

Temperature response of conducting Polypyrrole (Ppy) prepared with Ammonium per Sulfate (APS) doped with Dodecylbenzene sulfonic acid (DBSA)

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ABSTRACT

The procedures for the synthesis of Polypyrrole (PPy) doped with oxidizing agents such as Ammonium per Sulfate (APS) by means of chemical oxidative polymerization were presented. The bonding structure, morphologies, chemical nature of conducting polymers were studied by various methods like Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD) techniques. The temperature dependence of the electrical conductivity was studied at temperatures range from 300C up to 700C. Attempt was made to increase the electrical conductivity by using Dodecylbenzene sulfonic acid (DBSA) as dopant by adding 10% in weight of DBSA to the weight of pyrrole. It was observed that the electrical conductivity decreased gradually for all the samples. This behavior resembles the metallic conductors. It may be mentioned that pure Pyrrole is more like insulator but behaves like semiconductor in the doped form.

Key words : Conducting polymers, oxidants, dopants, electrical conductivity, semiconductor

Introduction:

Electro active conducting polymers have assumed a great importance in several technologies such as Transducers, Optical displays, Solar cells, and Gas sensors. Their ease of processing together with their chemically tunable properties makes them useful in electro-mechanical devices. As these polymers are Redox – active their conductivity can be changed by means of doping / de doping. A great deal of sensing applications are designed by exploiting the very nature of conducting polymers.

One of the main features of the Ppy system is the degree of freedom available to modify the electrical and physical properties by resorting to derivatives, copolymers or particular anion in order to active any desired matrix of polymer. Oxidative polymerization of pyrrole to polypyrrole proceeds via a one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the 2,2'-bipyrrole. This process is then repeated to form longer chains. The final form of polypyrrole is that of a long conjugated backbone. The polymer has resonance structures that resemble the aromatic or quinoid forms. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalised.

However, pristine PPy is insoluble and infusible because of the rigidity of its molecular chains of π -conjugated structure. This poor conductivity and processibility not only impede further investigation of its structure, but also limit its application in technology. So efforts to overcome these drawbacks have led to numerous studies on the synthesis of PPy by both electrochemical and chemical routes. It is well-known that using various dopants has contributed to the development of soluble PPy [5]. Currently, aromatic acid derivatives and organic sulfonates are widely used, such as dodecylbenzene sulfonic acid (DBSA), p-toluenesulfonic acid (TsOH) [6], etc. Lee *et al.* [7] developed DBSA with surface-active properties as anionic additive to realize Pyrrole (Py) solution. Further studies pointed out that adding other large dopants could reduce the interchain links, resulting in the increase of the conductivity and solubility [8–11].

The physical properties of conducting polymers strongly depend on the type of dopant and the doping levels. The doping levels can be easily changed by chemical reactions at room temperatures. In the present thesis we report preparation of polypyrrole in pure form and in the doped form by using dopants such as LiClO_4 , DBSA, p-TS and b-naphthalene sulfonic acid NSA.

Pyrrole is a five – member heterocyclic which polymerized via 2, 5 – position [12]. A radical cation mechanism is initiated in the presence of a strong oxidizing agent which is also serves as the dopant. The overall stoichiometry resulting from chemical polymerization of Ppy with ferric chloride oxidant is shown in Fig.1. Bipolaron result via the mechanism Fig.2 rendering the polymer electrically conductive.

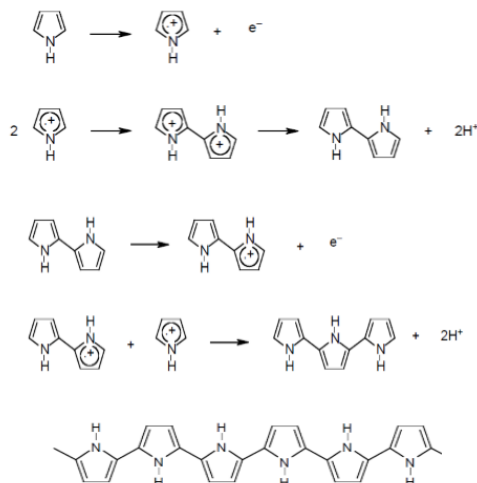


Fig. 1:Chemical polymerization of polypyrrole

The oxidative doping of polypyrrole proceeds in the following way. An electron is removed from the p system of the backbone producing free radical and a spin less positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. In this case, a sequence of quinoid-like rings is used. The distortion produced by this is of higher energy than the 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. In the case of polypyrrole it is believed that the lattice distortion extends over four Pyrrole rings. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates new localized electronic states in the gap, with the lower energy states being occupied by single unpaired electrons. The polaron state of polypyrrole is symmetrically located about 0.5 eV from the band edges.

Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it becomes possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypyrrole. This eventually, with continued doping, forms into a continuous bipolaron bands. Their band gap also increases as newly

formed bipolarons are made at the expense of the band edges. For a very heavily doped polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity. This is shown below in Fig. 2.

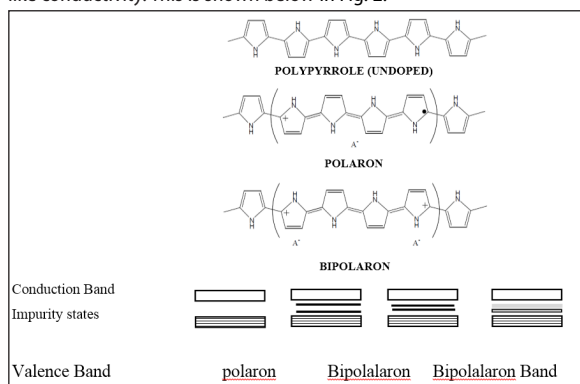


Fig.2 Conduction mechanisms in Polypyrrole

Experimental methods and preparations:

Pyrrrole (Sisco Research lab / Sepctrochem lab 99%) was distilled before use. All other reagents and solvents obtained from commercial sources were reagent grade purity and were used as received. All solutions were prepared using de-ionized water. All reactions were conducted at a room temperature [3]. The oxidizing agent APS was used in the ratio of 1: 2.4 (monomer: oxidants) prepared using de-ionized water. The dopant used was mixed with pyrrole solvent by taking 10% of it to the weight of pyrrole.

The Polypyrrole was prepared by chemical polymerization method. 1 M Pyrrole solution was prepared using de-ionized water and then mixed with oxidizing agent mentioned above and with the dopant mixture separately, slowly under constant stirring for 30 minutes. Then the polymerization was conducted for 4 hours under constant stirring. Polypyrrole produced was the kept unagitated for 24 hours so that Ppy powder settled down. The Polypyrrole powder was filtered out under vacuum and washed with distilled water several times to remove any impurities present. The Polypyrrole was dried for 2 days at room temperature.

The Polypyrrole was tested for conductivity by preparing its pellets of area of cross section of 1 sq.cm. and 1mm. thickness. The conductivity was tested by two probe method at room temperature and various temperatures up to 70° C in the voltage range from 0 to 12 V.

The required components for electronic circuit were brought from manufacturing company and are of international standard. The printed circuit board (PCB) for sensors was designed and assembled in our laboratory. The electronic circuit was designed indigenously and fabricated with our specifications.

Morphology of Polypyrrole was examined using Scanning Electron Microscope (SEM) JEOL make JSM – 5400 model. Chemical structure was examined by FTIR measurements on Perkin – Elmer Ltd. make FTIR spectrometer model system 2000 using KBr pellets.

The Polypyrrole was characterized by XRD using PAnalytical (Philips), Netherland model XpertPro. The XRD pattern was recorded between $2\theta = 10^\circ$ to 40° . The X – ray diffractometer uses CuK α radiation of $\lambda = 1.5418 \text{ \AA}$ generated at 40Kv/ 20 ma.

Electrical conductivity is the property, which distinguishes the conjugated polymers from other polymers. The Electrical conductivity can be studied by using two probe methods which gives an idea about the bulk conducting properties of the sample.

Two Probe Conductivity Measurements

The two probe apparatus used for the conductivity measurements was fabricated in our laboratory. It consists of a temperature control device, sample holder and a rotary pump. The sample holder is kept

at the center of the assembly and the upper electrode is spring loaded so that a pressure contact is made with the sample. The second electrode is at the bottom and rests on a firm support and is in contact with a heating device. The automatic temperature control device controls the necessary temperature to within $\pm 1^\circ \text{ C}$ and has a display unit for reading the temperature. The regulated power supply gives a variable DC voltage upto 15 volts. The voltage across the sample was measured with a digital multimeter and current through the sample was measured with the help of a digital ammeter. The sample pellet was approximately 1 cm in diameter and is sandwiched between two copper electrodes. The voltage was varied from 0 to 12V in steps of 1V and the current was recorded. The I-V characteristics were determined from room temperature to 70° C in steps of 10° C. The electrical conductivity σ of a conductor is given by

$$\sigma = \frac{I}{V} \times \frac{l}{A}$$

where l - length of the conductor in cm. (thickness of the film in this case).

A - Area of cross section in cm^2

I - Current through the sample and

V - Voltage across the sample

Characterization, Results and Discussions: Polypyrrole without dopant:

FTIR spectroscopy:

The FTIR spectrum of Ppy prepared is represented in Fig. 3. It shows strong absorption bands at around 3435 cm^{-1} corresponding to N-H stretching. Other medium intensity peaks are observed at around 2926 cm^{-1} - 2854 cm^{-1} which can be attributed to aromatic C-H stretching vibrations. The presence of 801 cm^{-1} band conforms that predominantly $\alpha - \alpha'$ bonding exists.

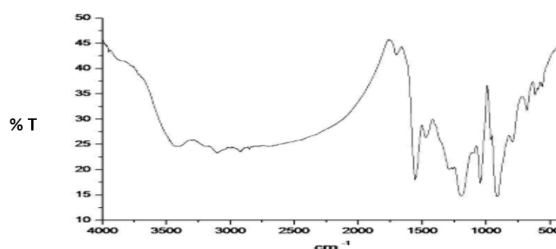


Fig.3 :FTIR pattern for polypyrrole prepared using APS as oxidant

X-ray diffraction analysis:

A typical X ray diffraction pattern for polypyrrole prepared using APS as oxidant is shown in Fig.4. The XRD pattern shows broad peaks in the region $15^\circ < 2\theta < 30^\circ$ revealing that the resulting polypyrrole powders is amorphous in nature. This agrees well with the structure reported in literature. Such broad peak usually indicates short range arrangement of chains.

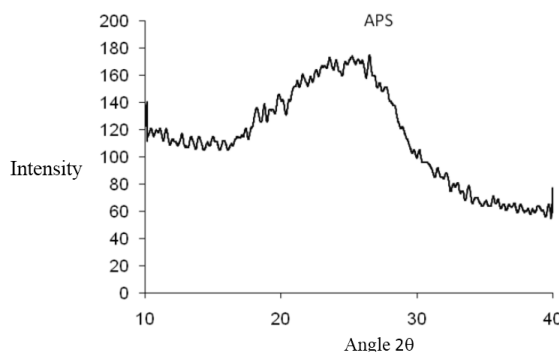


Fig. 4: X ray diffraction pattern for polypyrrole prepared using APS as oxidant

Morphology:

The morphological features of polypyrrole synthesized chemically has revealed that mostly the growth is in the globular form. Typical SEM image is shown in Fig.5. The micro graph shows a globular structure. It can be seen from Fig. that when polymerization was done with APS the average size of globules was found to be 0.59 μm . The individual globules observed were nearly spherical and have a close packing. Such morphological features are considered to be good for gas sensing applications.

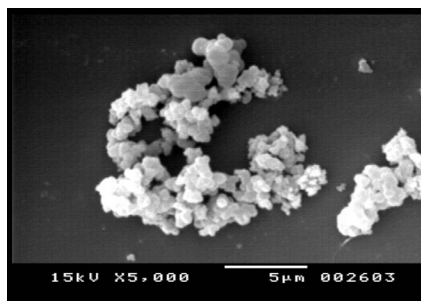


Fig.5: SEM of Ppy prepared by our method using APS as an oxidant

I-V characteristics:

Typical plots of I vs. V for polypyrrole prepared using APS as oxidant is given in Fig.6. Nearly linear relationship of the graph of I vs V curve was noted up to 8 volts. After this peak when voltage was increased further, a decrease in current was observed. The reason for such decrease is either that the current is now opposed by the flow of opposite charges in opposite direction of degradation of sample. This behavior was also seen when I vs V was studied for higher temperatures. However voltage for peak current (V_p) decreases with temperature. It shows that the charges of opposite kind are generated more in numbers as temperature increases. Additional evidences for the contribution to the current by ions are being explored. The conductivities were found in the range of 1.0 to $4.6 \times 10^{-3} \text{ S/cm}$.

The temperature dependence of the electrical conductivity of the polypyrrole, prepared with APS was studied at various temperatures from 30°C up to 70°C . It was observed that the electrical conductivity decreased gradually for all the samples.

Additional energy bands are formed above the valence band and just below the conduction band. This reduces the energy gap and the doping leads to semiconduction. Thus it is expected that increasing temperature will lead to increase of energy for an electron in the valence band which jumps to conduction band and hence the conductivity should increase with the temperature. However the present studies revealed that the materials do not behave like semiconductor but like metals where the conductivity is decreasing with temperature. Such behavior can be caused due to the large number of intermediate energy states in the energy gap region. Voltage for peak current decrease with increase in temperature. This shows that V_p is inversely proportional to temperature.

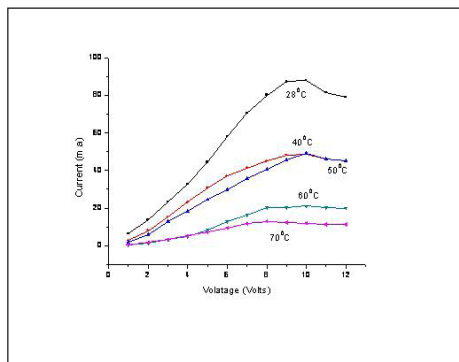


Fig. 6: I vs V graph of Ppy with APS as oxidant at various temperature

Effects of dopant:

The Polypyrrole was prepared by chemical polymerization method using APS as oxidant and dopants such as DBSA. The structure and morphology of these materials has been investigated using the methods of FTIR, X - Ray diffraction and SEM. The electrical conductivity has been measured by two probe method. All the samples were tested for conductivity for various temperatures from 30°C to 70°C

FTIR spectroscopy:

The Polypyrrole powders prepared in different dopants were analyzed by FTIR. FTIR spectra showed the main characteristic peaks around 685 cm^{-1} corresponds to C-C out of plane ring deformation vibrations or C-H rocking, 982 cm^{-1} to 925 cm^{-1} corresponds to C-H out of plane deformation vibration band of the ring, 1047 cm^{-1} C-H in plane deformation vibration, 1559 cm^{-1} corresponds to C=C / C-C stretching vibrations of the Pyrrole ring and 1487 cm^{-1} corresponding to the fundamental vibrations of polypyrrole ring, The peak at 2921 cm^{-1} corresponding to C-H stretching vibrations, 3430 cm^{-1} corresponds to the N-H bond. These peaks were observed in the present work for preparations using APS as oxidants and various dopants such as DBSA (Fig.3. 22). This agrees well with the ones available the literature, confirming the formation of Polypyrrole.

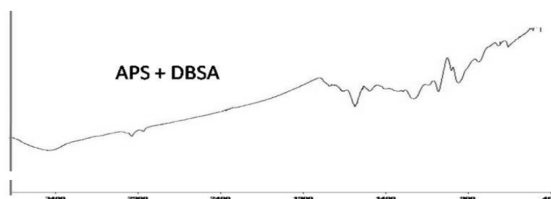


Fig.7.FTIR pattern for polypyrrole prepared using APS as oxidant and DBSA as dopant

X-ray diffraction analysis:

The diffraction peak centered at around 25.4° for pure pyrrole shows some displacement when we go to the doped ones. In general the doping leads to shift the peaks toward the lower angle. This indicates that the inter planer spacing increases with the addition of dopants. This would make the chains get apart from each other due to the large sizes of the dopant molecules.

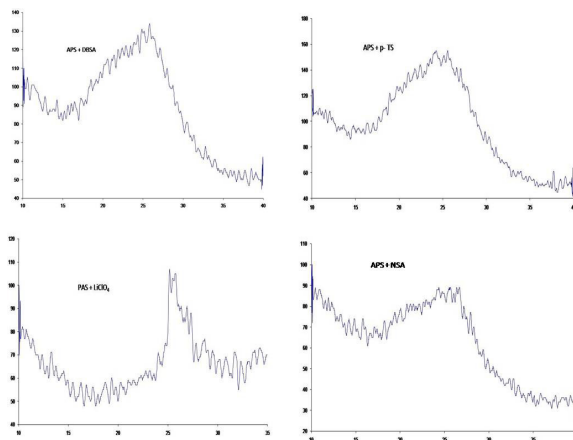


Fig. 8: XRD of Ppy prepared with APS as oxidant and DBSA as dopant.

Morphology:

The morphological features of polypyrrole synthesized chemically and electrochemically have revealed that mostly the growth is in the globular form but changes some time due to dopant molecules

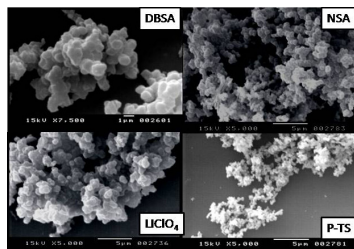


Fig. 9: SEM of Polypyrrole using APS as oxidant and DBSA as dopant.

I-V characteristics:

The temperature dependence of the electrical conductivity of the polypyrrole, prepared with APS and their doped varieties was studied at various temperatures from 30°C up to 70°C. It was observed that the electrical conductivity decreased gradually for all the samples. This behavior resembles the metallic conductors. It may be mentioned that pure pyrrole is more like insulator but behaves like semiconductor in the doped form. The mechanism of conduction is supposed to be by polarons and bipolarons formation due to the dopants molecules [113].

In case of polypyrrole the absence of electron in the chain leads to formation of holes i.e. p-type conduction. Thus addition of dopants leads to the modification of energy levels.

Additional energy bands are formed above the valence band and just below the conduction band. This reduces the energy gap and the doping leads to semiconduction. Thus it is expected that increasing temperature will lead to increase of energy for an electron in the valence band which jumps to conduction band and hence the conductivity should increase with the temperature. However the present studies revealed that the materials do not behave like semiconductor but like metals where the conductivity is decreasing with temperature. Such behavior can be caused due to the large number of intermediate energy states in the energy gap region. In the present studies the doping level was 10% which is comparatively high and leads to overlap of a large number of energy states. In addition the size of the dopants ions ClO_4^- is quite large and overlap of energy states can occur. Thus the temperature dependence can be understood.

Typical plots of I vs. V for polypyrrole prepared using APS as oxidant is given in and DBSA dopants are given in Fig.10. Nearly linear relationship of the I – V curve was noted except at room temperature for APS sample where it goes to saturation after 8 volts. It was observed that the electrical conductivity of polypyrrole increased when dopant like DBSA was used.

The temperature dependence of the electrical conductivity of the polypyrrole, prepared with APS and their doped variety was studied at various temperatures from 30°C up to 70°C. It was observed that the electrical conductivity decreased gradually for all the samples in the temperature range of 30°C to 70°C.

It was rather surprising to find that when the temp. Increases the conductivity decreases that mean Polymers behavior with temp. Increase is like a metal. But the conductivity level of polymer is like semiconductor.

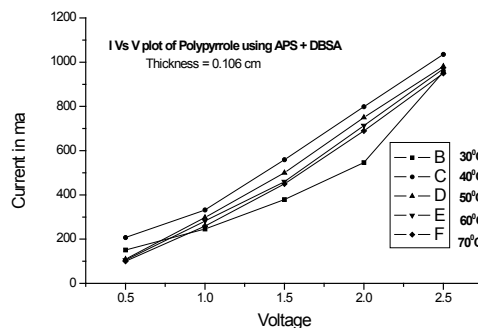


Fig. 10 : I vs V characteristic of Polypyrrole prepared using APS + DBSA at various temperatures

Table 2: X ray peak position, Half width, Globular size and conductivity of Ppy prepared using APS and various dopants.

Sample	X ray Peak position	X ray half width	SEM size of globule	Conductivity at R.T. over a linear portion of curve
Pure Polypyrrole	25.4°	8°	0.59 µm	1.70 X 10 ⁻³
Polypyrrole with DBSA	25.9°	7.2°	0.68 µm	2.84 X 10 ⁻³

Conclusion:

Polypyrrole was synthesized chemically in the pure form with oxidants like APS and doped with dopant DBSA. The ratio of 1: 2.4 monomers to oxidant is optimum. It was seen that there are structural and morphological differences which affects their electrical properties. The electrical conductivity gets enhanced due to addition of dopants. It may be mentioned that pure Pyrrole is more like insulator but behaves like semiconductor in the doped form. The mechanism of conduction is supposed to be by polarons and bipolarons formation due to the dopants molecules. Additional energy bands are formed above the valence band and just below the conduction band. This reduces the energy gap and the doping leads to semiconduction.

REFERENCES

- [1] Shirakawa H., Louis E. J., MacDiarmid A. G., Chiang C. K., Heeger A. J.: Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)_x. Journal of the Chemical Society, Chemical Communications, 16, 578–580 (1977). DOI: 10.1039/C39770000578 [2] Jang J., Nam Y., Yoon H.: Fabrication of polypyrrole–poly(N-vinylcarbazole) core–shell nanoparticles with excellent electrical and optical properties. Advanced Materials, 17, 1382–1386 (2005). DOI: 10.1002/adma.200401841 [3] Wu T-M., Lin S-H.: Synthesis, characterization, and electrical properties of polypyrrole/multiwalled carbon nanotube composites. Journal of Polymer Science Part A: Polymer Chemistry, 44, 6449–6457 (2006). DOI: 10.1002/pola.21724 [4] Carrasco P. M., Grande H. J., Cortazar M., Alberdi J. M., Areizaga J., Pomposo J. A.: Structure–conductivity relationships in chemical polypyrroles of low, medium and high conductivity. Synthetic Metals, 156, 420–425 (2006). DOI: 10.1016/j.synthmet.2006.01.005 [5] DeArmitt C., Armes S. P.: Colloidal dispersions of surfactant-stabilized polypyrrole particles. Langmuir, 9, 652–654 (1993). DOI: 10.1021/la00027a007 [6] Yuan X., Zeng X., Zhang H-J., Ma Z-F., Wang C-Y.: Improved performance of proton exchange membrane fuel cells with p-toluenesulfonic acid-doped Co-PPy/C as cathode electrocatalyst. Journal of the American Chemical Society, 132, 1754–1755 (2010). DOI: 10.1021/ja909537g [7] Lee J. Y., Kim D. Y., Kim C. Y.: Synthesis of soluble polypyrrole of the doped state in organic solvents. Synthetic Metals, 74, 103–106 (1995). DOI: 10.1016/0379-6779(95)03359-9 [8] Lee J. Y., Song K. T., Kim S. Y., Kim Y. C., Kim D. Y., Kim C. Y.: Synthesis and characterization of soluble polypyrrole. Synthetic Metals, 84, 137–140 (1997). DOI: 10.1016/S0379-6779(97)80683-2 [9] Oh E. J., Jang K. S., Suh J. S., Kim H., Kim K. H., Yo C. H., Joo J.: UV-Vis/NIR and transport studies of chemically synthesized soluble polypyrrole. Synthetic Metals, 84, 147–148 (1997). DOI: 10.1016/S0379-6779(97)80686-8 [10] Shen Y., Wan M.: In situ doping polymerization of pyrrole with sulfonic acid as a dopant. Synthetic Metals, 96, 127–132 (1998). DOI: 10.1016/S0379-6779(98)00076-9 [11] Wu T-M., Chang H-L., Lin Y-W.: Synthesis and characterization of conductive polypyrrole with improved conductivity and processability. Polymer International, 58, 1065–1070 (2009). DOI: 10.1002/pi.2634 [12] Eisazadeh H, Spinks G and Wallace G G, Material Forum , 1992, 16, 341-344. [13] Bocchi V and Gardini G P, Rapi S, J. Material Science Letters, 1987, 6, 1283-1284. [14] Armes S P and Vincent B, J. Chem. Soc., Chem. Commun., 1987, 287-294.