

Polypyrrole-coated electrospun polystyrene-Fe (III) composite fibres

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ABSTRACT

Polypyrrole (Ppy) was synthesized via a chemical oxidization method with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (FCHH) on electrospun polystyrene fibres ESPSF. The spinning process was achieved using Electrospinning for three solutions of polystyrene PS including 3, 5, and 9 % wt/v of FCHH in dimethyl formamide (DMF). The fibres diameters were monitored by scanning electron microscope SEM before and after coating, and it was found that the best results were achieved at low concentrations of FCHH. The Ppy coating was applied under four exposure periods (90, 150, 200, and 270 minutes) at 22C; Fibre diameter and coating quality are directly related in the study. The technique suggests a potential route towards producing conducting fibres with micro/nanoscale dimensions using Electrospinning followed by vapor chemical polymerization of pyrrole.

KEYWORDS: Key words: Pyrrole, Electrospinning, polystyrene, conducting polymer & Fibres.

1 INTRODUCTION

Research in conducting polymers is still attracting great interest. Since earlier report by Diaz[1], many prospective novel applications have been found that many prospective novel applications have been found that take advantage of these new polymers. Applications include chemical sensors[2], biochemistry and tissue engineering[3,4], energy storage[5] and catalysis[6]. Although conducting polymers have been widely investigated there are only limited application for commercial uses[7]; the poor processability of those materials, due to brittleness and poor solubility as well are the main reasons for such commercial limitations[8–10]. Many attempts have been made to develop alternative approaches to overcome these drawbacks including synthesis soluble conducting polymers by introducing a bulky side chains[11,12] and

forming them by dispersion and emulsion polymerization[13–15]. Nowadays the family of conducting polymers includes well-known polymers such as Polypyrrole (PPy), polyaniline (PANi) and Polythiophene (PTs). These have been reportedly prepared by a variety of methods such as chemical, electrochemical oxidization and photo synthesis [8,16,17]. The first two listed approaches are attracted more interesting due to their simplicity. PPy has been frequently studied as result to its stability. For instance, it has been used to coat other organic and inorganic material including polymers films[18], nano particles[19] and fibres[20].

Attempts to produce conducting Ppy fibres by electrospinning have faced constraints due to the poor solubility of Ppy in most organic solvents. To overcome this; number of attempts have been reported, which in general include using another polymer as a carrier to the Ppy[21] or as substrate on which polymerization of Ppy can occur[22].

This study has aimed to explore the routes of the production of polystyrene/polypyrrole composite fibres by polymerizing pyrrole following the formation of substrate fibre. Polystyrene-based fibres containing an oxidant (Ferric chloride) were selected following promising early reports from the reading electrospinning team [23].

2. Materials and methods

The chemistry department at the University of Reading provides the electrospinning setup. It has been designed and set, including a high voltage syringe pump injector and drum collector made locally of 17 cm circumference (usually covered by the aluminum foil for each run). A typical plastic syringe of 10 ml is attached to a blunt stainless-steel needle of 19 gauge. Figure 1 shows the schematic of the electrospinning setup. A micro ultrasonic disrupter was used to speed up polymer solution preparation and enhance homogeneity. Electron microscopy was performed with a scanning Stereoscan 360 from Cambridge Co., and X-ray diffraction XRD analysis was carried out using a Gemini S Ultra from Oxford Diffractometer. Finally, the imaging with transmission electron microscopy was conducted using JEOL JEM-1200EX II.

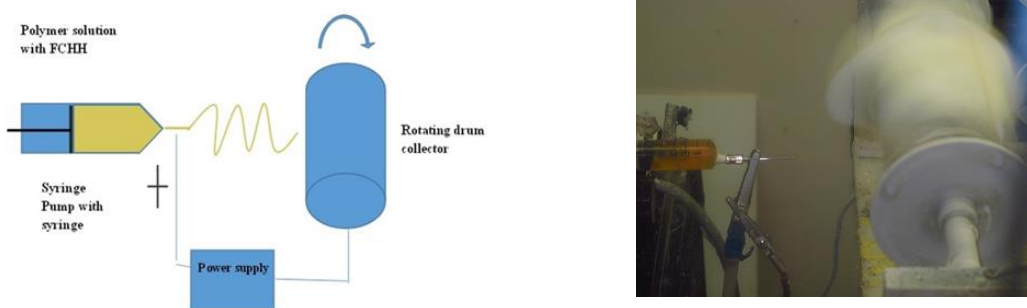


Figure 1 represents the setup of ES process.

2.2. Polymer solutions:

Three solutions of PS of 20% wt/v in DMF were prepared by dissolving 2.0 gm of PS in 10 ml of DMF with the assistance of the ultrasonic probe and left for 24 hours. A 0.9, 0.5, and 0.3 gm of FeCl₃ were added subsequently to the PS solution, and this was re-treated again with the Ultrasonic probe until there was no undissolved material. ¹Electrospinning process was carried out at room temperature at (recorded 22-23C) and relative humidity of 46-50. (Table 1.) After collecting the spun fibres, these were dried inside the oven under vacuum at 45C for 6 hours to ensure the fibre was free from solvent.

Table (1): Electrospinning parameters of PSF

.Exp No	Polymer qty (g)	DMF volume (ml)	Qty FCHH (g)	Applied voltage	flow rate ml/h	Collection Distance cm	Drum rpm
Py11	2.0	10	0.9	16 Kv	7.62	4.0	150-200
Py14	2.0	10	0.5	16 Kv	7.62	4.0	150-200
Py15	2.0	10	0.3	16 Kv	7.62	4.0	150-200

2.3. Coating with Polypyrrole

Coating of spun PS/FCHH fibres were performed by exposing the fibres to pyrrole vapour at a fixed temperature. The setup used a three glass jars of 150 ml with lids; to prepare the reaction condition, about 0.57 gm of pyrrole was transfer to each jar before it put into a set temperature water bath at 22 C. After that three glass vials of 7ml volume were provided with a measured amount of the spun fibre from each sample and placed in the pyrrole reaction jar for four different periods 90, 150, 200 and 270 min, between each run the reaction jar was washed several time by acetone and methanol, then dried by a stream of air , this to make sure the quantity of pyrrole will be the same for each run, Table 2 list the various experiments.

Table (2): Illustrates conditions of Ppy coating of PSF

Sample	Exposure time min	Quantity of fibre mg	Temp	Quantity of Pyrrole g
Py11-a	90	13.1	22	0.579
Py11-b	150	12.6	22	0.577
Py11-c	200	12.1	22	0.580
Py11-d	270	10.8	22	0.582

Py14-a	90	24	22	0.581
Py14-b	150	22.8	22	0.581
Py14-c	200	21.9	22	0.578
Py14-d	270	17.3	22	0.581
Py15-a	90	17	22	0.578
Py15-b	150	16.1	22	0.577
Py15-c	200	18	22	0.579
Py15-d	270	12.8	22	0.581

3.Results and Discussion

Three different samples of spun fibre as a matrix of PS fibre with included FeCl_3 were prepared, the primary observation show a coloured fibre containing salt as an oxidation agent for the next step. It is obvious as the amount of ferric chloride increased the yellow colour of fibres became more vivid, this clearly demonstrated by the Figure 2, which represent an image of the three spun fibres samples after spinning.

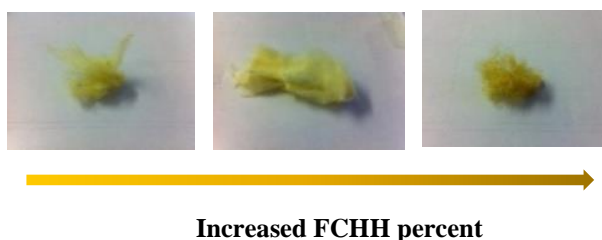


Figure 2 Image of spun fibres from three solutions of PS with different content of FCHH

Twelve specimens of fibres were exposed to pyrrole. The Primary observation was that as the time of exposure to pyrrole increased, a change in fibres colour from pale yellow to grey and then to black was seen in Figure 3 represents an image of 12 samples of fibres of the three different spun fibres arranged in, and each group includes four specimens showing different exposure times. It was observed that fibres of Py15 (with a lower amount of the oxidant) responded more readily to coating in all exposure periods, and it lost its structure as a fibre after 270 min. At the same time, specimens Py14 a-d still retained the shape of fibre but suffered from shrinking. Sample Py11 did not appear to be coated entirely for all the fibres, even at the longest exposure period.

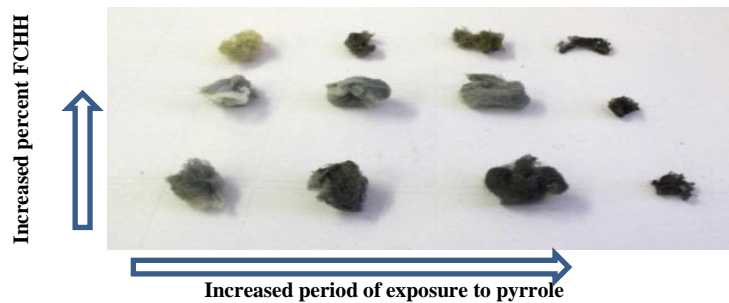


Figure 3 Images of 12 specimens of three spun fibres with different amount of FCHH after exposing to pyrrole vapour in various periods,

All the fibres at 270min of exposure became more brittle in comparison with starting coating stage or before coating. The morphology of these fibres was examined by a SEM to determine their shape and later to determine the mean diameter of them; as it expected this diameter will related to the amount of salt, this was done by using of a Scandium software from Olympic. The mean diameter values calculation of the three collected fibre is illustrated in Table 3. The data in Table 3 shows that the spun from the lower concentration of Ferric ions has smaller diameter in compared to that spun from high Fe^{+3} concentration PS solutions.

Table (3): Lists average diameter calculation of the spun fibres.

Sample	Percent of FCHH	Mean diameter μm	Minimum Diameter μm	Max Diameter μm	Standard Deviation
Py 11	9%	10.97	3.42	18.82u	3.63
Py 14	5%	3.56	1.65	7.38u	1.96
Py 15	3%	1.67	0.73	3.67u	0.94

The SEM images in Figure (4) show PS/FCHH fibres before and after coating with Ppy and indicates fibres welding which leads to shrinking of fibres volume. In this instance, Py15a-d (lower FCHH content) showed a good response to coating, and SEM images indicate the Ppy layer was inhomogeneous. In contrast, fibres spun from higher ferric chloride solutions, like Py14a-d or Py11a-d, become more distinguishable as their diameter increases[24]. In addition, the TEM images in figure (5) prove that Ppy developed as an inhomogeneous coating after the Ppy coating had been applied to the fibres. Accordingly, the morphology of Ppy layer will be related to both the concentration of oxidization agent and to the diameter of the substrate (the electrospun fibres)

Due to its low solubility characterisation of Polypyrrole is difficult. However here we are able to identify of Ppy using X-ray diffractometer which was performed for best coated sample at the longest period of exposure of sample Py15 and before coating. XRD results show two main zones for spun fibre of PS/FCHH, the first zone includes two peaks (a and b) in region of 12 and 20 respectively both peaks are belong to coating syndoatactice polystyrene[25–27] as it illustrates in figure (6).

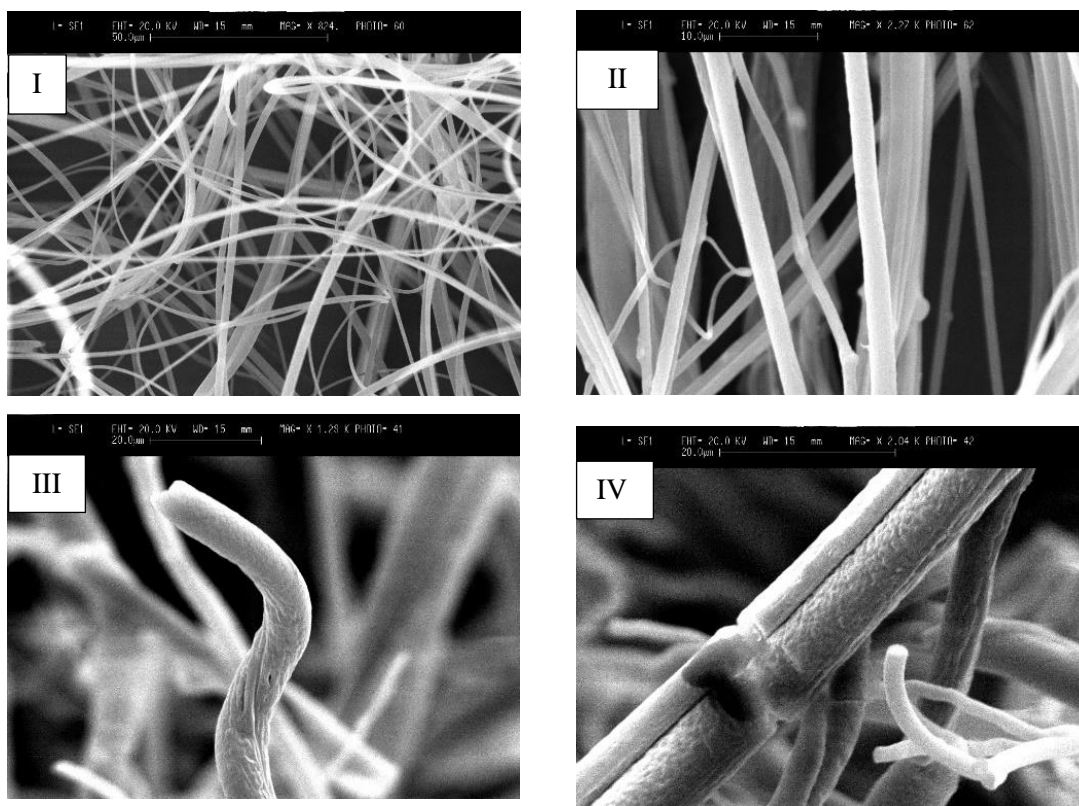


Figure (4) A group of images taken by SEM for spun fibres before and after treated by pyrrole, from the top image I represents a spun PS fibre of solution Py15 before exposing to pyrrole, Image II show sample Py15-c, Image III illustrates pattern of coating with Ppy of large diameter single fibre of sample Py11-d, and image IV shows the welding pattern of two fibre inside experiment Pv14-d.

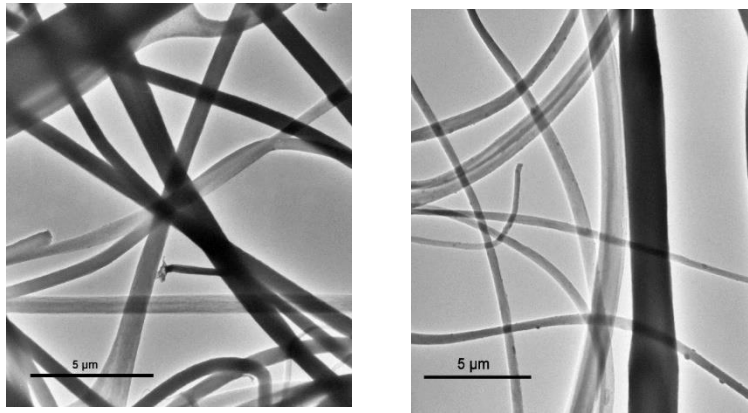


Figure (5) Images taken by TEM; before coating with Ppy (left) and after coating (right).

Another zone came as abroad peak with lower intensity in region 35-45 related to Ferric ion (III). After process a new zone can be seen as shoulder to the second peak which is marked as **d** zone, this zone can be found around 20 degree which is pointing directly to Ppy ; usually this peak came as abroad peak even with a pure Ppy prepared by the same oxidizing agent[28] Another technique was used to confirm Ppy formation, where a sample of a coated PS fibres with Ppy where dissolved in DMF, both of PS and Ferric inorganic halogen were dissolved while the PPy filtered out as black precipitate and washing with DCM several time to remove any DMF and dried inside a vacuumed oven at 40C for 1 h, then tested with XRD diffractometer.

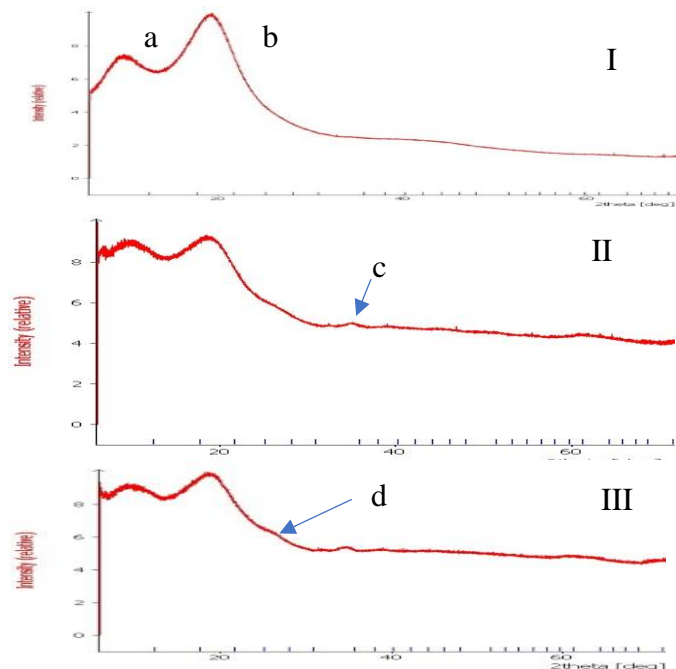


Figure (6) Shows three diagrams of XRD from I to III of electrospun PS fibres, Py15 and Py15-d in sequence from top to bottom respectively.

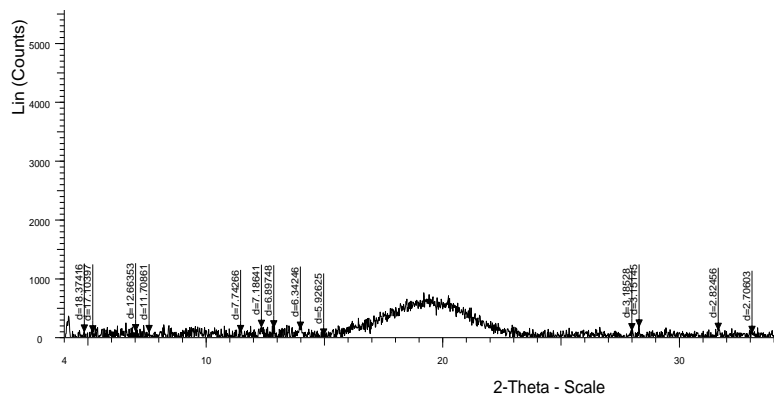


Figure (7) XRD pattern of prepared Ppy by same oxidant agent

Conclusions

A route to producing pyrrole-coated fibres has been explored and developed. The optimum conditions for coating ferric chloride-doped fibres with pyrrole require reasonably high concentrations. What is more, particular needs to be taken after the period of exposure as a long exposure, the fibre will lose its discrete structure. The result of the XRD test shows a light peak close to 20, which refer to Ppy. The morphology of the coated Ppy was examined with TEM, and the images reveal that the Ppy coated the whole fibres and cumulated as attached beads on the fiber's surface. Moreover, fibres spun from solution with a lower amount of Ferric chloride show better coating response comparably. It may also be explained by the fact that as the diameter of electrospun fibres becomes finer, the surface area increases, so pyrrole vapor can develop more readily.

REFERENCES

- [1] Diaz, A.F., K.K. Kanazawa, and G.P. Gardini, *Electrochemical polymerization of pyrrole*. Journal of the Chemical Society, Chemical Communications, 1979. 14: p.635–636.
- [2] Ramanavičius A., A. Ramanavičienė, and A. Malinauskas, *Electrochemical sensors based on conducting polymer—polypyrrole*. Electrochimica Acta, 2006. 51: p.6025–6037.
- [3] Zarei, M., A. Samimi, M. Khorram, M.M. Abdi, and S.I. Golestaneh, *Fabrication and characterization of conductive polypyrrole/chitosan/collagen electrospun nanofiber scaffold for tissue engineering application*. International Journal of Biological Macromolecules, 2021. 168: p.175–186.
- [4] Sajesh, K.M., R. Jayakumar, S.V. Nair, and K.P. Chennazhi, *Biocompatible conducting chitosan/polypyrrole-alginate composite scaffold for bone tissue engineering*. International Journal of Biological Macromolecules, 2013. 62: p.465–471.
- [5] Kausar, A., *Overview on conducting polymer in energy storage and energy conversion system*.

- Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 2017. 54: p.640–653.
- [6] Zhou, Q., and G. Shi, *Conducting Polymer-Based Catalysts*. Journal of the American Chemical Society, 2016. 138: p.2868–2876.
- [7] Roth, S., W. Graupner, and P. Mcneillis, *Survey of Industrial Applications of Conducting Polymers*. Acta Physica Polonica A, 1995. 87: p.699–711.
- [8] Namsheer, K., and Rout CS. , *Conducting polymers : a comprehensive review on recent advances in synthesis , properties and*. RSC Advances, 2021: Royal Society of Chemistry 11: p.5659–5697.
- [9] Ravichandran, R., S. Sundarrajan, J.R. Venugopal , S. Mukherjee, and S. Ramakrishna , *Applications of conducting polymers and their issues in biomedical engineering*. Journal of the Royal Society Interface, 2010. 7. p. 635-636.
- [10] Maiti, S. , *Recent trends in conducting polymers: Problems and promises*. Journal of Chemistry, 1994. 33: p.524–539.
- [11] Zhang, S., G. Wang , Lv. Guowei, D. Yu, and Y. Ding, *Synthesis and fluorescence properties of a soluble polypyrrole derivative based on a dipyrrole monomer*. Synthetic Metals, 2014. 195: p.185–192.
- [12] Wang, W., D. Yu, and F. Tian, *Photoluminescence of a soluble polypyrrole based on N-vinylpyrrole*. Journal of Luminescence, 2010. 130: p.494–497.
- [13] John, J., P. Saheeda, K. Sabeera, and S. Jayalekshmi, *ScienceDirect Doped polypyrrole with good solubility and film forming properties suitable for device applications*. Materials Today: Proceedings, 2018. 5: p.21140–21146.
- [14] Ju, E., K. Sik, and A.G. Macdiarmid, *High molecular weight soluble polypyrrole*. Synthetic Metals, 2002. 125: p.267–272.
- [15] Zha, Z., et al., *Engineering of perfluorooctylbromide polypyrrole nano-/microcapsules for simultaneous contrast enhanced ultrasound imaging and photothermal treatment of cancer*. Biomaterials, 2014. 35: p.287–293.
- [16] Guo, X., and A. Facchetti, *The journey of conducting polymers from*. Nature Materials, 2020. 19: p. 922-928.
- [17] Fang, Q., D.G. Chetwynd, and J.W. Gardner, *Conducting polymer films by UV-photo processing*. Sensors and Actuators, A: Physical, 2002. 99: p.74–77.
- [18] Washburn, S., E. Townsend, J. Lauterbach, and C.M. Snively, *Desorption and photopolymerization behavior of mixed and multilayered styrene-pyrrole nanofilms*. Applied Surface Science, 2006. 252: p.6228–6235.
- [19] Yang, X., and Y. Lu, *Preparation of polypyrrole-coated silver nanoparticles by one-step UV-induced polymerization*. Materials Letters, 2005. 59: p.2484–2487.
- [20] Wang, H., J. Ding, B. Lee, X. Wang, and T. Lin, *Polypyrrole-coated electrospun nanofibre membranes for recovery of Au (III) from aqueous solution*. Journal of Membrane Science, 2007. 303: p.119–125.

- [21] Chronakis, I.S., S. Grapenson, and A. Jakob, *Conductive polypyrrole nanofibers via electrospinning: Electrical and morphological properties*. Polymer, 2006. 168: p.175-186.
- [22] Merlini, C., R.D.S. Almeida, M.A. D'Ávila, W.H. Schreiner, and G.M. De Oliveira Barra, *Development of a novel pressure sensing material based on polypyrrole-coated electrospun poly(vinylidene fluoride) fibers*. Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 2014. 179: p.52–59.
- [23] Sen, S., F.J. Davis, G.R. Mitchell, and E. Robinson, *Conducting nanofibres produced by electrospinning*. Journal of Physics: Conference Series, 2009. 183: p.1–6.
- [24] Stanger, J.J., *Charge Transfer Mechanisms in Electrospinning*. University of Canterbury, 2008. University of Canterbury.
- [25] Hwang, S.H., M.J. Kim, and J.C. Jung, *Mechanical and thermal properties of syndiotactic polystyrene blends with poly(p-phenylene sulfide)*. European Polymer Journal, 2002. 38: p.1881–1885.
- [26] Fang, J., Y.Xuan, and Q. Li, *Preparation of polystyrene spheres in different particle sizes and assembly of the PS colloidal crystals*. Science China Technological Sciences, 2010. 53: p.3088–3093.
- [27] Couvrat, N., Y.Cartigny, S. Tisse, M.N. Petit, and G. Coquerel, *Binary phase diagram between phenanthrene and its main impurity: Dibenzothiophene*. JEEP 2011 - 37th Conference on Phase Equilibria, 2011: 4: p.1–5.
- [28] Chitte, H.K., N.V. Bhat, V.E. Walunj, and G.N. Shinde, *Synthesis of Polypyrrole Using Ferric Chloride (FeCl₃) as Oxidant Together with Some Dopants for Use in Gas Sensors*. Journal of Sensor Technology, 2011. 1(2): p.47–56.