

Facile Preparation And Investigation Of New Electroactive Poly (Aniline-Co-M-Chloroaniline) Nanocomposites

P.S.Vijayanand, J.Vivekanandan, A.Mahudeswaran, K.S.Usha

Abstract: Novel copolymers of dodecylbenzenesulfonic acid aided poly (aniline-co-m-chloroaniline) nanocomposites of various compositions were prepared by oxidative method in micellar solution. The nanocomposites were analyzed by using UV-Vis and FT-IR spectroscopic methods. The crystalline nature of the polymer was evidenced through XRD patterns. SEM revealed the presence of particles with spherical morphology 100 nm in diameter. These copolymer nanocomposites showed a remarkably improved solubility in organic solvents. The electrical activity of the doped polymer was found to be content increasing from 3:1 to 3:3 0.08×10^{-2} S/cm to 5.64×10^{-7} S/cm with chloroaniline.

Keywords: aniline, m-chloroaniline, copolymers, DBSA, nanocomposites, self assembly, conductivity.

I. INTRODUCTION

Preparation of a nanostructured conducting polymer was first developed by Martin et al. [1]. In recent times there has been a great awareness in the field of nanoparticles research, because the nanostructure provides interesting properties and useful applications. Amongst PANI is the most environmental stability, redox properties [1]. It is used in different important fields of industrial application [2]. synergistically combine the benefits of both components and thus lead to highly conductive polymer. However to our knowledge a few studies on the oxidative polymerization of aniline derivatives have been reported [3-5]. Several efforts have been made to incorporate metallic nanoparticles into the conductive polymers for the improvement of mechanical stability and electrical conductivity performances. For instance, polymer metallic nanocomposites have been developed as functional materials for electronic devices [6-8]. There are many that protocols have been developed to create nanomaterials of precise size, shape and properties for the device applications [9]. Doping of silver nanoparticles has great impact of attention due to their fabrication ease.

However, the usage of PANI has been limited for the reason of its lesser solubility in organic solvents Utilization of substituted PANI primarily made to increase the processability of PANI. Latest methods are handled to get better the processability of PANI copolymer preparation.

There are hardly any reports behind the use of dopants in the polymer chain to improve the conductivity [11]. The aniline was copolymerized with different derivatives for example alkyl [12,13], alkoxy [14] and carboxylic acid [15-17]. Snauwaert et al. [18] prepared poly (halogen anilines) by chemical and electrochemical methods. For instance, it was found that polychloroanilines exhibit poor electrical conductivity (10^{-6} – 10^{-8} S/cm) most likely owing to the existence of electronegative chlorine groups. The electrical and electronic properties of PANI also depend on the torsional angle between the neighbouring rings [19]. The properties of polyaniline and polyaniline derivatives are extremely desired because the resulting copolymer can Aniline copolymerization through other monomer possesses good solubility and conductivity.

In particular, nanostructures of the copolymer are especially attractive because of their low dimensionality and high surface area. The purpose of using chloroaniline in the copolymer structure was to improve the solubility, processability and mechanical stability of the resulting copolymer.

In the literature survey no research report so far about the preparation of poly (aniline-co-m-chloroaniline) with dodecyl benzene sulfonic acid (DBSA) silver nanoparticles. Here we report the preparation and investigation of novel copolymers of DBSA doped poly (aniline-co-m-chloroaniline) by self assembled method. The copolymer nanocomposites of different compositions of aniline and chloroaniline 3:1, 3:2 and 3:3 molar ratios with DBSA were synthesized to recognize the result of electron-withdrawing groups. Our objective is to create a new functional nanostructured conducting polymer with good solubility, multifunctionality and to understand the electrical properties associated with a 1-D nanostructure. The chemical structure and conducting behavior induced by polymerization are investigated by spectroscopic, morphological and electrical measurements. This copolymerization reaction promotes relations between additives and monomers for polymerization reaction [20].

II. INVESTIGATION TECHNIQUES

A. Materials used and techniques

Aniline (Rankem, India), m-chloroaniline (Sigma Aldrich, USA), Ammonium persulfate, dodecylbenzenesulfonic acid (MERCK, India), and hydrochloric acid (Emplura India) were purchased. Double distilled water was used.

Revised Manuscript Received on December 22, 2018.

P.S.Vijayanand, Department of Chemistry, Bannari Amman Institute of Technology, Sathyamangalam, 638 401, Erode District, Tamil Nadu, India. (E-mail: vijayanandps@bitsathy.ac.in)

J.Vivekanandan, Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, 638 401, Erode District, Tamil Nadu, India.

A.Mahudeswaran, Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, 638 401, Erode District, Tamil Nadu, India.

K.S.Usha, Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, 638 401, Erode District, Tamil Nadu, India.

FACILE PREPARATION AND INVESTIGATION OF NEW ELECTROACTIVE POLY (ANILINE-CO-M-CHLOROANILINE) NANOCOMPOSITES

B. Preparation of poly (An-co-m-ClAn) DBSA nanocomposites

The DBSA based poly (aniline-co-*m*-chloroaniline) were prepared as follows: 0.01 M DBSA (0.326 gm) was mixed in 80 ml of purified water as micelles. Aniline (An) 0.465 gm and 0.638 gm of *m*-chloroaniline (*m*-ClAn) (3 (Aniline): 3 (*m*-Chloroaniline)) were added into the DBSA micelles. 10 ml of 1 M aqueous HCl solution was gradually passed into the mixture. Lastly 2.28 gm solution of APS was slowly put in to begin polymer reaction. The green colour precipitate of DBSA based copolymer obtained after 12 h then the precipitate was filtered under suction. Then the filtered precipitate was treated with purified water, acetone and methanol for removing the impurities DBSA molecules, oligomers. The attained polymer product was dried. The similar procedure was adopted for preparing different concentration of copolymers such as 3:3, 3:2 and 3:1 molar ratios.

III. CHARACTERIZATION

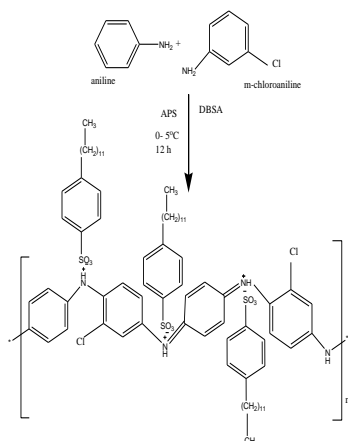
Electronic spectra of samples with DMSO were analyzed ELICO SL-218 (India) spectrophotometer. FT-IR analysis was performed using a Nicolet Magna 560 (USA). XRD patterns of the synthesized polymer samples were analyzed by Bruker GADDS (Germany). The copolymer nanocomposites structure was carried out by a JEOL JSM-6335F (Japan). A standard (KEMI) electrometer was utilized to measure the conductivity of the prepared copolymer.

IV. RESULTS AND DISCUSSION

The scheme of synthesized poly (An-co-*m*-ClAn) DBSA polymer (Scheme 1) is shown in below.

A. Solvability

Solvability tests for the prepared polymer materials were performed in polar and non-polar solvents such as water, concentrated H₂SO₄, acetone, CH₃OH, DMF and DMSO. The DBSA based poly (An-co-*m*-ClAn) polymers were found to have better solubility in DMF and DMSO [9]. The solvability of poly (An-co-*m*-ClAn) are presented in Table 1. Improved solubility characteristics of the polymers are due to Cl groups and dopants. The surfactant modifies the flexibility of the polymer backbone and solubility. The higher solubility characteristics of the polymers is due to the higher content of the comonomer [21].



Scheme.1 Preparation of poly (An-co-*m*-ClAn) DBSA nanocomposite

Polymers	H ₂ O	dil.H ₂ SO ₄	Acetone	CH ₃ OH	DMF	DMSO
P(An-co- <i>m</i> -ClAn)DBSA 3:3	IS	MS	SS	MS	S	S
P(An-co- <i>m</i> -ClAn)DBSA 3:2	IS	S	MS	MS	S	S
P(An-co- <i>m</i> -ClAn)DBSA 3:1	IS	S	S	MS	S	S
PANI	IS	MS	IS	IS	IS	IS

Table.1 Solubility nature of copolymers in different solvents (IS: insoluble, MS: moderately soluble, SS: slightly soluble, S: soluble)

B. Electronic spectra

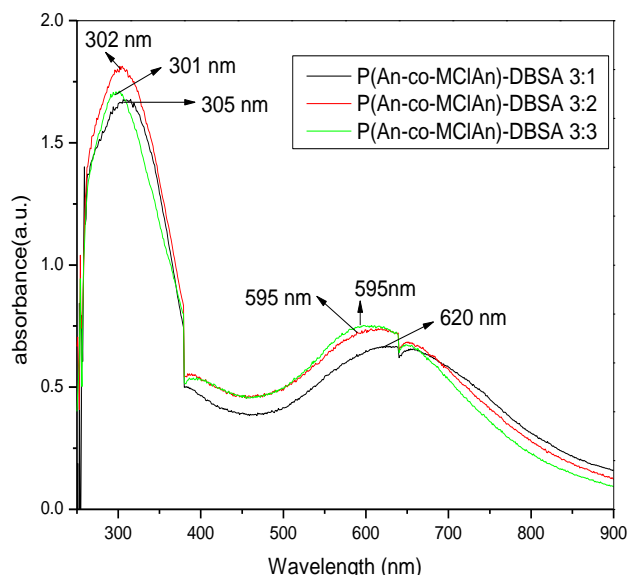


Fig. 1 Absorbance spectra of poly (An-co-*m*-ClAn) DBSA nanocomposites

Electronic spectrum of poly(An-co-*m*-ClAn) nanocomposites and homopolymer are presented in Fig.1. The bands around 301 to 305 nm because of the π - π^* electronic transition [9]. The conjugation of π orbitals for maximum resonance interaction is accountable for conductivity. The quinoid ring transition around 595 to 620 nm [22-24].

There was a hypochromic shift observed in copolymers when compared to PANI-DBSA. The presence of chloro groups, which changes the planarity and control the π orbital overlapping. Thus, a blue shift was observed due to the presence of the chloro groups and ultimately, it increased the band gap of the copolymers. Therefore, *m*-chloroaniline increased the oxidation state of the copolymers decreased [11]. The absorption bands at 410-450 nm confirm polaronic transitions [25] and their existence specifies the enhanced solubility.

C. FT-IR Spectra

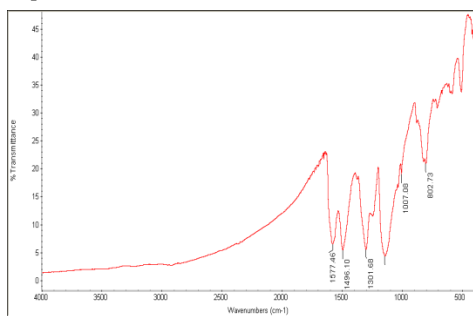


Fig. 2(a) FT-IR spectra of poly aniline

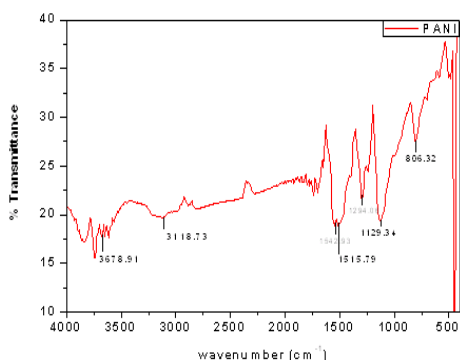
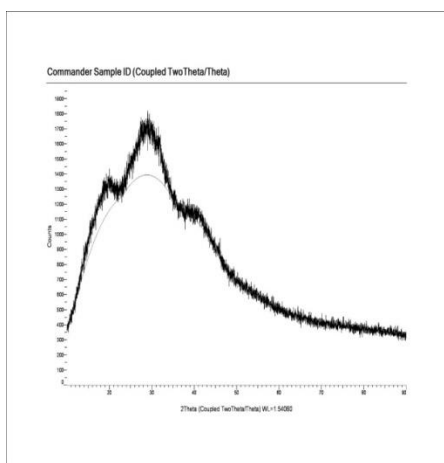


Fig. 2(b) FT-IR spectra of DBSA based poly (An-co-m-ClAn) (3:3) nanocomposites

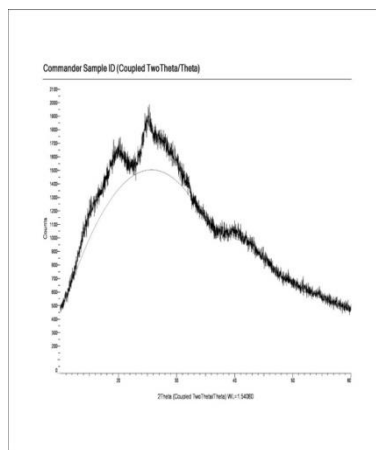
The Fig. 2 (a) shows pure PANI. NH stretching in $C_6H_4NH_2C_6H_4$ around 3118 and 3678 cm^{-1} . C=C and C=N vibrations are attributed at 1543 and 1515 cm^{-1} . N-H bending vibration at 1294 cm^{-1} . In-plane and out-of-plane C-H bending vibrations observed at 1129 and 806 cm^{-1} .

We also compared the spectra of copolymer (3:3) molar ratio of DBSA based poly (aniline-co-m-chloroaniline) with that of PANI, the spectrum of the copolymer shows four new peaks at 1557 , 1469 , 1301 , 1090 cm^{-1} . The DBSA based poly (An-co-m-ClAn) (3:3) nanocomposite are shown in Fig. 2 (b). C=C and C=N vibration of benzenoid and quinoid rings are observed at 1577 and 1496 cm^{-1} and conforming the polyaniline units. C=C stretching and N-H bending vibration are attributed at 1090 cm^{-1} and 1301 cm^{-1} . Band at 1140 and 802 cm^{-1} corresponds to in-plane and out-of-plane C-H bending vibration.

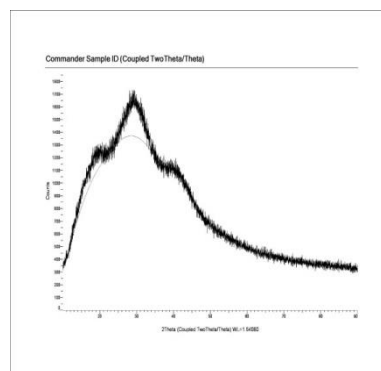
D. X-ray diffraction



(a)



(b)

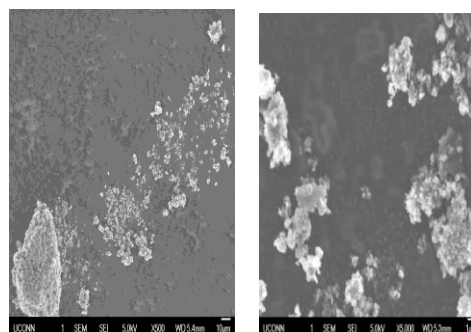


(c)

Fig. 3 X-ray diffraction of DBSA based (a) poly (An-co-m-ClAn) (3:1) nanocomposites (b) poly (An-co-m-ClAn) (3:2) nanocomposites (3:3) (c) poly (An-co-m-ClAn) (3:3) Nanocomposites

The powder XRD of DBSA based poly (An-co-m-ClAn) nanocomposites of various copolymer compositions are shown in Fig. 3. The band around $2\theta = 30$ is because of non crystalline nature of the DBSA based poly (An-co-m-ClAn). The amorphous characteristics is partially due to irregular arrangement of the monomers. A more amorphous nature was observed in the polymer (3:2) (3:3) than the (3:1). The diffraction angle is smaller while increasing the m-chloroaniline in the polymer chain. The m-chloroaniline units into PANI chain causes steric effect, intramolecular chain spacing leading to amorphous characteristics.

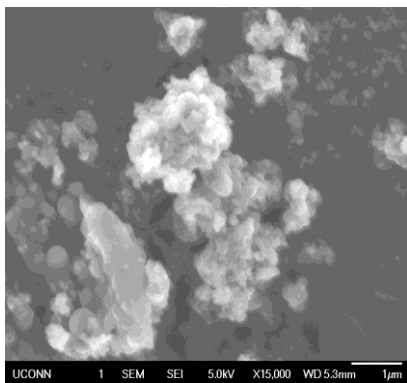
E. Sem



(a)

(b)

FACILE PREPARATION AND INVESTIGATION OF NEW ELECTROACTIVE POLY (ANILINE-CO-M-CHLOROANILINE) NANOCOMPOSITES



(c)

Fig. 4 (a,b & c) SEM image of DBSA based poly (An-co-m-ClAn)(3:3) nanocomposites

Figure 4 a represents the SEM micrograph of polymer (3:3) nanocomposites. The surface morphology shows the uniform granular structure of agglomerated nature. The micelle character changes from spherical to lamular layered shape structure only by increasing the DBSA concentration. Figures 4 (b) & (c) show the higher magnifications indicating a spherical granular structure was obtained. It is due to the increasing of the copolymer composition which impose boosted viscosity to polymer matrix. Thus, the new creative ordered nanostructure morphology has been observed [26].

The shape of nanogranules is due to the combined of nucleates. This may occur at higher concentration of nucleates at shorter induction time. Initially homogeneous nucleation occurs and later growth of the polymer is in heterogenous nature. Thus the fused morphology as conducting island is produced directly. It predicts the occurrence of highly conducting areas, in disarrayed nature. Some ordered phases of 20–50 nm size have been observed. Thus a new nanostructured morphology of conducting copolymer nanocomposites has been observed.

F. Conductivity

The electrical conductivity of homopolymer (PANI) and poly(An-co-mClAn) nanocomposites are listed in Table 2. The poly(An-co-mClAn) 3:1 composite has good conductivity 0.08×10^{-2} S/cm and possesses good solubility characteristics. Further adding the co-monomer feed (*m*-ClAn) ratio, the electrical activity of copolymer nanocomposite decreased from 0.08×10^{-2} S/cm to 5.64×10^{-7} S/cm. The decreased conductivity due to increased disorderness, decreased conjugation and electron delocalization.

The decreased electrical conductivity of the copolymer is due to the following reasons (i) the steric effect of the chloro group that induces deformation and enhances the inter-chain distances [27]. Higher concentrations of chloroaniline decrease the conjugation and quinone-imine formation. (ii) the decreases in the electron distribution because of electron withdrawing effect (iii) due to the electrostatic repulsion and steric hindrance the chlorine substituent will avoid acid doping of the polymers. (iv) the stabilization of isolated semiquinone imines would hinder conjugation through the chain.

Polymers	Conductivity (S/cm)
PANI	1.98×10^{-1}
Poly(An-co- <i>m</i> -3ClAn)-DBSA nanocomposites 3:1	0.07955×10^{-2}
Poly(An-co- <i>m</i> -3ClAn)-DBSA nanocomposites 3:2	3.40×10^{-5}
Poly(An-co- <i>m</i> -3ClAn)-DBSA nanocomposites 3:3	5.64×10^{-7}
P- <i>m</i> -ClAn	1.16×10^{-7}

Table.2 Electrical Conductivity of DBSA based poly (An-co-*m*-ClAn) nanocomposites at room temperature

In this manuscript we described the successful synthesis of a novel nanostructured poly(An-co-*m*ClAn) and characterized the nanoscale materials. In the resulting nanocomposite DBSA based poly(An-co-*m*-3ClAn), DBSA plays a twin role as template and dopant, leading to a highly stable leucoemeraldine base form of polyaniline copolymer nanostructure. The obtained green coloured precipitate of the polymers were analyzed using UV, FT-IR, XRD and electrometer. These nanocomposites showed improved solvability, which facilitates the industrial processability. UV-Visible spectra indicated that the *m*-chloroaniline concentration increased in the copolymer the oxidation state of the copolymers decreased. FT-IR measurements confirmed the molecular structure. The presence of a band around $2\theta = 30^\circ$ is in the X-ray diffraction pattern due to the non crystallinity of the copolymer. The surface of the copolymer nanocomposites has visually rougher surface with the presence of spherical granular structures of agglomerates with average size of around 100 nm. Lower electrical conductivity of the nanocomposite may be due to the less number of inter chain charge carriers. The DBSA doped copolymer nanocomposites exhibited lower crystallinity and Cl in backbone better solubility characteristic compared to the polyaniline. The great attention has been made for self template controlled polymerization method for the preparation of micro/nano structure materials.

ACKNOWLEDGEMENTS

The authors thankfully acknowledged the CSIR, India for the grant and the Management of Bannari Amman Institute of Technology for providing the facilities. The authors also thank Sri Ramakrishna Mission Vidyalaya College of Arts and Science for their help rendered for electrical conductivity study.

REFERENCES

1. MacDiarmid, A.G. A novel role for organic polymers, Synth. Met. 2001, 125, 11-22.
2. Ravikumar, G.; Vivekanandan, J.; Mahudswaran, A.; Vijayanand, P.S. Synthesis and characterization of novel poly(aniline-co-*m*-aminoacetophenone) copolymer nanocomposites using dodecylbenzene sulfonic acid as a soft template, Iran. Polym. J. 2013, 22, 923-929.



3. Neoh, K.G.; Kang, E.T. Chemical copolymerization of aniline with halogen-substituted anilines, *Eur. Polym. J.* 1990, 26, 403-407.
4. Palaniappan, S. Chemical copolymerization of aniline with *o*-chloroaniline: thermal stability by spectral studies, *Polym. Int.* 2000, 49, 659-662.
5. Sharma, A.L.; Saxena, V.; Annapoorni, S.; Malhotra, B.D. Synthesis and characterization of a copolymer: Poly(aniline-*co*-fluoroaniline), *J. Appl. Polym. Sci.* 2001, 81, 1460-1466.
6. Di'az, F.R.; Sa'ncnez CO; Del Valle M.A.; Torres, J.L.; Tagle, L.H. Synthesis, characterization and electrical properties of poly(2,5-, 2,3- and 3,5-dichloroaniline)s: Part II. Copolymers with aniline, *Synth. Met.* 2001, 118, 25-31.
7. Collier, C.P.; Saykally, R.J.; Shiang, J.J.; Henrichs, S.E.; Heath, J.R. Reversible Tuning of Silver Quantum Dot Monolayers Through the Metal-Insulator Transition, *Science.* 1997, 277, 1978-1981.
8. Klein, D.L.; Roth, R.; Lim, A.K.L.; Alivisatos, A.P.; McEuen, P.L. A single-electron transistor made from a cadmium selenide nanocrystal, *Nature.* 1997, 389, 699-701.
9. Sastry, M.; Gole, A.; Sainkar, S.R. Formation of Patterned, Heterocolloidal Nanoparticle Thin Films, *Langmuir.* 2000, 16, 3553-3556.
10. Velev, O.D.; Kaler, E.W. In Situ Assembly of Colloidal Particles into Miniaturized Biosensors, *Langmuir.* 1999, 15, 3693-3698.
11. John, H.; Thomas, R.M.; Mathew, K.T.; Joseph, R., Studies on the dielectric properties of poly(*o*-toluidine) and poly(*o*-toluidine-aniline) copolymer, *J. Appl. Polym. Sci.* 2004, 92, 592-598.
12. Pradeep Kumar, U.; Afaq Ahmad. Chemical Synthesis, Spectral Characterization and Thermal Degradation of Poly(aniline-*co*-*m*-chloroaniline), *Anal. Bioanal. Electrochem.* 2009, 1, 11-26.
13. Wang, S.L.; Wang, F.S.; Ge, X.H. Polymerization of substituted aniline and characterization of the polymers obtained, *Synth. Met.* 1986, 16, 99-104.
14. Wei, Y.; Hariharan, R.; Patel, S.A. Chemical and electrochemical copolymerization of aniline with alkyl ring-substituted anilines, *Macromolecules.* 1990, 23, 758-764.
15. Leclerc, M.; Guay, J.; Dao, L.H. Synthesis and characterization of poly(alkylanilines), *Macromolecules.* 1989, 22, 649-653.
16. Salavagione HJ, Acevedo DF, Miras MC, Motheo AJ, Barbero CA Comparative study of 2- amino and 3- aminobenzoic acid copolymerization with aniline synthesis and copolymer properties, *J. Polym. Sci. Part A: Polym. Chem.* 2004, 42, 5587-5599.
17. Karyakin, A.A.; Maltsev, I.A.; Lukachova, L.V. The influence of defects in polyaniline structure on its electroactivity: optimization of 'self-doped' polyaniline synthesis, *J. Electroanal. Chem.* 1996, 402, 217-219.
18. Fan, J.; Wan, M.; Zhu, D. Synthesis and characterization of water-soluble conducting copolymer poly(aniline-*co*-*o*-aminobenzenesulfonic acid), *J. Polym. Sci. Part A: Polym. Chem.* 1998, 36, 3013-3019.
19. Wei, Y.; Focke, W.W.; Wnek, G.E.; Ray, A.; MacDiarmid, A.G. Synthesis and Electrochemistry of Alkyl-ring Substituted Polyanilines, *J. Phy. Chem.* 1989, 93, 495-499.
20. Ruckenstein, E.; Sun, Y. Polyaniline-containing electrical conductive composite prepared by two inverted emulsion pathways, *Synth. Met.* 1995, 74, 107-113.
21. Borkar, A.D. Effect of copolymer composition on solubility and electrical conductivity of poly(aniline-*co*-*o*-chloroaniline), *J. Chem. Pharm. Res.* 2012, 4, 3526-3528.
22. Chan, H.S.O.; Ng, S.C.; Sim, W.S.; Tan, K.L.; Tan, B.T.G. Preparation and characterization of electrically conducting copolymers of aniline and anthranilic acid: evidence for self-doping by x-ray photoelectron spectroscopy, *Macromolecules.* 1992, 25, 6029-6034.
23. Kim, Y.H.; Foster, C.; Chiang, J.; Heeger, A.J. Localized charged excitations in polyaniline: Infrared photoexcitation and protonation studies, *Synth. Met.* 1989, 29, 285-290.
24. Roe, M.G.; Ginder, J.M.; Wigen, P.E.; Epstein, A.J.; Angelopoulos, M.; Macdiarmid, A.G. Photoexcitation of Polarons and Molecular Excitons in Emeraldine Base, *Phys. Rev. Lett.* 1988, 60, 2789-2792.
25. Dhanalakshmi, K.; Saraswati, R. Electrochemical preparation and characterization of conducting copolymers: poly(pyrrole-*co*-indole), *J. Mat. Sci.* 2001, 36, 4107-4115.
26. Amarnath, C.A.; Kim, J.W.; Kim, K.B.; Choi, J.Y.; Sohn, D.W. Nanoflakes to nanorods and nanospheres transition of selenious acid doped polyaniline, *Polymer.* 2008, 49, 432-437.
27. Proke's, J.; Stejskal, J. Polyaniline prepared in the presence of various acids: 2. Thermal stability of conductivity, *Polym. Degrad. Stab.* 2004, 86, 187-195.