

## SYNTHESIS OF POLY PYRROLE, IT'S COMPOSITE WITH POLYCARBONATE RESIN AND STUDY OF THEIR ELECTRICAL PROPERTIES

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### ABSTRACT

*A composite of polypyrrole and Polycarbonate resin was prepared and identified by FTIR and UV spectroscopy. The x-ray diffraction shows some crystal structures and the d-spacing of the crystallites were calculated. The morphology of the compounds was studied by scanning electron microscope. The dc electrical conductivity of the doped and un-doped compounds was measured and compared. The dc conductivity of the composite is higher than that of its components.*

**KEYWORDS:** *Poly Pyrrole, Polycarbonate Resin, SEM, TG, X-Ray Diffraction, Dc Electrical Conductivity*

### INTRODUCTION

The polymers have brought recently great interests due to their applications in different fields, such as medical industrial and engineering. The reasons for that they have a wide range of interesting, optical, electrical and mechanical properties in addition to their cheap prices compared to the nonorganic materials(1).

The studies in the 1970s show that it is possible to get electrical conductive polymer materials. Polyacetylene shows good have conducting metallic properties after doping with n or p dopants (2). The studies show that the electrical conductivity depends on many factors, such as dopants types, chemical and, structural, crystalline temperature and applied field (3).

The electrical conductivity in the semiconducting polymer increases with temperature due to an increase of the charge carriers with temperature in the conduction band according to the band theory (4,5). Polymers are composed of long molecular chains which form irregular, entangled coils in the melt. Some polymers retain such a disordered structure upon freezing and thus convert into amorphous solids. In other polymers, the chains rearrange upon freezing and form partly ordered regions with a typical size of the order 1 micrometer(6). Although it would be energetically favorable for the polymer chains to align parallel, such alignment is hindered by the entanglement. Therefore, within the ordered regions, the polymer chains are both aligned and folded. Those regions are therefore neither crystalline nor amorphous and are classified as semi-crystalline. Crystallization of polymers is a process associated with the partial alignment of their molecular chains. These chains fold together and form ordered regions called lamellae, which compose larger spheroidal structures named spherulites(7) .

The idea of using additives to the polymers starts with the beginning of using polymers. The additives have a clear effect on rigidity, electricity resistivity, thermal stability, electrical conductivity, and other properties. Such additives are, fillers, solidifiers, elasticizers, oxidants and reluctant(8).

In this work, a composite of polypyrrole and polycarbonate resin were prepared and then doped with iodine. Both doped and un-doped composite were studied by spectroscopic, x-ray, thermal, electron microscopy and dc electrical conductivity method.

### Synthesis of the Polymers

Synthesis of polypyrrole (PPY): In a 250 ml conical flask, a solution of 1.48 ml of the monomer, pyrrole, in 50 ml ethanol was added and stirred for 15 minutes. In a 250 ml beaker, another solution was prepared by dissolving 1.623 gm of anhydrous Ferric chloride ( $\text{FeCl}_3$ ) in a mixture of 75 ml ethanol and 25 ml of distilled water. The second solution two was added, by using a separating funnel, to the first solution with continuous stirring by using. The stirring was continued for 24 hours. A black precipitate was formed(9). The black precipitate was filtered and washed with distilled water then with acetone to remove the unreacted pyrrole and ferric chloride. The black precipitate, PPY, was dried at 650C. Figure 1 shows the synthesis reaction.

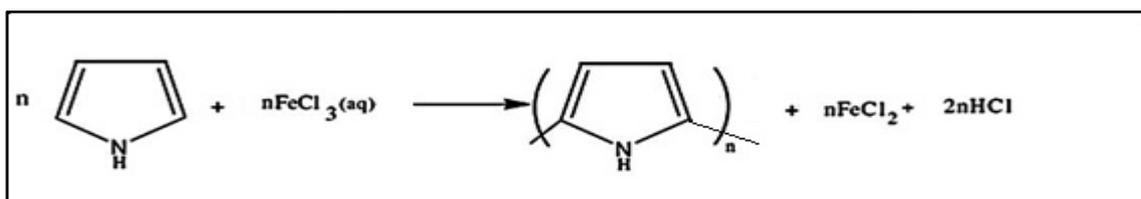


Figure 1: Synthesis of PPY

Bisphenol polycarbonate Resin(Pc-resin): was purchased from Aldrich company, it was synthesized from Bisphenol-A. and phosgene. Unit Molecular weight 254, average Mw 3600 g/mol, Its structure is shown in figure 2.

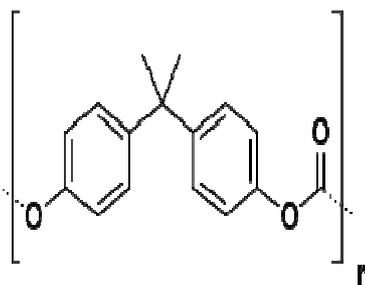


Figure 2: Polycarbonate Formula

Preparation of composite of Polypyrrole and polycarbonate (PPY/Pc-resin)

One ml of pyrrole was to a mixture of 4.8 gram of anhydrous ferric chloride dissolved in 50 ml f ethyl acetate and 0.6 gram of both of polycarbonate- resin dissolved in50 ml of chloroform(10).

The mixture was mixed wellon a magnetic stirrer for 5 hours. The solid product then filtered and washed with water and then with acetone and left to dry in room temperature.

## Doping with Iodine

A mixture of 0.1 gram of the polymer or the composite was mixed well then the solid mixture dissolved in less amount of the solvent, DMF(dimethylformamide). The thick solution was then casted on a glass substrate which prepared for measuring the electrical conductivity(11). The solvent then evaporated and then left to dry to be ready for electrical measurements.

## IR Spectroscopy

Figure 3 shows the Ir spectrum for the PPY. It shows a band in the 3419  $\text{cm}^{-1}$  which is related to the C-H stretching vibration. The bands at 1558  $\text{cm}^{-1}$  and 1315  $\text{cm}^{-1}$  and 1685  $\text{cm}^{-1}$  which are related to C=C, C-N and C=N stretching vibrations respectively(12).

Figure 4 shows the IR spectrum for Pc-resin. It shows the main band at 1780  $\text{cm}^{-1}$  for C=O stretching vibration.

Figure 5 shows the Ir spectrum for the composite of PPY/Pc- resin. It shows the main bands at 3400  $\text{cm}^{-1}$ , 1771  $\text{cm}^{-1}$ , for C-H aromatic stretching and C=O stretching respectively. And shows the band at 1543  $\text{cm}^{-1}$ , 1396 $\text{cm}^{-1}$ ,1616  $\text{cm}^{-1}$  for the C-C, C-N and C=N stretching respectively.

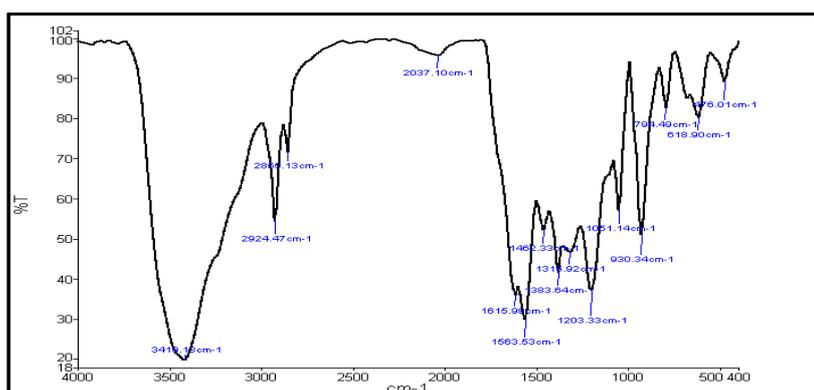


Figure 3: IR Spectrum of PPY

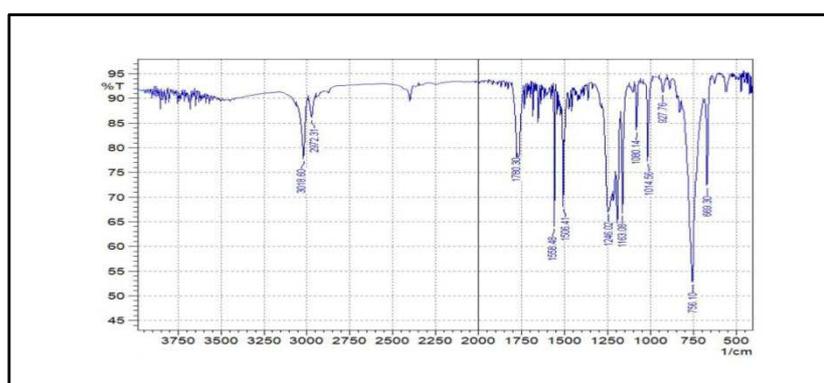


Figure 4: IR Spectrum of Pc-Resin

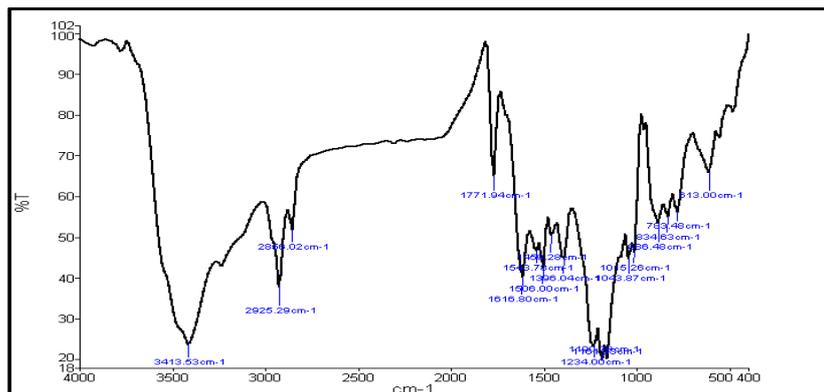


Figure 5: Ir Spectrum of Composite PPY/Pc-Resin

### Ultra-Violet Spectroscopy

The Uv spectra were measure in DMF solutions. Table 1 shows the UV bands for the polymers and their composite. The spectra show that the composite has of lower energy may be due to the interaction between the two polymers. The  $\pi \rightarrow \pi^*$  transition appears in the lower wavelength too(12,13).

Table 1 and the figures 6-8 show the Uv data for the measured spectra of the compounds.

Table 1: The Uv Spectra Bands Data for the Polymers and their Composite

Compounds		Absorbance	$n \rightarrow \pi^*$ (nm)	Absorbance	$\pi \rightarrow \pi^*$ (nm)
PPY		0.426	475	0.460	343
Pc-resin		3.076	271	-----	---
PPY/Pc-resin composite	1.258   516	3.729			361

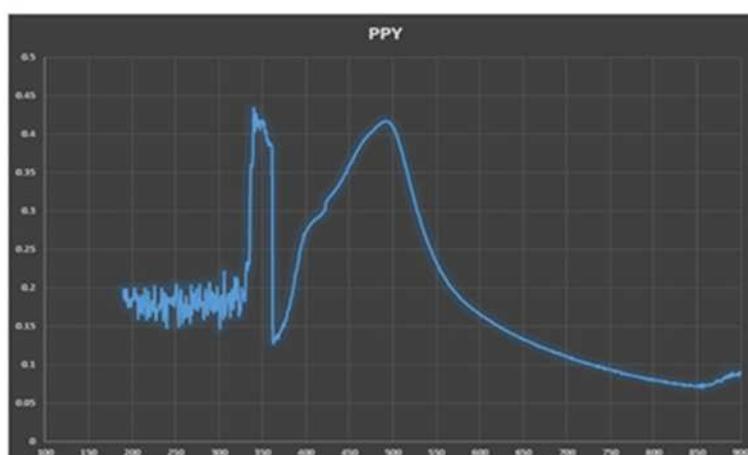


Figure 6: The Uv spectrum of the PPY

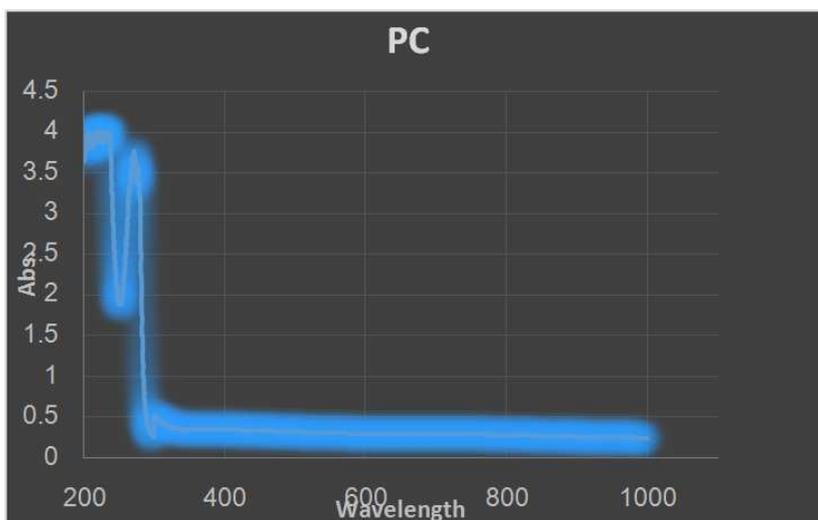


Figure 7: The UV Spectrum of the Pc-Resin

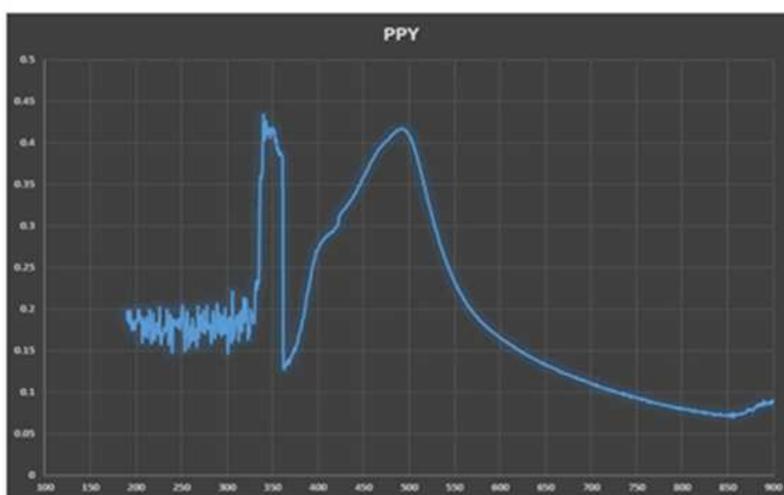


Figure 8: The UV Spectrum of the Composite PPY/Pc-Resin

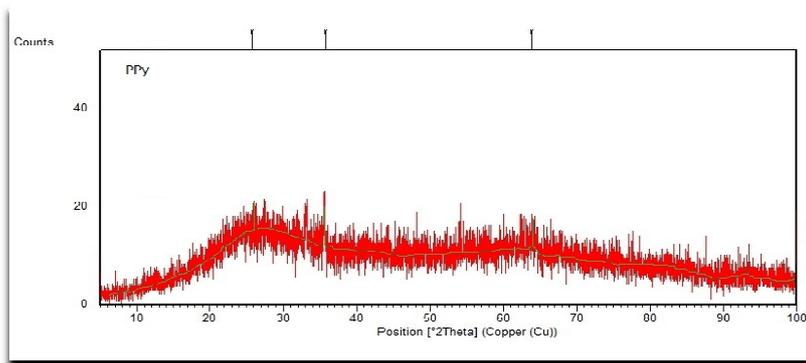
**X-Ray Diffraction (XRD)**

The figures9 and 10 shows the x-ray diffraction pattern for the PPY and the composite(the Pc-resin is very amorphous). The diffraction patterns doesn't

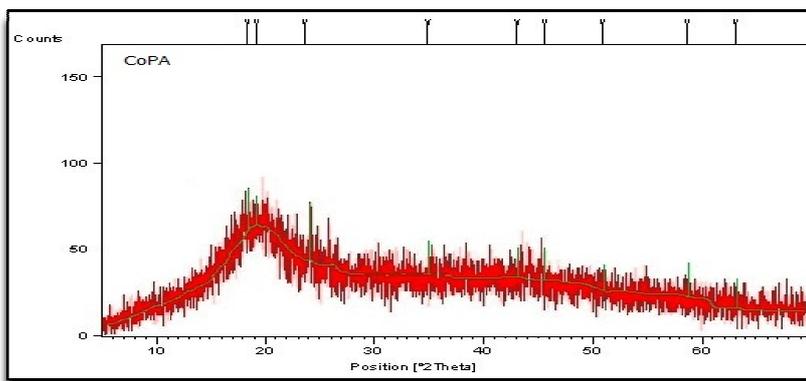
show well crystalline compounds. The figures and table 2 shows the values of 2θ and the calculated d-spacing according to Braggs law(14,15).

**Table 2: The X-Ray Diffraction Data**

Compounds	2θ	d-Spacing(Å)
PPY	26.03	3.35
	35.31	2.95
	64.85	1.75
PPY/Pc-resin composite	13.33	7.70
	21.43	4.80
	26.90	3.84



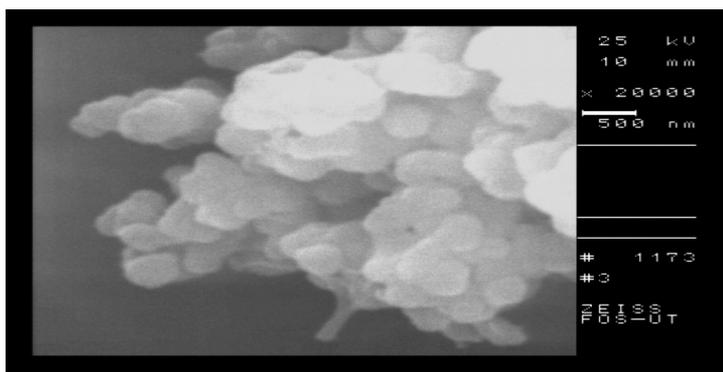
**Figure 9: the x-Ray Diffraction Pattern of PPY**



**Figure 10: The x-Ray Diffraction of the PPY/Pc-Resin Composite**

### Scanning Electron Microscopy (SEM)

The figures (11-13) shows the SEM of the studied polymers and their composite, under voltage of 25 keV and amplification of 5000-20000 and depth range 500 nm and 2 $\mu$ m . The morphological shapes show an amorphous structure which is might affect the electrical conductivity(16,17).



**Figure 11: The SEM of the Pc-Resin**

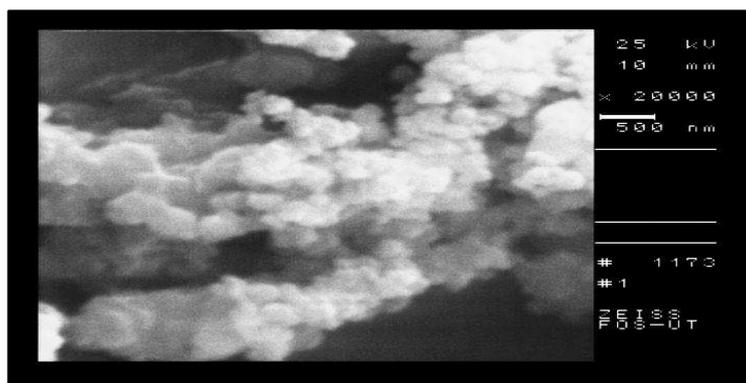


Figure 12: the SEM of the PPY

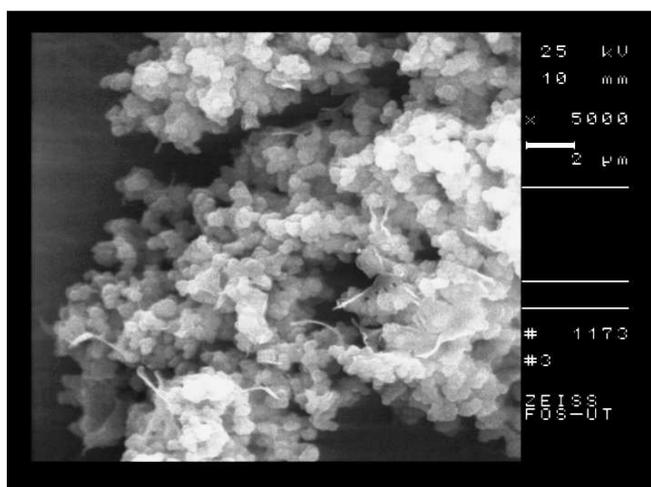


Figure 13: The SEM of the Composite PPY/Pc-Resin

### The Dc Electrical Properties

The DC electrical properties of the prepared compounds (Iodine doped and undoped) were carried out using a circle containing voltmeter and ammeter. The samples were casted as thin films on glass cells made up of fluorine tin oxide (FTO) as sandwich cells. The FTO is conductive from one side which is connected to the circuit electrodes. The sample thickness (L) was 0.5 mm (measured by micro Vernier). The area of the electrode (A) is 1 cm<sup>2</sup>. The cell constant (L/A) is 0.05 cm<sup>2</sup>. The cells were placed in variable temperature cryostat (18-20). The DC conductivity was measured in a temperature range of 300- 400 K.

$$\text{Using Arrhenius question } \ln\sigma = \ln\sigma_0 - \frac{\Delta E}{KT}$$

Were and are  $\sigma$  the  $\sigma_0$ dc conductivity and pre-exponential factor.  $\Delta E$  is the activation energy. k is Boltzmann constant.

The relations between  $\ln\sigma$  and the reciprocal temperature were drawn and the activation energy for each relation was calculated from the slope of the graphs.

Figure 8 shows the dc electrical conductivity for the studied iodine undoped compounds. The figure shows that the conductivities of the three compounds increases with temperature which refers to the semiconducting behavior, and the

conductivity of the composite is higher than that of its components PPY and Pc- resin.

Figure 9 shows the dc electrical conductivity of the iodine doped composite is higher than that of its components and the conductivity sequence is as following:

Composite. I > PPY.I >Pc-resin. Comparing the conductivities of the doped and undoped compounds in both figures shows the conductivity of the doped is higher than the conductivities of the undoped. Which could be attributed to the oxidation-reduction reactions of the compounds by the iodine to form (I-3)(21), leaving a hole in the oxidized polymers which increases the conductivity

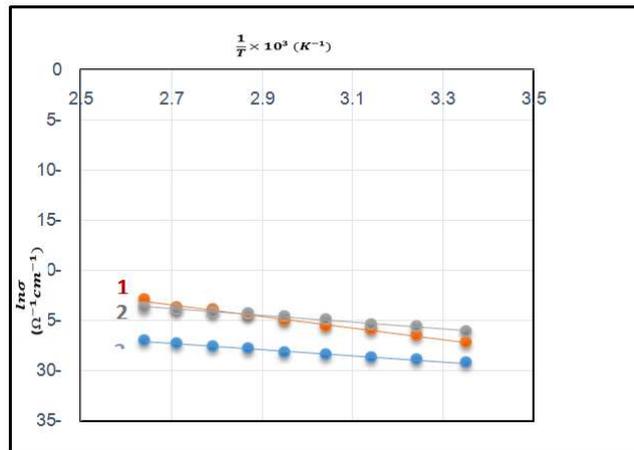


Figure 8: Relations between  $(\ln\sigma)$  and Reciprocal Temperature. For: 1-the Composite, 2-PPY and Pc-Resin

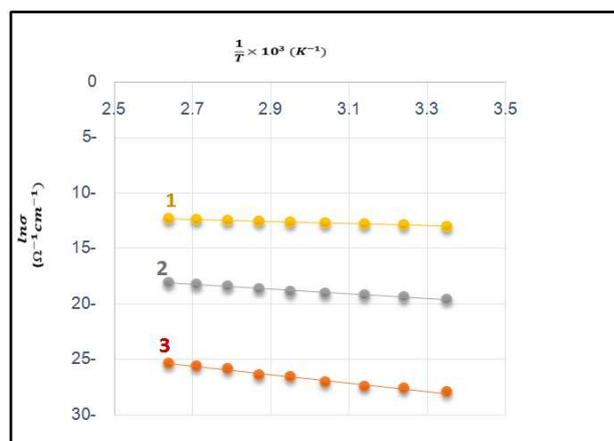


Figure 9: The Relations Between  $(\ln\sigma)$  and Reciprocal Temperature for the Iodine Doped Compounds: 1- the Composite, PPY/Pc-Resin. I, 2-PPY.I, Pc-Resin

## CONCLUSIONS

From the experimental results, we can conclude that the composite is more electrically conductive than the PPY and polycarbonate resin. The compounds shows amorphous and crystalline regions.

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## REFERENCES

1. W. Xi, H. Peng, A. Aguirre-Soto, C. J. Kloxin, J. W. Stansbury, and C. N. Bowman; *Macromolecules*, 47 (18), 6159(2014)
2. W.J. Feast, J. Tsibouklis, K. L. Pouwer; L. Groenendaal, E.W. Meijor " *polymer*" 37(22) 5017(1996).
3. 3-M.A.G. Martins, C. A. C. Sequeira " *Journal of Power Sources*" 32(2), 107( 1990) 4- S. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am Chem. Soc.*, 95 (3): 948(1973)
4. C. Kittel " *Introduction to solid state physics*" 8th ed., John Wiley and Sons(2005).
5. H. Christopher " *Polymer materials*" (2nd ed.). London, (1989).
6. E. Piorkowska G. C. Rutledge " *Handbook of polymer crystallization*" John wiley and sons, online(2013)
7. Zeming He, Juhwan Ma, Yuanfang Qu, Xuemei Feng; *Journal of European Ceramic Society*; 22(13)2143(2002)
8. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire and, and P. Teasdale " *Conductive Electroactive Polymers*" CRC Press, New York( 2003)
9. Y. A. Gowayed, R. Vaidyanathan, M. El-Halwagi; " *Journal of elastomers and plastics*", 27(1) 79(1995).
10. N. A. Hussein, A. J. Kadhim, " *International Journal of Applied and Natural Sciences*" 6(6)21(2017)
11. B. K. Sharma, " *Spectroscopy*" GOEL publishing house, India(2005) . 13- G. J. Cruz, M. G. Olayo, O. G. López, O. M. Gómez, J. Morales and R. Olayo " *Polymer*" 19, 4314 (2010)
12. J. Loiseau, N. Doerr, J. M. Suau, J. B. Egraz, M. F. Liauro and N. Ladayire; " *Macromolecule*" 36(9), 2066(2003).
13. V. Vetrivelvi and R. J. Santhi; *Res, J, Chem. Sci*, 4(5), 1(2014)
14. Y- Linda C. Sawyer; David T. Grubb; Gregory F. Meyers " *Polymer microscopy*" Springer. Press.(2008).
15. J. Kanicki, " *Polymer Semiconductor Contacts and Photovoltaic Applications*, In: *Handbook of Conducting Polymers*' Marcel Dekker, New York (1986).
16. -K. Hemant, V. B. Narendra. E. Vasant and N. Ganesh " *Journal of Sensor Technology*" 1, 47(2011)
17. P. J. Ichikadokawa, M. Akimurakumi and Y. Kaneko " *Composite science and technology*" 68(2), 493(2008).
18. D. S. Patil, S. A. Pawar, A. S. Kamble, P. S. Patil " *Silver Incorporated Polypyrrole/Polyacrylic*., *International conference on recent trends in applied physics and materials science AIP Conf. Proc.*, 1182(2013).
19. J. Simon and J. J. Andre " *Organic semiconductors*" John Wiley and sons, London(1985).



