

Investigations on new nanostructured poly (M-Toluidine-Co-3-Aminobenzoic Acid) Copolymer in Presence of DBSA Surfactant molecule by Insitu-Polymerisation

A. Mahudswaran, J. Vivekanandan, P. S. Vijayanand, J. Chandrasekaran

Abstract: A novel nanostructured poly (m-toluidine-co-3-aminobenzoic acid) copolymer has been prepared using dodecylbenzenesulphonic acid as surfactant and ammonium persulphate as oxidant at different monomer concentrations. The synthesized copolymer was soluble in solvents like DMSO, NMP, DMF and THF. The copolymers were subjected various analytical characterization methods such as electronic spectroscopy, FTIR spectroscopy, X-ray diffraction method, scanning electron microscopy and electrical conductivity. The UV-visible spectra reveals the $\pi - \pi^*$ and $n - \pi^*$ transitions at 313 nm and 517 nm respectively. FTIR absorption bands confirm benzenoid and quinoid rings in the copolymer chain. The X-ray diffraction study reveals that the copolymer is amorphous in nature. The DC electroactive nature of the copolymer is found to be 10^{-9} to 10^{-10} S/cm. The synthesized copolymer will show a change in resistance when exposed to the humidity and ammonia vapor sensors.

Keywords: Conjugated Polymer, Copolymer, Surfactant, Sensors

I. INTRODUCTION

Electro active polymers are special type of polymers which possess remarkable optical and electrical properties which led to great industrial revolution in the field of optoelectronics. Advantages of these conjugated polymers are the excellent environmental stability, easy synthesis, tunable optical and electronic properties etc. The properties of the electroactive polymers can be altered with some changes in its oxidation and protonation states. These conducting polymers are used in fabricating sensors [1], LEDs [2], solar cells [3], rechargeable batteries [4], conductive coatings [5] electromagnetic shielding [6] electrochromic devices [7]. Homopolymers of polyaniline, polythiophene and polypyrrole are the commonly studied electroactive polymeric materials during the past three decades [8-11]. However these conjugated polymers were not soluble in common organic solvents and so the application perspectives are much limited.

Manuscript published on 30 November 2018.

*Correspondence Author(s)

A. Mahudswaran, Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, Erode, Tamil Nadu, India.
J. Vivekanandan, Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, Erode, Tamil Nadu, India.
P. S. Vijayanand, Department of Chemistry, Bannari Amman Institute of Technology, Sathyamangalam, Erode Tamil Nadu, India.
J. Chandrasekaran, Department of Physics, Sri Ramakrishna Mission Vidyalyaya College of Arts and Science, Coimbatore, Tamilnadu, India.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

The delocalization nature, polarizability and rigidity of the poor solubility. In order to improve the application perspectives, Copolymerization method has been introduced material lead for improving the solubility without affecting the conductive nature [12-13]. Copolymerization is a method of synthesizing polymers by mixing two different monomers under specific chemical and physical conditions. The conjugated copolymers have more advantages than the conventional polymers because of good solubility and notable electrical conductivity [14]. Introducing the functional groups such as methyl, bromine, carboxylic acid groups at 1, 2 and 3 positions of the benzene ring of aniline inhibits inter-chain interaction and degree of cross linking and results in short chain flexible polymers lead to increase in solubility in common organic solvents [15]. These conjugated polymers can be oxidized and reduced using dopants for better activity. The doping in conjugated polymer means by adding external molecules into the material. The morphology of the synthesized polymer greatly depends on the concentration of the monomers, surfactant concentration and the surfactant chain length. Reverse micro-emulsion is also a possible mechanism to prepare micro and nanostructures of conducting polymers through surfactants acting as soft templates [16]. Dodecylbenzene sulfonic acid (DBSA) contributes an important position in conducting polymer area making the insoluble polymer salt into more soluble and processable. DBSA acts as a good micelle and a very good dopant molecule [17-18].

Synthesizing nanostructured conducting polymers has attracted many researches due to its remarkable and unique morphology and structures. There are many methods available to synthesize nanostructured conducting polymer such as electrospinning [19], seeding polymerization [20] and template polymerization method [21]. In hard template method, the polymer nanostructures are formed in an anodimensional porous membrane which are fixed template. The synthesized nanostructures may get disrupted during the post treatment methods. The most preferable method is the soft template method also called templateless method in which the polymerization takes place within the mesostructures which are formed hydrogen bonding, van der Waals force and other chemical bonds. Some of the soft templates are liquid crystals, micelle, gas bubbles and interphase of block copolymers [22]. In our work we highlight the preparation method of novel nanostructured conducting copolymer using soft template method and its optical and electrical properties.



II. MATERIALS USED AND TECHNIQUES

A. Preparation of the Copolymer

The copolymer was synthesized using the following procedure. Initially 0.326 g of DBSA was dissolved in 80 mL of purified water. 0.5358 g of m-toluidine and 0.685 g of 3-aminobenzoic acid were added and allowed to stir well. 10 mL of 1M HCl solution is added. Then 10 mL of 2.28 g of APS solution was passed in drop wise to initiate the polymerization reaction. The reaction temperature is 0 and 5°C for 24 hours. The obtained green precipitate is filtered and purified with acetone. The samples are dehydrated in vacuum oven for 6 hours at 40°C. The above said procedure was for 3:3 monomer ratio. Similar procedure was followed to synthesize the 3:1 and 3:2 ratio of m-toluidine and 3-aminobenzoic acid respectively.

B. Instrumentation

The UV-Visible spectra of the dissolved samples were characterised using ELICO SL-218 double beam spectrophotometer in the range of 300 to 900 nm using NMP as solvent. The Fourier Transform Infra Red spectra of the copolymers were measured by using SHIMADZU 8400S, Bruker Tensor 27 Nicolet Magna 560 spectrophotometer in the region of 4000 – 400 cm⁻¹ using potassium bromide as pellets. The X-ray diffraction results were recorded using Philips X'pert Pro X-ray diffractometer with Nickel filtered Cu K_α radiation (λ = 1.5402 Å) and Shimadzu 6000B diffractometer with Ni-Cu K_α-radiation with the operation of 40kV. The analysis was carried from 10° to 90°. The surface morphology was studied using scanning electron microscopy by HITACHI-SU 6600L instrument operative at 25 kV. The electrical conductivity was measured using Keithley 6517 B electrometer. The pelletized samples of diameter of 1.3 cm and thickness of 1.10 to 1.55 mm were prepared. The reaction scheme of preparing DBSA aided poly (m-tol-co-3-ABA) copolymer is shown in the Figure 1.

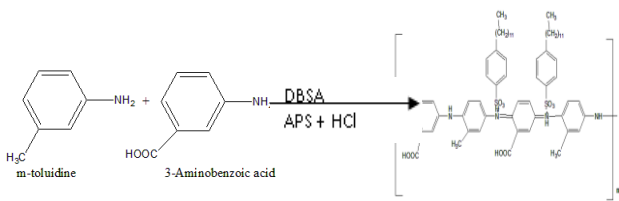


Figure 1 Synthesis of DBSA doped poly (m-tol-co-3-ABA) copolymer

III. RESULTS AND DISCUSSION

A. Solubility

The solubility test has been carried out for the DBSA doped poly (m-tol-co-3-ABA) copolymer and it has been found that the synthesized samples are soluble in various solvents like DMSO, DMF, NMP and THF. And insoluble in acetone and water. The increase in the solubility is due to bulky functional groups such as methyl group and carboxylic acid attached to the aromatic ring in the copolymer [23]. The presence of the large dopant molecule such as DBSA reduces inter and intra molecular interactions in the copolymer and litheness property gets increased [24].

B. Absorption Spectra

The electronic spectra for DBSA aided poly (m-tol-co-3-ABA) copolymer for different ratio between m-toluidine and 3-aminobenzoic acid is shown in the Figure 2. The absorption wavelength are show in the table 1. All the spectra were recorded using NMP as solvent. Figure 2 depicts characteristic absorption peaks at 313, 314 and 316 nm and these peaks are associated with π – π* transition that occurs in the benzenoid ring. It is seen that as the concentration of the m-aminobenzoic acid is increased the absorption peak shifted to the higher wavelength. A small peak around 393 nm to 402 nm is observed and these are associated with π - polaron band transition. These polaron states may be associated with new restricted electronic states. This energy level gives unstabilized bonding orbital and it has more energy than that of the valence band. Figure 2 also depicts the weak absorption band around 571 to 513 nm and these bands are associated with the excitonic transition that occurs from highest occupied molecular orbital to the lowest unoccupied molecular orbital. These peaks also show shift to higher wavelength in the absorption peak as the increase of aminobenzoic content.

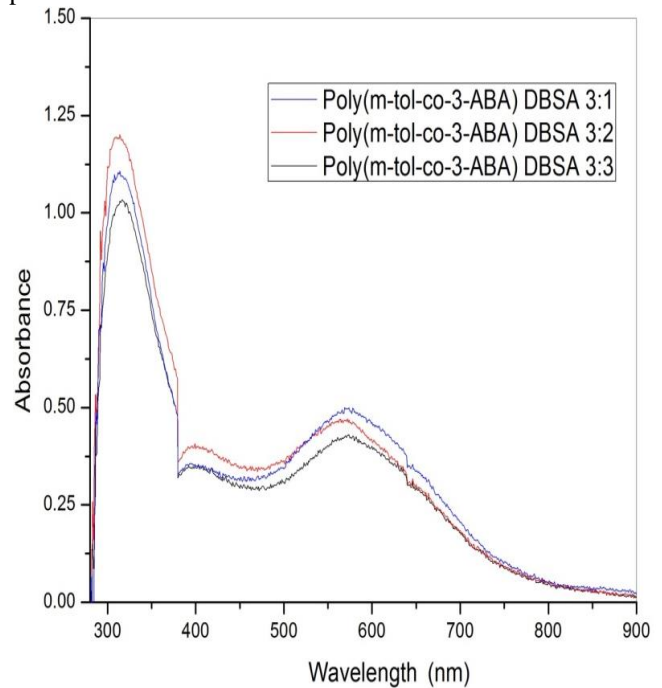


Figure 2 UV-Vis spectra of DBSA doped poly (m-tol-co-3-ABA)

It is also observed that there is a small π – polaron transition occurs and this is associated with formation of new delocalized electrons. The broad peak centered around 565 to 580 nm is associated with the transition of n – π* transition that occurs in the quinoid ring. The excitonic transition peak also shifts to the lesser wavelength or blue shift [25] and this is due to the reduction in the charge density and extent in conjugation. These extended conjugations of π orbits are responsible for the conductivity and co-planarity of the atoms in the π-electron delocalization with maximum resonance interaction.

Table 1.UV-Visible absorption values of doped poly (m-tol-co-3-ABA)

Sl. No.	Electronic transition	Wavelength (nm)		
		Poly(m-tol-co-3-ABA) DBSA copolymer		
		3:1	3:2	3:3
1.	$\pi - \pi^*$ benzenoid ring transition	313	314	316
2.	Polaronic band	393	399	402
3.	$n - \pi^*$ quinoid ring transition	571	572	573

C. FTIR Spectra

The FTIR spectra of doped poly (m-tol-co-3-ABA) copolymer for different ratios of m-toluidine and 3-aminobenzoic acid are depicted in figure 3 and the corresponding band values are shown in the Table 2. The spectra reveal characteristic peaks at 3419, 3031, 2945, 1708, 1591, 1490, 1290, 1151 and 817 cm^{-1} . The band at 3419 cm^{-1} represents nitrogen-hydrogen stretching of the amine group in the toluidine and aminobenzoic acid. The peak at 3031 and 2945 cm^{-1} confirm the C-H stretching in aromatic and DBSA unit, respectively.

The presence of carboxylic acid is confirmed with C=O stretching peak appeared on 1708 cm^{-1} . The formation of quinoid and benzenoid moiety in the copolymer is confirmed by the peak values at 1591 and 1490 cm^{-1} . The peak at 1290 cm^{-1} is attributed to the presence of Carbon-Nitrogen stretching. The characteristic Carbon-Hydrogen vibration in quinoid ring which is responsible for the electron delocalization is observed 1151 cm^{-1} and the peak at 817 cm^{-1} confirms carbon-hydrogen out of plane bending [26].

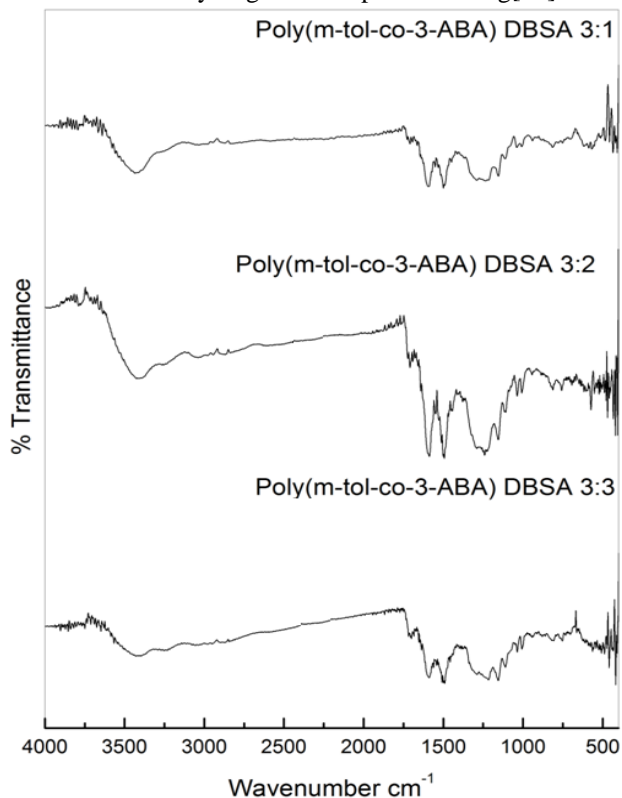


Figure 3 FTIR Spectra

Table 2 FTIR band values of DBSA doped poly (m-tol-co-3-ABA) copolymer

Sl. No	Stretching vibration	Wave number (cm^{-1})		
		Poly(m-tol-co-3-ABA) DBSA copolymer		
		3:1	3:2	3:3
1.	N-H stretching	3419	3423	3427
2.	C-H stretching of Aromatic ring	3031	3038	3048
3.	C-H stretching	2945	2944	2919
4.	C = O stretching of carboxylic acid	1708	1708	1701
5.	C=C quinoid	1591	1585	1587
6.	C=C benzenoid	1490	1490	1490
7.	C-N stretching	1290	1288	1300
8.	C-H stretching in quinoid	1151	1155	1153
9.	C-H out of plane bending	817	815	817

D. XRD Analysis

The X-ray diffraction results of DBSA aided poly (m-tol-co-3-ABA) copolymer is illustrated in the Figure 4 for the different molar ratios of m-toluidine and 3-aminobenzoic acid. The diffraction patterns show a peak revealing the amorphous character [28]. The amorphous character is due to the weak intermolecular force of attraction and random arrangement of the copolymer chain. Also the presence of substituted groups and chain length makes a polymer amorphous and they are unable to crystallize.

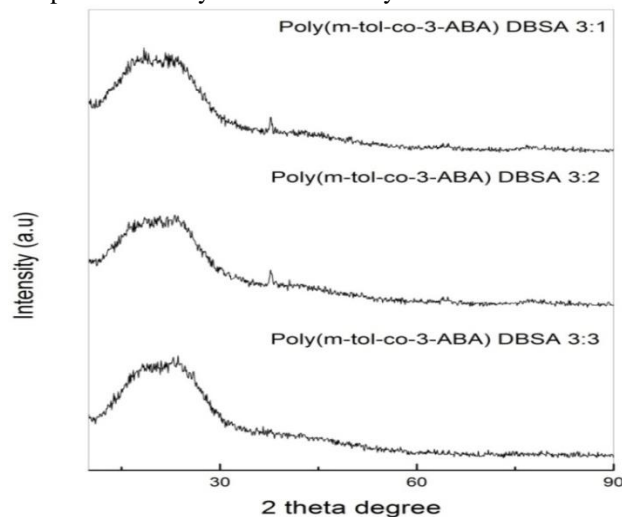


Figure 4 X-Ray Diffraction Results

Investigations on newnanostructuredpoly (M-Toluidine-Co-3-Aminobenzoic Acid) Copolymer in Presence of DBSA Surfactantmolecule by Insitu-Polymerisation

It is observed from the Figure 4 as increase of 3-aminobenzoic acid content in the feed, the peak intensity at 20° is also decreasing and the copolymer shows more amorphous in nature. It reveals a broad amorphous characteristic peak at $2\theta = 20$ to 25° . This is because of the periodicity parallel and perpendicular arrangement of molecules in the polymer chain [28].

E. Morphological Studies

Figure5 (a & b) illustrates the SEM pictures of doped poly (m-tol-co-3-ABA) copolymer 3:3 ratio at different magnifications. The microscopic image shows large number spherical particles are agglomerated to each other and the size each particles ranges from 100 to 200 nm. Each particle consists of huge curled polymer chains resulting in spherical shape. This spherical morphology is formed because of DBSA molecule. At first, polymerization occurs over the surface of the micelle. The morphology of the polymer solely lies on the concentration of the dopant used and micelle shape[29]. Higher magnification shows cluster of particles agglomerated each other. During polymerization process the individual particle grains are formed and further polymerization process makes the each particle to attach with another particle to give cluster appearance. Again the cluster are merged together to give continuous phases of solid structure with hallow spaces in between them.

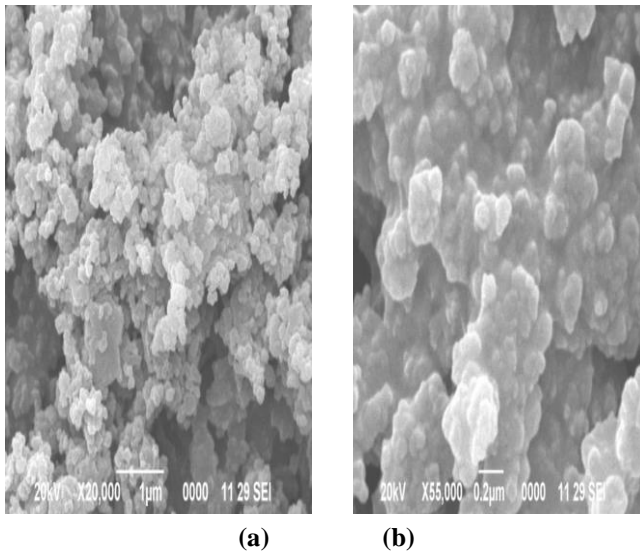


Figure 5(a & b) SEM imafe of DBSA doped poly (m-tol-co-3-ABA) (3:3)

Table 3 DC conductivity values of DBSA doped poly (m-tol-co-3-ABA)

Copolymer and its molar ratio	Conductivity S/cm
Poly(m-tol-co-3-ABA) DBSA 3:1	2.5×10^{-9}
Poly(m-tol-co-3-ABA) DBSA 3:2	3.91×10^{-10}
Poly(m-tol-co-3-ABA) DBSA 3:3	4.55×10^{-9}

F. Conductivity Studies

The electrical conductivity values of DBSA doped poly (m-tol-co-3-ABA) copolymer for different molar ratio between m-toluidine and 3-aminobenzoic acids are shown in the Table 3. It is found that the electrical conductivity value is found to vary from 2.5×10^{-9} to 3.91×10^{-10} S/cm. The lower electrical nature of the DBSA aided copolymer is

dueto the presence of the bulky substituents such as methyl group, nitrogen and carboxylic acidic group in the polymermolecule and also incorporation of DBSA makes the material to be more amorphous nature resulting in decreased conductivity.

IV. CONCLUSION

A new copolymer series of poly (m-toluidine-co-3-aminobenzoic acid) polymer materials has been prepared successfully in presence of dodecyl benzenesulfonic acid and its properties were studied. The synthesized material was soluble in organic solvents. The synthesized copolymers showed the characteristic absorption peaks in UV-visible spectra. FTIR spectra revealed the absorption bands and confirmed benzenoid and quinoid rings. X-ray diffraction results indicate non-crystalline nature. SEM image shows the agglomerated particles which are about 100 to 200 nm in diameter. The electrical conductivity ranges 10^{-9} to 10^{-10} S/cm. The synthesized materials will showsome change in resistivity when exposed to ammonia gas or water vapor and these materials can be used in the field of sensors.

ACKNOWLEDGEMENTS

The authors are pleased to CSIR, Govt. of India for economic support for carrying out the research work. The authors are also grateful to the Management of Bannari Amman Institute of Technology for providing the research facility to complete the work.

REFERENCES

- Lange, U, Roznyatovskaya, NV & Mirsky, VM 2008, 'Conducting polymers in chemical sensors and arrays', *Analytica Chimica Acta*, vol. 614, no.1, pp. 1-26.
- Qiu, Y, Duan, L & Wang, L 2002, 'Flexible organic light-emitting diodes with poly-3,4-ethylenedioxythiophene as transparent anode', *Chinese Science Bulletin*, vol. 47, no.23, pp. 1979-1982.
- Bejbouji, H, Vignau, L, Miane, JL, Dang, MT, Oualim, EM, Harmouchi, M & Mouhsen, A 2010, 'Polyaniline as a hole injection layer on organic photovoltaic cells', *Solar Energy Materials and Solar Cells*, vol. 94, no. 2, pp. 176-181.
- Zhang, J, Sun, B, Ahn, HJ, Wang, C & Wang, G 2013, 'Conducting polymer-doped polypyrrole as an effective cathode catalyst for LiO₂ batteries', *Materials Research Bulletin*, vol. 48, no. 12, pp. 4979 – 4983.
- Diniz, FB, Andrade, GF, Martins, CR & Azevedo WM 2013, 'A comparative study of epoxy and polyurethane based coatings containing polyaniline-DBSA pigments for corrosion protection on mild steel', *Progress in Organic Coatings*, vol. 76, no.5, pp. 912-916.
- Panigrahi, R & Srivastava, SK 2015, 'Tollen's reagent assisted synthesis of hollow polyaniline microsphere/Ag nanocomposites and its applications in sugar sensing and electromagnetic shielding', *Materials Research Bulletin*, vol. 64, no.1 pp. 33-41.
- Ram, MK, Maccioni, E & Nicolini C 1997, 'The electrochromic response of polyaniline and its copolymeric systems', *Thin Solid Films*, vol. 303, no.1-2, pp. 27-33.
- Shi, B, Ren, J, Wang, A, Liu, X & Wang, Y 2009, 'Synthesis and characterization of wormhole-like mesostructured polyaniline', *Journal of Materials Science*, vol.44, pp. 6498-6504.
- Cao, Y, Smith, P & Heeger, AJ 1992, 'Counter-ion induced processability of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers', *Synthetic Metals*, vol. 48, no.1, pp. 91-97.



10. Vogel, S & Holze, R 2005, 'Spectroelectrochemistry of intrinsically conducting aniline-thiophene copolymers', *Electrochimica Acta*, vol.50, no.7-8, pp. 1587-1595.
11. Aleshin, AN, Lee, K, Lee, Y, Kim, DY & Kim CY 1999, 'Comparison of electronic transport properties of soluble polypyrrole and soluble polyaniline doped with dodecylbenzene sulfonic acid', *Synthetic Metals*, vol.99, no.1, pp. 27-33.
12. Massoumi, B & Mozaffari, Z 2014, 'Synthesis and properties of electroactive polyaniline-graft-poly (2-hydroxy ethyl methacrylate) copolymers', *Functional Polymers: Polymer Science Series B*, vol.36, no.3, pp. 369-376.
13. Sevil, UA, Emel, C & Olgun, G 2014, 'Electrical conductivity and spectroscopic characterization of Blends of poly(2-chloroaniline)/ polyaniline P(2ClANI)/PANI copolymer with PVC exposed to gamma-rays', *Radiation Physics and Chemistry*, vol. 94, no. 1, pp. 45-48.
14. Mu, S 2004, 'Electrochemical copolymerization of aniline and o-aminophenol', *Synthetic Metals*, vol. 143, no. 3, pp. 259-268.
15. Sharma, S & Kumar D 2010, 'Study on solvatochromic behavior of polyaniline and alkyl substituted polyanilines', *Indian journal of Engineering Materials Science*, vol. 17, no.3, pp. 231-237
16. Shreepathi, S & Hoolze R 2007, 'Benzoyl-Peroxide-Initiated Inverse emulsion copolymerization of Aniline and o-Toluidine: Effect of Dodecylbenzenesulfonic Acid on the Physicochemical Properties of the Copolymers', *Macromolecular Chemistry and Physics*, vol. 208, no.6, pp. 609-621
17. Taka, T, Laakso, J & Levon, K 1994, 'Conductivity and structure of DBSA protonated polyaniline', *Solid State Communications*, vol.92, no. 5, pp. 393-396.
18. Vijayanand, PS, Mahudeswaran, A, Vivekanandan J & Kumbar, SG, 2015, 'Efficient synthesis of nanostructured poly (aniline-co-m-aminobenzoic acid) copolymer in presence of DBSA Surfactant', *Tenside Surfactants Detergents*, vol. 52, no.3, pp. 230-235.
19. Shahi, M., Moghimi, A., Naderizadeh, B., & Maddah, B. (2011). Electrospun PVA-PANI and PVA-PANI-AgNO composite nanofibers. *Scientia Iranica*, vol. 18, pp.1327-133
20. S Feng, X. M. (2010). Synthesis of Ag/polypyrrole core-shell nanospheres by a seeding method. *Chinese Journal of Chemistry*, vol. 28, pp.1359-1362.
21. Chen, W & Xue, G 2010, 'Formation of conducting polymer nanostructures with the help of surfactant crystallite templates', *Frontiers of Materials Science*, vol. 4, no. 2, pp. 152-157.
22. Ren, L Li, K & Chen, X 2009, 'Soft template method to synthesize polyaniline microtubes doped with methyl orange', *Polymer Bulletin*, vol. 63, no.1, pp. 15-21.
23. Kumar, D 2000, 'Synthesis and characterization of poly (aniline-co-o-toluidine) copolymer', *Synthetic Metals*, vol. 114, no. 3, pp. 369-372.
24. Jonforsena, M, Grigalevicius, S, Andersson, MR & Hjertberg, T 1999, 'Counter-ion induced solubility of polypyridines', *Synthetic Metals*, vol.102, no. 1-3, pp. 1200-1201.
25. Gupta, K, Jana, PC & Meikap AK 2010, 'Optical and electrical transport properties of polyaniline-silver nanocomposite', *Synthetic Metals*, vol. 160, no. 13-14, pp. 1566-1573.
26. Chiang, JC & MacDiarmid, AG 1986, 'Polyaniline': Protonic acid doping of the emeraldine form to the metallic regime', *Synthetic Metals*, vol.13, no.1-3, pp. 193-205
27. Biswas, S, Dutta, B & Bhattacharya, S 2014, 'Consequence of silver nanoparticles embedment on the carrier mobility and space charge limited conduction in doped polyaniline', *Applied Surface Science*, vol. 292, pp. 420-431.
28. Zhang, L & Wan, M 2003, 'Self-Assembly of polyaniline-from nanotubes to hollow microspheres', *Advanced Functional Materials*, vol. 13, no.13, pp. 815-820.
29. Haba, Y, Sega, E, Narkis, M, Titelman, GI & Siegmann, A 2000, 'Polyaniline-DBSA/polymer blends prepared via aqueous dispersions', *Synthetic Metals*, vol.110, no.3, pp. 189-193.