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Temperature dependence of electrical conduction in pure and doped polypyrrole

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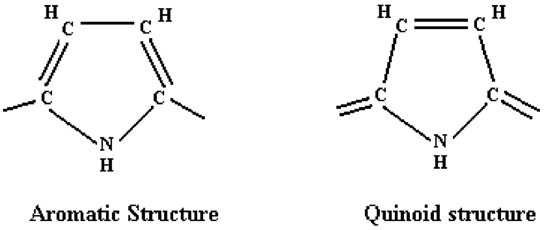
Summary

Pure polypyrrole and polypyrrole in salt form were synthesized using NaOH as reducing agent in aqueous HCl, respectively. Electrical conduction in these pure and doped polypyrrole samples was studied through the I-V characteristics of these materials. I-V characteristic curves for both pure and doped polypyrrole were found to be linear. The conductivity of chlorine-doped polypyrrole is about 10^4 times that of pure polypyrrole. An attempt has been made to study the dependence of conductivity on temperature, in order to understand the application of these systems. It has been observed from the variation of conductivity vs. temperature curve in both the samples that the conductivity increases with the increase in temperature. This behaviour is indicative of semiconducting nature of the samples with a variation in electrical conductivity of each, which is a strong function of doping and temperature of the environment. Activation energies for both the samples have been found to be in millielectron-volt range, 101.94 meV and 121.68 meV for pure and doped polypyrrole, respectively. An effort has also been made to understand the charge transport in these conductive polymers through models.

Introduction

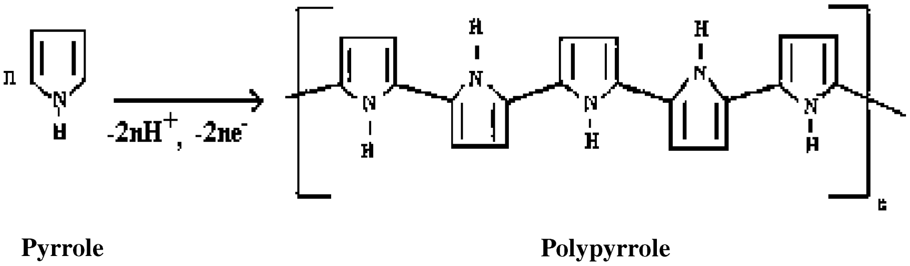
The intrinsically conducting polymers have been attracting the attention of countless groups of researchers all over the world because of their potential application in modern technology. Such polymers exhibit mechanical, electrical, optical and magnetic properties, which sometimes resemble metals and inorganic semiconductors. Also the ease of processing makes these materials attractive. These characteristics turn conducting polymers into the category of so-called synthetic metals. When doped with weak oxidizing or reducing agent these conducting polymers undergo a transition from an insulator to semiconductor [1-3]. Recently, polypyrrole and polyaniline have been the focus of many studies and they are preferred over other conducting polymers because of their high chemical, atmospheric and electrical stability at ambient temperature [4, 5]. Their unique properties have led to some commercial applications such as manufacturing of printed circuit boards, corrosion protection, electrochromic displays, electrolytic capacitors, rechargeable batteries and conductive coating for textiles [6-8].

Polypyrrole is a non-degenerate ground state polymer with two different type of chain configuration containing repeating units of aromatic as well as quinoid scheme 1.



Scheme 1. Structures in polypyrrole

During oxidative polymerisation, pyrrole (Py) typically polymerizes by linkage at α position, along with the loss of a proton at each of these positions as shown in scheme 2 [9]. The process of polymerisation is expressed by:



Scheme 2. Oxidative polymerisation

The reaction for the formation of a polymeric unit [10] is

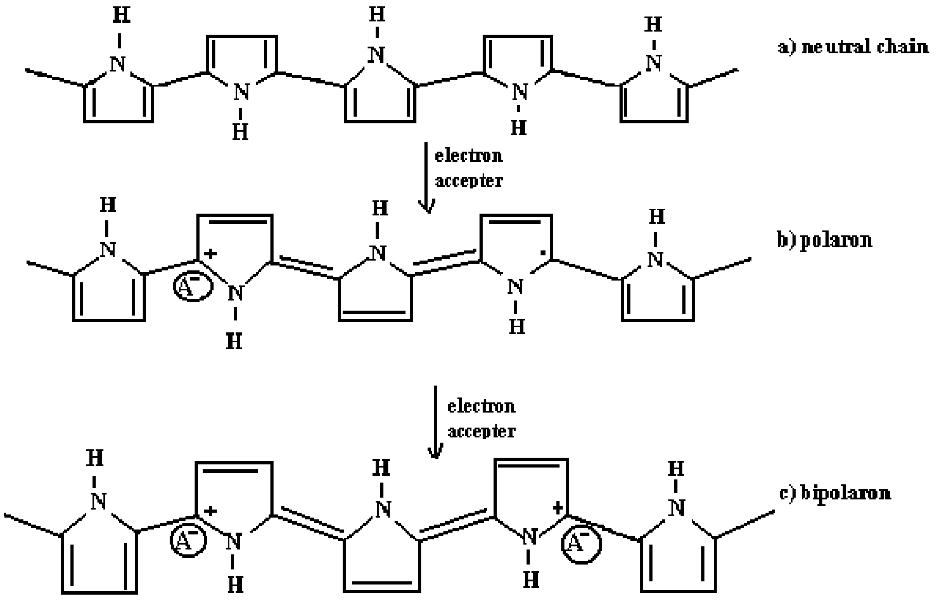
$$nPy + Cl^- \longrightarrow (PPy)^+ Cl^- + 2nH^+ + (2n+1)\, e^- \quad \textbf{(1)}$$

(Chlorine doped polypyrrole)

$$(PPy)^+ Cl^- + NaOH \longrightarrow (PPy)^0 + NaCl + H_2O \quad \textbf{(2)}$$

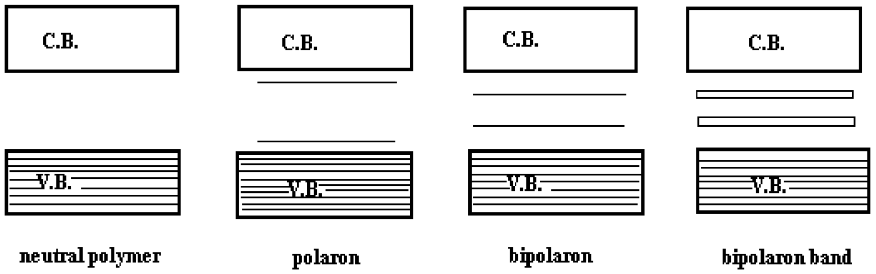
(Pure polypyrrole)

In an oxidative doping of polypyrrole, an electron is removed from the π- system of the backbone producing free radical and spinless positive charge. The radical ion and cation are coupled to each other via local resonance of the charge and the radical. In this case, the sequence of quinoid rings gets distorted rendering higher energy site compared to remaining portion of the chain. The creation and separation of these defects costs a considerable amount of energy. This limits the number of quinoid like rings that can link these two bound species together. This combination of a charge site and a radical is called as polaron as shown in scheme 3 (b). Upon further oxidation, free radical of the polaron is removed, creating a new spinless entity called as bipolaron, which is of lower energy than that of two distinct polarons. At higher doping levels it becomes possible that two polarons combine to form bipolaron as shown in scheme 3 (c)[11]. It is inferred that doping affects the packing dimensions and pyrrole rings are linked by a double bond $(\pi\text{-}\sigma)$ in a quinoid form rather than the normal aromatic form scheme 1[12].



Scheme 3. Formation of polarons and bipolarons

Thus for a highly doped polymer, it is conceivable that the upper and lower bipolaron bands will merge with the conduction and valence band, respectively to produce partially filled bands or states as shown in scheme 4 [11].



Scheme 4. Bands in conducting polymer

A good deal of work has been done on polypyrrole doped with different anions such as PF_6^-, TSO^-, BF_4^-, Cl^-etc.[13-15] in the film form. However, a very few attempts have been made to study the properties of polypyrrole in its bulk form. In this work, we focus on the temperature dependence of electrical conductivity of pure and doped polypyrrole in bulk form.

Material preparation and Experimental techniques

Polypyrrole was prepared by oxidative polymerisation of double distilled pyrrole using ammonium persulfate, $(NH_4)_2S_2O_8$ as an oxidant. A calculated amount of ammonium persulfate was dissolved in HCl (1M) solution. The polymerisation was performed at 0^oC temperature with oxidant/ monomer molar ratio 0.2. The black precipitate resulting from the reaction is washed with distilled water and methanol and then dried under vacuum for 6-8 hrs [16]. This precipitate of polypyrrole in its salt form is reduced by NaOH solution and the precipitate resulting from the reaction is washed with distilled water and dried under vacuum.

For electrical measurements, bulk sample in the form of pellets (diameter 12mm and thickness of approx 2 mm) were prepared by compressing the fine powder of polypyrrole and chlorine-doped polypyrrole under a load of 6 tonnes. The pellets were mounted between two copper electrodes in a sample holder for I-V measurements. For that purpose, voltage was applied across the pellet and the resulting current was measured by Keithley electrometer/high resistance meter –6517 A. The temperature range of the study was from room temperature to 100 ^oC approximately. The circuit diagram used for this study is given elsewhere [17]. This electrometer has an inbuilt capability of output independent voltage source of ± 1000 V. So the same equipment was used to apply voltage across the sample and to measure the current through the sample. To ensure proper connection of the sample, an indigeneously designed sample holder was used with copper electrodes.

Result and discussion

I-V characteristics of pure polypyrrole and chlorine-doped polypyrrole were recorded at different temperatures and are found to be linear as shown in Figure 1-2. In conducting polymers, there are no permanent dipoles. However, there exists a strong charge trapping in the sample. Under the influence of applied external field the localized (short range) motions of the trapped charges in the sample serves as effective electric dipoles [18]. Such short-range distortions contribute to the formation of polarons and bipolarons as shown in the scheme 3. These polarons and bipolarons are dominant charge carriers, which are responsible for the electrical conduction in these samples. As the strength of the applied field increases the degree of such distortion increases, resulting in the increment of current. It is also observed that the current increases with the increase in temperature. Elevations in temperature lead to an increase in lattice vibration, which results in chain stretching. This stretching of polymer chain leads to an effective charge distribution all over the chain and increment in alignment of polymer chains with potential for longer conjugation length [12]. This leads to intra and inter chain hopping of charge carriers which inturn increase the conduction. Therefore, in these bulk samples, charge transports involve both intra and inter chain contributions. From the measured I-V characteristics of these two samples, the values of electrical conductivities have been obtained at different temperature. The electrical conductivity (σ) of the samples has been determined using the relation,

$$\sigma = [(I \times L) / (V \times A)] \qquad \mathbf{(3)}$$

where I is the current , V is the voltage , L the thickness, and A the cross-section area of the sample.

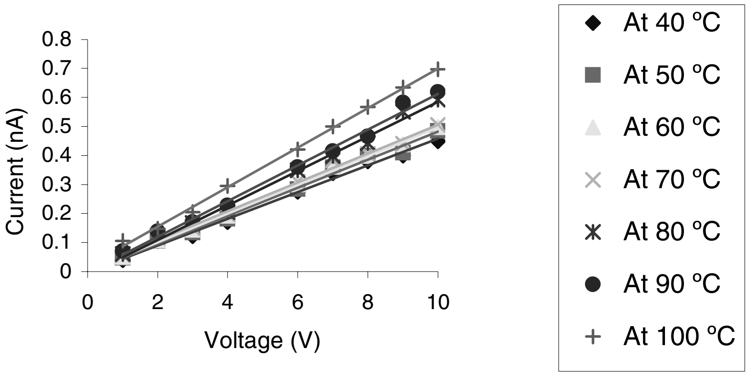


Figure 1. I-V Characteristics of pure polypyrrole

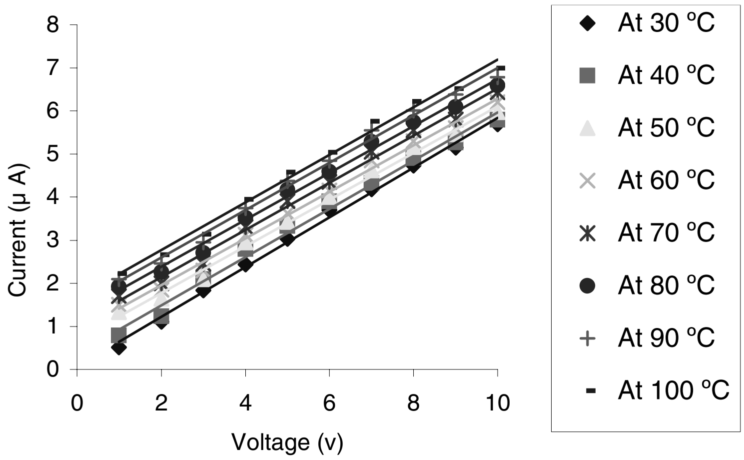


Figure 2. I-V Characteristics of chlorine doped polypyrrole

A comparative study for pure polypyrrole and chlorine-doped polypyrrole suggests that the conductivity of chlorine-doped polypyrrole is about 10^4 times that of pure polypyrrole. The non-degenerate ground states of pure polypyrrole possess an aromatic configuration in which aromatic rings are linked via long bonds. Doping with HCl causes bond alternation from aromatic configuration to quinoid configuration with short bond length. This structure has spinless positive charge ion and unpaired electron in quinoid configuration that is higher in energy and confines the charge and spin density to a single self-localized structural deformation that is mobile along the chain as shown in scheme 3. This polaronic and bipolaronic structures result in a widening of the bonding and antibonding levels into the band gap which is responsible for an increase in the electrical conductivity with doping [19].

Theoretical models

The electrical conductivity of both the samples has been determined in the temperature range from 313 to 373K. The electrical conductivity of both the samples increases with the increase in temperature showing the semiconducting nature of the samples. This behaviour of electrical conductivity can be explained using two different models:

1. Electrical conductivity data for both the polypyrrole samples were found to follow the Arrhenius model [20].

$$\sigma = \sigma_0 \exp [-E_{ac} / kT] \qquad \textbf{(4)}$$

where σ_0 is the conductivity at room temperature , E_{ac} is the carrier activation energy and k is the Boltzmann constant. Plots of ln(σ) vs 1000/T have been shown in Figure 3-4.

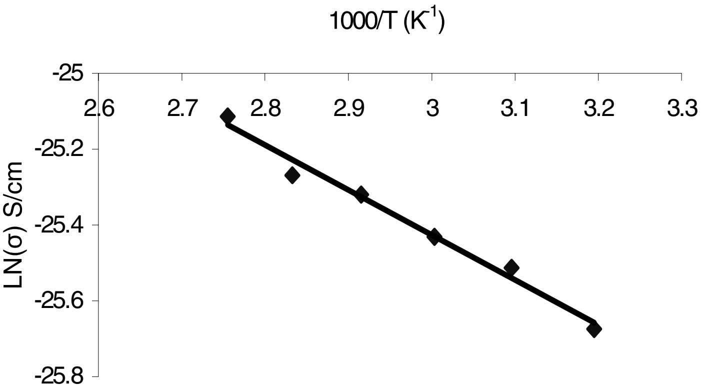


Figure 3. Plot of LN(σ) Vs. 1000/T of pure polypyrrole

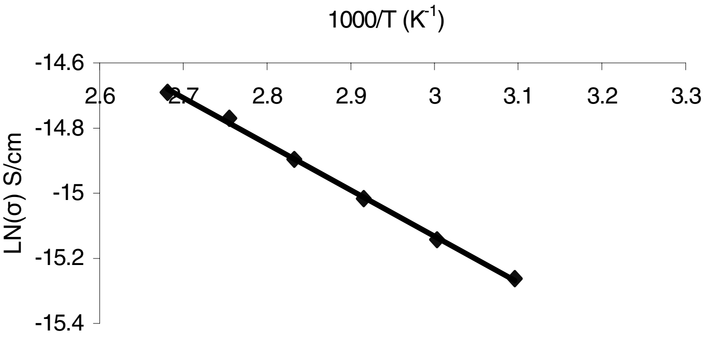


Figure 4. Plot of LN(σ) Vs. 1000/T of chlorine doped polypyrrole

The slope [equal to E_{ac} /1000k] of these plots provides information about activation energies E_{ac}. It was found that activation energy is of the order of millielectron volt.

Activation energies were found to be 101.94 meV and 121.68 meV for pure polypyrrole and polypyrrole doped with HCl respectively. It is an interesting fact that the activation energy of pure polypyrrole is smaller as compared to doped sample, but conductivity is large for the doped sample. This is due to the fact that doping of the anions, so introduced into the sample, produce varying fields along the chain. As a result larger number of polarons and bipolarons are created in the sample and the availability of these contribute to the conduction enhancement in the conductivity of the sample. With the increase in doping, formation of continuous bipolaron bands take place. The separation between these bipolaron bands increases at the expense of the band edges. For a very heavily doped polymer it is conceivable that the upper and lower bipolaron bands will merge with conduction and valence band, respectively leading to a wider separation between these bands [11] and hence such an inherent change in the nature of the doped material leads to a higher value of activation energy.

2. The temperature dependence of the conductivity σ(T) of disordered semi conducting materials is generally described by the Mott's variable range hopping (VRH) model, which is another possible charge transport mechanism in conducting polymers. Mott's VRH mechanism is a phonon assisted quantum-mechanical transport phenomena in which the movement of charge carriers to a nearby localized state of different energy is explained through the thermodynamic procedures, where as the movement of a charge carriers to a farther off localized state of similar energy is given by quantum mechanical tunneling [21]. The details worked out on this process leads to a characteristic temperature dependence of conductivity of the form $\ln \sigma (T) \alpha T^{\{-1/(1+d)\}}$, where σ is the conductivity of the sample and T is the temperature.

Mott's model for hopping is given by

$$\sigma (T) = \sigma_0 \text{ Exp } [-T_0/T]^{\gamma} \qquad \textbf{(5)}$$

where σ_0 is the high temperature limit of conductivity, T_0 is the Mott's characteristics temperature associated with the degree of localization of the electronic wave function. The exponent $\gamma = 1/(1+d)$ determines the dimensionality of the conducting medium [22].

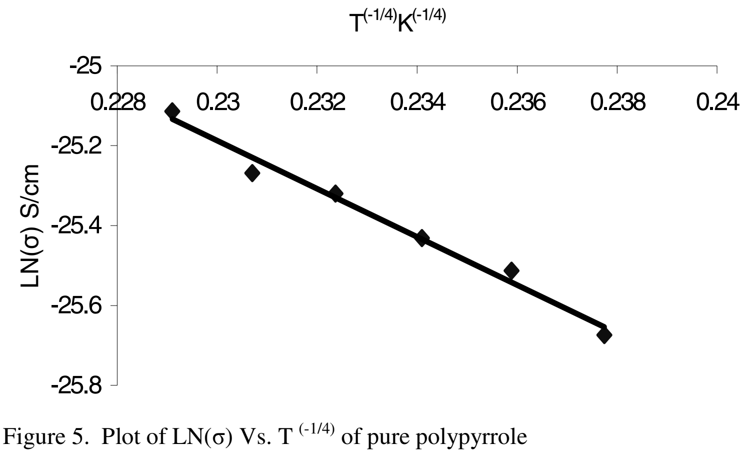


Figure 5. Plot of LN(σ) Vs. $T^{(-1/4)}$ of pure polypyrrole

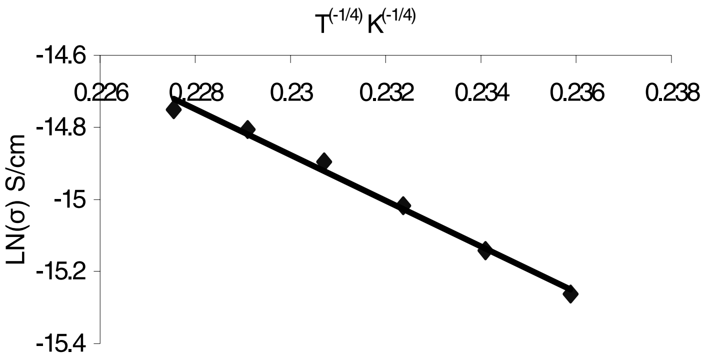


Figure 6. Plot of LN(σ) Vs. T $^{(-1/4)}$ of chlorine doped polypyrrole

The plot of ln σ (T) vs. $T^{(-1/4)}$ is a straight line as shown in Figure 5-6 and indicates that three dimensional (3D) charge transport occurs in both the samples. The values of T_0 and ln σ_0 obtained from the slopes and intercept from the above mentioned plots are 1.31 x 10^7 K and –11.336 S/cm for pure polypyrrole and 1.62 x 10^7 K and -0.2816 S/cm for chlorine doped polypyrrole sample, respectively. The values of T_0 are very sensitive to the nature of the sample and increase with the increase of electrical conductivity.

Conclusion

Variation of electrical conductivity of polypyrrole is suggestive of the fact that system can be modified from insulating to semiconducting by doping with chlorine. With the increase of doping a wider separation of bipolaron band takes place, which in turn enhances the activation energy. Mott's VRH model for the temperature dependence of electrical conductivity gives a better representation of the experimental data and suggests that the possible linkage in the system is followed by three-dimensional networking.

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References

1. Nalwa HS(1997) Hand book of Organic Conductive Molecules & Polymers. John Wiley & sons Ltd. 2.
2. Soares DAW, deSouza PHO, Rubinger RM, deQueiroz AAA, Higa OZ, deSouza LR (2004) Brazilian Journal of Physics 34 no.2B.
3. Pratt C, Conducting Polymers.http://hompage .dtn.ntl.com/colin pratt/cpoly.htm.
4. Anuar K, Murali S, Fariz A, MahmudEkramul HNM (2004) Material Science 10:255-58.
5. Kassim A, Basar ZB, Mahmud HNME (2002) Chem.Sci.114:155-162.
6. Smitha G, Kundy A, Rajagopalan R, Iroh JO (2002) J.of App.Poly.Sci. 83:1970-77.
7. Chehimi MM, Abdelijalil E (2004) Synth. Met.145:15-22.
8. Fried JR (1999) Polymer science and Technology. New Delhi: Prentice Hall India 461.
9. Bunting RK, Swarat K, Yan D (1997) J.of Chem.Edu 74 no. 4:421-22.

10. Henry MC, Hsueh CC, Timko BP, Freund MS (2001) J. of The Electrochemical Soc. 148(11): D155-D162.
11. G.P.Joshi, Ph.D. Thesis, "Thermal and Optical properties of conducting polymers" India (2003) 6-7.
12. Davidson RG, Hammond LC, Turner TG, Wilson AR (1996) Synth. Met.81: 1-4.
13. Kohlman RS, Ishiguro T, Kancko H, Epstein AJ (1995), Synth. Met. 69:325-328.
14. Singh R, Narula AK (1996) Synth. Met.82: 245-49.
15. Wang PC, MacDiarmid AG (2001) Synth. Met.119: 367-68.
16. Turcu R, Giurgia LV, Ordean R, Grecu R, Brie M (2001) Synth.Met.119: 287-88.
17. Saraswat Vibhav K., Singh K, Saxena NS, Kishore V, Sharma TP, Saraswat PK (2006) Current Applied Physics 6:14-18.
18. Bengoechea MR, Aliev FM, Pinto NJ (2002) J. Phys.: Condens. Matter 14:11769.
19. NaveenKumar M, Nagabhooshanam M, AnandRao M, BhagvanthRao M (2001)Cryst. Res. Technol.36:309-17.
20. Gosh M, Barman A, Meikap AK, De SK, Chatterjee S (1999) Phys. Lett. A 260:138.
21. Maddison DS, Tansley TL (1992) J.Appl.Phys.72. 10: 4677-82.
22. Dey A, De S, De A, De SK (2004) Nanotechnology 15: 1277-83.