changes of the DC electrical conductivity. A change in composition by heat would lead to a change in properties and measured quantities. Hence, the thermal analyses (TGA and DSC, Figure 8) attempted to follow up the change of properties by heat.

In order to check the thermal stability of the polymer complex, and to determine the decomposition patterns, TGA measurements were made. The destruction patterns of the complex can be observed from TGA and is summarized in Table 4. It can be concluded that the destruction pattern of the material starts by loss of three water molecules

Table 3
Calculations for the activation energies of the annealed, non-annealed, and doped complex

	Temp range C°	Activation energy eV	Assignment
Non Ann	22–81	0.15	P +
	81–118	—	Water
	118–225	0	Recombination
Ann	22–38	0	Recombination
	38–103	0.41	P −
	103–225	0	Recombination
I_2 5%	22–87	0.15	P +
	87–124	—	Water
	124–199	0	Recombination
	199–225	0.56	Valence band
I_2 Chem. Ann.	22–137	0	Recombination
	137–225	0.08	Recombination
$FeCl_3$ 5%	22–85	0	Recombination
	85–105	—	Water
	105–186	—	Water
	186–225	0.56	Valence band
$FeCl_3$ Chem. Ann.	22–78	0	Recombination
	78–165	0.15	P +
	165–215	—	Water
	215–225	0	Recombination
$CuSO_4 \cdot 5H_2O$ 5%	22–75	0.56	Valence band
	75–86	—	Water
	86–137	—	Water
	137–225	0.56	Valence band
$CuCl_2 \cdot 2H_2O$ Chem. Ann.	22–74	0	Recombination
	74–137	0.15	P +
	137–225	0	Recombination

followed by two through approximate calculations. The polypyrrole-zirconium lost 5% of its weight at 95, 10% at 175°C and 20% at 281°C. A residue of 57.70% is left at 625°C.

A summary of the DSC analyses of the complex is shown in Table 5. The table shows four exothermic steps.

Conclusions

Polypyrrole-zirconium complex has been synthesized and characterized. The DC electrical conductivity variation for non-annealed, annealed and doped polypyrrole-zirconium complex has been studied in the temperature range 300–500 K. The doping was done by mixing, (I_2, $FeCl_3$ and $CuSO_4 \cdot 5H_2O$) and chemically (I_2, $FeCl_3$ and $CuCl_2 \cdot 2H_2O$). The later is annealed in a vacuum oven for 24 h at 100°C. The intrinsic non-annealed

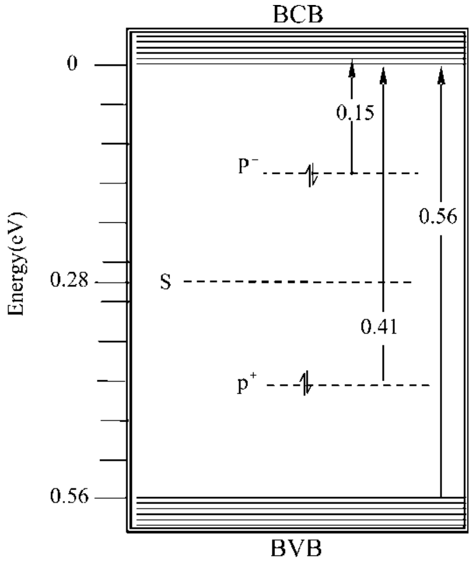


Figure 7. A schematic diagram for the activation energies of the annealed and doped polypyrrole metal complexes.

polypyrrole-zirconium complex and that doped by mixing with dopants containing adsorbed water was noted to eliminate water in the range 82–125°C as confirmed in FTIR, TGA and DSC. The chemical doping of polypyrrole-zirconium complex did not show a great enhancement of DC electrical conductivity. An attempt has been made to interpret the DC electrical conductivity behavior and thermal properties to chain length, dopant used, polymer structure and attached groups.

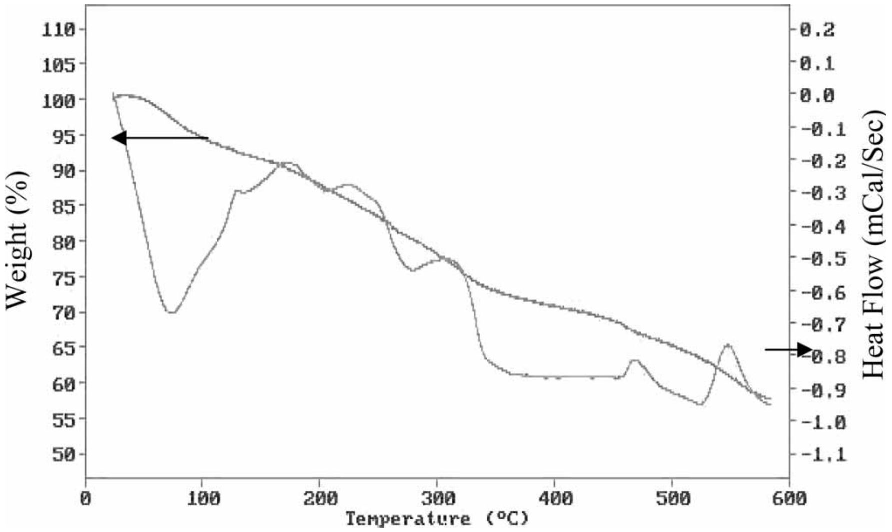


Figure 8. TGA and DSC of polypyrrole-zirconium complex.

Table 4
Summary of the thermogravimetric analysis destruction pattern and suggested assignment

1st stage	
Temp. range °C	30–120°C
DT_{DTG} °C peak	51.29°C
Wt loss %C(F)	8.54(7.5)%
Assignment	3 H_2O
2nd. stage	
Temp. range °C	120–194°C
DT_{DTG} C peak	179°C
Wt loss %C(F)	5.69(4.76)%
Assignment	2 H_2O
3rd. stage	
Temp. range °C	194–256°C
DT_{DTG} °C peak	236°C
Wt loss %C(F)	5.38(5.72)%
Assignment	2 NH_3
4th stage	
Temp. range °C	256–377°C
DT_{DTG} °C peak	289°C
Wt loss %C(F)	12.35(11.35)%
Assignment	1.5 $(CN)_2$
5th stage	
Temp. range °C	377–465°C
DT_{DTG} °C peak	441°C
Wt loss %C(F)	4.11(4.29)%
Assignment	0.5$(CN)_2$
6th stage	
Temp. range °C	465–570°C
DT_{DTG} °C peak	525°C
Wt loss %C(F)	9.81(9.07)%
Assignment	NO_3

Table 5
A summary of the DSC analyses of the complex

	Ti	Tmd	Tf	E[a]
1st step	25	73	128	72.58
2nd step	174	207	224	2.31
3rd step	251	280	309	8.34
4th step	469	524	548	16.09

a: mcal/mo.

Acknowledgements

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