

Green synthesis of nano polypyrrole using urea-hydrogen peroxide

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Abstract

Polypyrrole is one of the most useful conductive polymers, but green synthesis of this polymer has been restricted until now. The objective of the present study is green synthesis of nano polypyrrole (PPy) by oxidative polymerization using urea-hydrogen peroxide. It was found that conductivity and morphology of polypyrrole are highly dependent on the reaction conditions such as the molar ratio of oxidized to monomer, temperature, reaction time, kind of solvents, the presence of a catalyst such as *p*-toluene sulfonic acid, and specially concentration and addition time of hydrochloric acid. After understanding the relationship between these factors, we turned this enormous variability into improved polypyrrole properties.

Keywords: Conductive polymer; green chemistry; oxidation polymerization; nano PPy; *P*-toluene sulfonic acid.

Introduction

These days, conductive polymers have promising application in different fields. These polymers can be more easily processed than metals; they can cover large surfaces and also are lighter than metals. PPy is one of the most studied and most useful conductive polymers due to its chemical stability, high

conductivity and easy synthesis method. PPy also has many potential applications such as in electronic devices, electrodes for rechargeable batteries [1,2], supercapacitors [3,4], solid electrolytes for capacitors [5,6], electromagnetic shielding materials [7], sensors [8], corrosion-protecting materials [9-13], actuators [14], electrochromic devices

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[15], and membranes [16].

Study of nano-size particles of this polymer is of great interest. Nano PPy can be synthesized by electrochemical or oxidative chemical methods, but green synthesis of this polymer would be interesting. UHP (urea-hydrogen peroxide), as an oxidant, is one of the best choices because it is easy to handle, safe, more stable than hydrogen peroxide and it can be considered as a carrier of the unstable and hazardous hydrogen peroxide. Considering these aspects, UHP was used for metal-free chemical oxidation of pyrrole. It has been observed that the ultimate size, morphology and shape of polypyrrole nanoparticles are highly subjective to the reaction conditions. Fundamental understanding of how size and morphological changes influence the physico-chemical properties of polypyrrole nanoparticles are of great technological interest.

Though, UHP is a cheap, mild and an environmentally benign oxidant with highly active oxygen, but with slow oxidizing properties in the absence of activators. Direct oxidation by this compound is often kinetically unfavored. The use of a catalytic system with electron-transfer mediators (ETMs) usually facilitates the procedure by transporting the electrons from the catalyst to the oxidant along a low-energy pathway,

thereby increasing the efficiency of the oxidation and thus complementing the direct oxidation reactions.

Over the past few years, TSA (*p*-toluene sulfonic acid) was used as a catalyst in different areas of organic synthesis [17-26]. In this study, we attempt to characterize the effect of various probable UHP catalysts such as TSA, anthraquinone-2-sulfonic acid (ASA) and HCl to determine what actually controls the rate of oxidative polymerization and hence the structure of the polymer.

Experimental

Urea and hydrogen peroxide were commercially purchased (Aldrich). Pyrrole was distilled under reduced pressure and stored at 4 °C. Scanning electron microscopy (SEM) measurements were performed with a LEO 1455 VP microscope. Transmission electron microscopy (TEM) experiments were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 200 KV. FT-IR Spectra of KBr powder-pressed pellets were recorded on a Bomem FT-IR spectrometer. Bulk conductivity measurements were measured by using four-point probe method. Reaction monitoring was accomplished by TLC on silica gel Polygram SILG/UV 254 plates.

Procedure for the synthesis of nano polypyrrole

Freshly distilled pyrrole (3.35 g, 0.05 mol) was added dropwise through a dropping funnel to a magnetically stirred mixture of 15 mL aqueous solution of UHP (0.05 mol) and TSA (0.95 g, 0.005 mol) at room temperature. The color of the mixture gradually turned black. The resulting products in each time interval was then centrifuged, filtered, washed with copious amount of distilled water and dried at ambient temperature.

Sample A: The reaction was allowed to proceed for 30 min. The conductivity of the product was 0.0033 S/cm.

Sample B: The reaction was allowed to proceed for 4 h. The conductivity of the product was 5.88×10^{-5} S/cm.

Sample C: The reaction was allowed to proceed for 20 h. The conductivity of the product was 9.26×10^{-9} S/cm.

Sample D: At the beginning of the reaction, 15 mL HCl solution (1 M) was added to the mixture of UHP, PY and TSA. Morphology of product was amorphous with 10^{-6} S/cm conductivity.

Sample E: After 25 min, 1 mL HCl (1M) was added to the reaction mixture, and the reaction was allowed to proceed for next 5 min at room temperature. The conductivity of the product was 0.005 S/cm.

Sample F: The resulting product was washed

with 50 mL HCl (1 M) and dried at ambient temperature. The conductivity of the product was 0.025 S/cm.

Sample G: In the beginning the reaction, 15 mL HCl solution (3 M) was added to the mixture of UHP, PY and TSA. Morphology of product was amorphous and nonconductive. The effect of Py/UHP molar ratio, the effect of TSA (dopant) amount at the time of reaction, conductivity, and the morphology of the resulting products are given in **Tables 1-3**.

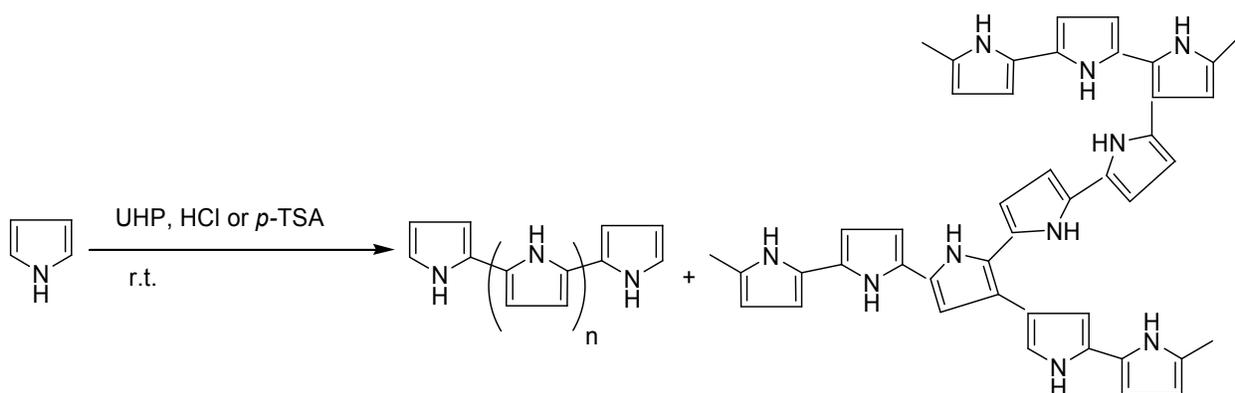
Results and discussion

Literature survey on the use of *p*-toluene sulfonic acid as an oxidant activator shows that it was used by Yang *et al.* [27] as an activator for oxidation of sulfides to sulfoxides by iodobenzobenzene, selectively. Furthermore, Berkessel *et al.* [28] reported that the oxidation of cyclohexanone with hydrogen peroxide was catalyzed by this compound. Furthermore, the autoxidation of *p*-xylene was carried out by the $\text{Co}(\text{OAc})_2/\text{Mn}(\text{OAc})_2/\text{Br}^-$ as a catalyst in the presence of *p*-toluenesulfonic acid [29]. Finally, *p*-toluene sulfonic acid catalyzed oxidation of monoterpenes in combination with palladium [30].

At the first stage, in order to evaluate the effect of oxidant, reactions of UHP with different molar ratios of oxidant to monomer

(from 1/4 to 4/1) were studied. There was no sign of reaction progress appeared after 7 days. Thus, four proposed catalysts (TSA, hydrochloric acid, ASA and its sodium salt) were examined. In the first attempt, TSA was selected as a catalyst (and dopant). The reaction started immediately and it was completed after 30 minutes in 1:1 molar ratio of Py/UHP. No reaction occurred when this catalyst was used in the absence of UHP.

Since this compound cannot act as an oxidant, two important and helpful factors would be its acidic proton that helps in proton-assisted electron transfer during oxidation of pyrroles, and its surfactant-like behavior in that the radicals are stabilized and protected from unwanted side reactions with the solvent, oxygen or other nucleophile (**Scheme 1**).



Scheme 1. Schematic representation of PPy formation

In the third set of conditions, ASA sodium salt was chosen in combination with UHP. The reaction was very slow and incomplete even after several days. In the fourth study for checking the proton effect, anthraquinone-2-sulfonic acid was used as a catalyst. This acid can accelerate the reaction the same as TSA. According to the results mentioned above, the presence of acid is an important factor for acceleration of

polymerization of pyrroles by UHP as shown in the literature survey.

The effect of hydrochloric acid was examined in different situations. When the polymer was washed with this acid (six times, 50 mL, 1 M), due to doping effect, conductivity was raised from 0.0033 to 0.025 S/cm. Therefore, acid can change the aromaticity of pyrroles in polymer and transform sp^2 orbital of nitrogen into sp^3 . In

another attempt through which hydrochloric acid (1 M) was added at the beginning of the polymerization of Py, it was found that the conductivity has diminished. When, the concentration of acid was changed to 3 M, the reaction was accelerated vigorously together with gas generation (H_2) [31]. Under this circumstance, morphology control was impossible and a nonconductive aggregate was formed. However, one can say that the addition of the high concentration of acid at the beginning of the reaction can change the morphology of polymer and cause crosslink, in a manner that PPy would lose its conductivity. This situation has occurred even after completion of the reaction and keeping the obtained polymer in 3 M hydrochloric acid resulting in an aggregated, nonconductive polymer. For 1M hydrochloric acid, the rate of the reaction is very high and creates aggregated polymer, but it is very low to evolve a remarkable hydrogen gas. Thus, high concentration of acid isn't suitable for this reaction and creates crosslinked polymer.

Finally, hydrochloric acid (1 M) was added in the presence of UHP but in the absence of TSA. In this case, the reaction was at the same rate as when TSA was present but the conductivity was low. Thus, it is likely that the presence of TSA is

important due to its surface activity, which acts as a template and a uniform morphology is obtained.

In the continuation of our research, the effects of different solvents on the reaction time were studied. The best result was gained from water, and no reaction was occurred in other solvents such as methanol, ethanol, and a mixture of water/ethanol.

This reaction was studied under different temperatures in combination with Py, UHP, and TSA. At 0 °C, the reaction rate was low and the conductivity of polymer was low too; it is may be due to decrease of surfactant ability of TSA. Under identical conditions, but at 50 °C, the reaction was very slow, which it could be as a result of decomposition of UHP. The best result was obtained at room temperature.

It was found that the conductivity measurement could be a facile and simple way to guess the morphology of obtaining PPy prior to SEM and TEM studies. Sample with low conductivity has an aggregate structure and sample with high conductivity has uniform morphology. This enhancement in conductivity is related to better polymer chain orientation that, in turn, enhances conjugation lengths.

In conclusion, we report a new successful strategy for the synthesis of nano

PPY. The attractive features of this protocol compared with previous work are, 1:1 ratio of oxidant to monomer, absence of transition metal catalysts, need of room temperature, short reaction time, and showing a tailor-made reaction whose dimensions and morphology of the product varies with reaction time. This nano PPY can be used as a conducting filler in making conducting polymer composites [32-34].

Characterization of polymers

IR spectra of the PPys obtained here were identical to the literature reports [35-38]. The broadband in the range of 4000-2000 cm^{-1} which is known as “tail of the electronic absorption band” is one of the characteristics of the conducting form of polypyrrole that is clearly visible in our polymer samples. The bands centered at 1537, 1470, 1295 and 1185 cm^{-1} can be assigned to be due to C=C (str.) and C=N (in plane), C-C (str.) and C-N (str.) vibrations, respectively (Figure 1).

Different nanopolypyrrole samples were obtained by changing the reaction time of the

polymerization. The weak absorption around 1686 cm^{-1} due to the presence of carbonyl groups (as a sign of formation of pyrrolidinone, isolated or conjugated) was seen in some of the samples. Under optimized conditions (Py/UHP/TSA=1/1/0.1, 15 mL water, room temperature), this absorption appeared after 4 hours reaction time (Table 1, Entry 3), under the same conditions, but bubbling the reaction mixture with N_2 gas, carbonyl group was formed very quickly (after 1.5 hours). This phenomenon could be due to the faster agitation of the reaction mixture and strong collision between water and the hydroxyl group as a nucleophile and formed polypyrrole. Thus, carbonyl formation was time dependent. Nanopolymer formed at the beginning of the reaction was free of this group. This result is also appeared in conductivity of polymer, and the best conductivity was obtained during the first 4 hours of the reaction time.

Table 1. The effect of Py/UHP molar ratio in 15 mL of water in the presence of 0.005 mol TSA

Entry	Py/UHP	Py (mol)	UHP(mol)	Reaction time
1	4	0.05	0.0125	>10 h
2	2	0.05	0.025	>3 h
3	1	0.05	0.05	30 min

4	0.5	0.025	0.05	30 min
5	0.25	0.0125	0.05	30 min

Table 2. The effect of TSA (dopant) on the time of reaction for molar ratio of Py/UHP=0.05/0.05

Entry	TSA (mol)	Time of reaction (min)
1	0.001	2
2	0.0005	2
3	0.00025	10

Table 3. Time and pH effects for Py/UHP/TSA =1/1/0.1 in 15 mL of water

Entry	HCl (mL, M)	Other condition	Time	Conductivity (S/ cm)	Morphology	Yield (%)
1	-	-	30 min	0.0033	Nano globular particles (predominant) + nano fiber	77
2	-	-	4 h	5.88×10^{-5}	globular particles + fiber	89
3	-	-	20 h	9.26×10^{-9}	Micron size globular particles (predominant)	91
4	15, 1	Acid was added at first	30 min	10^{-6}	Amorphous	84
5	1, 1	25 min after	30 min	5×10^{-3}	Nano globular particles + nano	77

		reaction started			fiber	
6	50, 1	Washing with acid	30 min	2.5×10^{-2}	Nano globular particles (predominant) + nano fiber	77
7	15, 3	Acid was added at first	30 min	-	amorphous and nonconductive	

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the morphology of the obtained PPy samples. The images show one-dimensional fiber like structures of polypyrrole in nanodimensions when the reaction is conducted for a short duration of time (30 min, Figures 2 and 3). As the time increases, there is a tendency by the polymer to acquire a granular form (4 h, Figures 4 and 5; 20 h, Figure 6). The width of obtaining nanofiber is around ~50-105 nm. These structures show uniform morphology and were grown almost parallel to each other. Therefore, one can say that varying the reaction time intervals can be helpful in morphological control of polypyrrole nanostructures obtained using UHP as an oxidant.

Conductivities of the resulting polypyrrole nanostructures synthesized were measured by the four-probe method. The obtained polypyrrole nanostructures show typical nonmetallic behavior with a maximum conductivity of 2.5×10^{-2} S/cm at room temperature. The low room temperature conductivity of the optimized polypyrrole nanostructures is in accordance with the PPy reported by Zhang *et al.* [39] and Kaiser *et al.* [40] due to the low doping level.

The proton nuclear magnetic resonance spectrum ($^1\text{H-NMR}$), the carbon-13 nuclear magnetic resonance spectrum ($^{13}\text{C-NMR}$), and the X-ray scattering (XRD) pattern of nano PPy are presented in Figures 7-9, respectively.

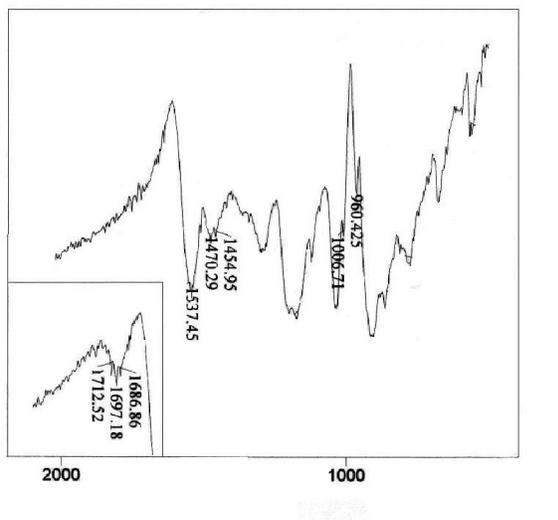


Figure 1. IR of PPY. Inset: carbonyl group

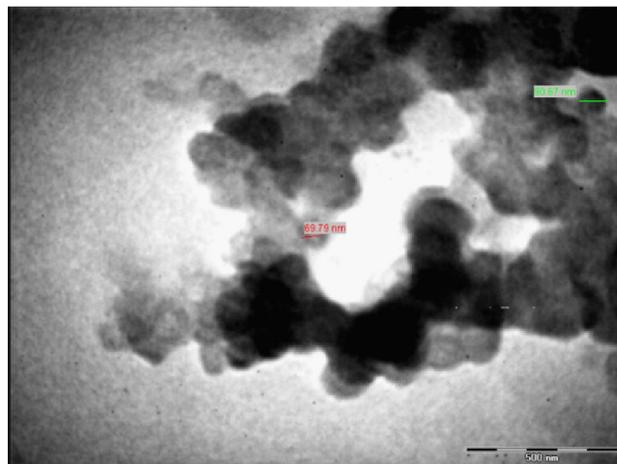


Figure 2. SEM image showing globular particles

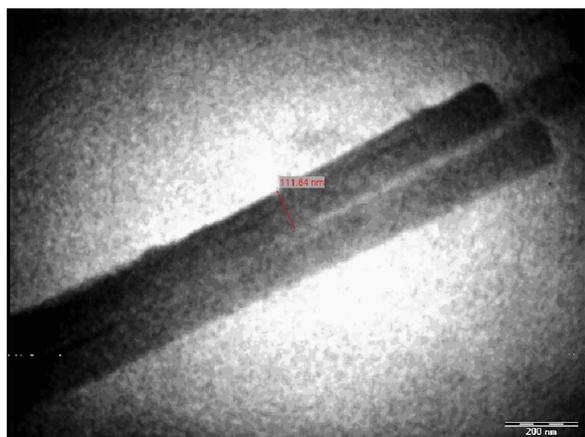


Figure 3. SEM image showing PPY fibers

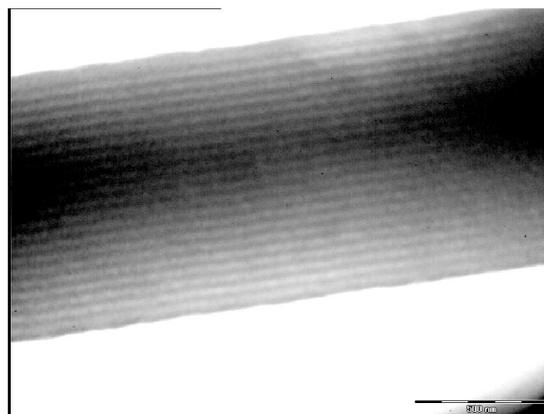


Figure 4. TEM image showing PPY fibers

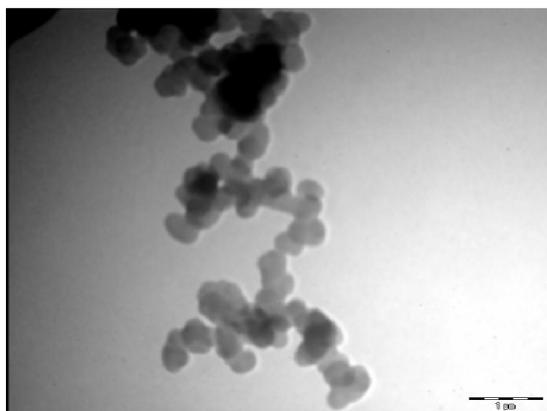


Figure 5. TEM image showing PPY globular particles

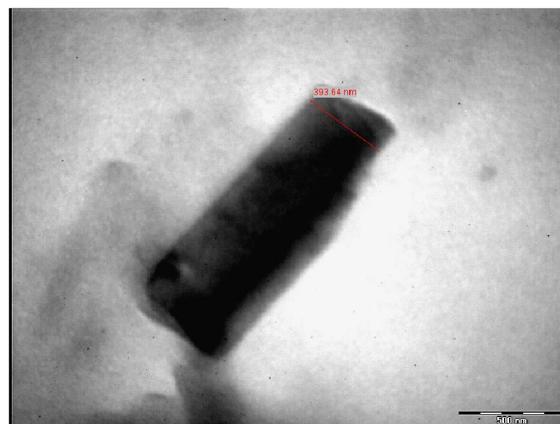


Figure 6. SEM image showing poly PPY fiber

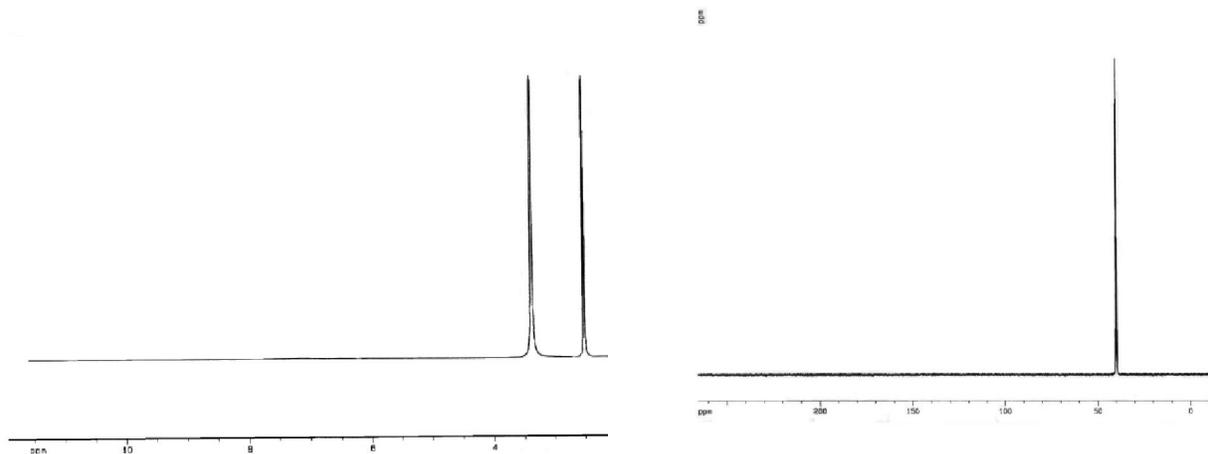


Figure 7. ^1H -NMR of PPy

Figure 8. ^{13}C -NMR of PPy

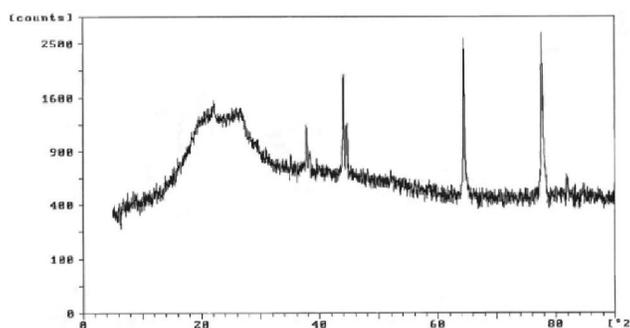


Figure 9. XRD of PPy

Conclusion

Despite the progress on the synthesis of nano polypyrrole, there are still some limitations with respect to using green conditions for this reaction. In this research, we found that using TSA as a surfactant, dopant and oxidant activator, water as solvent and 30 minutes for reaction time offers the best conditions for green synthesis of nano PPy by UHP. Hydrochloric acid can play different roles in this polymerization depending on its concentration and time of addition. PPY size

and morphology and pyrrolidinone appearance, as side products, are also time dependant.

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References

- [1] H. Saito, S. Uegusa, *J. Adv. Sci.*, **2001**, *13*, 76-77.

- [2] H.-K. Song, G.T.R. Palmore, *Adv. Mater.*, **2006**, *18*, 1764-1768.
- [3] L. Liu, , Y. Zhao, Q. Zhou, H. Xu, C. Zhao, Z. Jiang, *J. Solid State Electrochem.*, **2007**, *11*, 32-37.
- [4] S.A. Hashmi, R.J. Latham, R.G. Linford, W.S. Schlindwein, *Polym. Int.* , **1998**, *47*, 28-33.
- [5] F. Larmat, J. R. Reynolds, Y.-J. QIU, *Synth. Met.* , **1996**, *79*, 229-233.
- [6] S.A. Hashmi, H.M. Upadhyaya, *Solid State Ionics*, **2002**, *152/153*, 883-9.
- [7] M.S. Kim, H. K. Kim, S. W. Byun, S. H. Jeong, Y.K. Hong, J.S. Joo, K.T. Song, J.K. Kim, C.J. Lee, J.Y. Lee, *Synth. Met.*, **2002**, *126*, 233-239.
- [8] N.R. Stradiotto, H. Yamanaka, M. Valnice, B. Zanoni, *J. Braz. Chem. Soc.*, **2003**, *14*, 159-173.
- [9] J.I. Martins, T.C. Reis, M. Bazzaoui, E. A. Bazzaoui, L. Martins, *Corros. Sci.*, **2004**, *46*, 2361.
- [10] M. Bazzaoui, E.A. Bazzaoui, J.I. Martins, L. Martins, *Mat Sci Forum.*, **2004**, *484*, 455-6.
- [11] M. Bazzaoui, L. Martins, E. Bazzaoui, A.J.I. Martins, *J Electroanal Chem.*, **2002**, *537*, 47-57.
- [12] M. Bazzaoui, E.A. Bazzaoui, L. Martins, J. I. Martins, *Synth. Met.*, **2002**, *128*, 103-114.
- [13] M. Bazzaoui, J.I. Martins, E.A. Bazzaoui, T.C. Reis, L. Martins, *J. Appl. Electrochem.*, **2004**, *34*, 815-822.
- [14] A.S. Hutchison, T.W. Lewis, S.E. Moulton, G.M. Spinks, G.G. Wallace, *Synth. Met.*, **2000**, *113*, 121-127.
- [15] P. Schottland,; K. Zong,; C.L. Gaupp, *Macromolecules*, **2000**, *33*, 7051-7061.
- [16] S. Brahim, A.D. Narinesingh, Guiseppi-Elie, *Electroanalysis*, **2005**, *17*, 556-570.
- [17] M.P.D. Mahindaratne, K. Wimalseena, *J. Org. Chem.*, **1998**, *3*, 2858-2866.
- [18] J.A. Malero, G.D. Stucky, R. Grieken, G. Morales, *J. Mater. Chem.*, **2002**, *12*, 1664-70.
- [19] A. Khorramabadi-Zad, S.A. Akbari, A. Shiri, H. Veisi, *J. Chem. Res.*, **2005**, *2005*, 277-9.
- [20] A.R. Khosropour, M.M. Khodaei, H. Moghannian, *Synlett*, **2005**, *2005*, 955-8.
- [21] A.S. Dias, M. Pillinger, A.A. Valente, *J. Catal.* , **2005**, *229*, 414-423.
- [22] L. Bonardi, G. Ulrich, R. Ziessel, *Synlett.*, **2006**, *2006*, 450-4.
- [23] V. Nadaraj, S.T. Selvi, R. Sasi, *Arkivoc*, **2006**, *2006*, 82-89.
- [24] T. Li, Y. Souma, O. Xu, *Catal. Today*, **2006**, *111*, 288-291.
- [25] K.B. Wang, G. Y. Wang, *Chin. Chem. Let.*, **2007**, *18*, 811-813.

- [26] H. Xiangming,; M. Huiqing, W. Yulu, *Arkivoc*, **2007**, 2007,150-154.
- [27] R.-Y. Yang, L.-X. Dai, *Synth. Commun.*, **1994**, 24, 2229-36.
- [28] A. Berkessel, M.R.M. Andreae, *Tetrahedron Lett.*, **2001**, 42, 2293-5.
- [29] B. Saha, J.H. Espenson, *J. Mol. Catal. A: Chem.*, **2005**, 241, 33-8.
- [30] J.A. Gonçalves, A.C. Bueno, E.V. Gusevskaya, *J. Mol. Catal. A: Chem.*, **2006**, 252, 5-11.
- [31] T.A. Skotheim, J.R. Reynolds, handbook of conjugated polymers, CRC Press. **2007**.
- [32] N.A. Rahman, . I.T. Kudin, Ab. M. M. Ali and M.Z.A. Yahya, *J. Mater. Sci., Eng. A*, **2012**, 190-195.
- [33] N. Su, H. B. Li, S. J. Yuan, S. P. Yi, E. Q. Yin, *Express Polym. Lett.*, **2012**, 6(9), 697-705.
- [34] Ch.R.K. Rao, R. Muthukannan, J. Adriel Jebin, T. Antony Raj. , M. Vijayan, *Indian J. Chem.*, **2013**, 52A, 744-748.
- [35] G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, **1994**.
- [36] T. Hanawa, S. Kuwabata, H. Yoneyama, *J. Chem. Soc., Faraday Trans.*, **1998**, 84, 1587-92.
- [37] G. Maia, E.A. Ticianelli, F.C. Nart, *Zei Phys Chem, Int. J. Res. Phys. Chem. Phys.*, **1994**, 186, 245-57.
- [38] L. Chierici, G.P. Gardini, *Tetrahedron*, **1996**, 22, 53-56.
- [39] X. Zhang, J. Zhang, W. Song, Z. Lu, *J. Phys. Chem. B*, **2006**, 110, 1158-1165.
- [40] A.B. Kaiser, *Adv. Mater.*, **2001**, 13, 927-941.