

Synthesis and Characterization of Nanostructured Polyaniline in Tergitol Mediated Reverse Micellar Medium

Nuruddin Ahmed* and Dilip Kr Kakati

*Department of Chemistry, Jawaharlal Nehru College, Boko Guwahati, Assam, Pin code: 781123, India

ABSTRACT

Nanoparticles of polyaniline have been synthesized by an inverse microemulsion technique. Polymerization of aniline was confined to a nanoreactor named 'water pool' surrounded by surfactant molecules Tergitol and co-surfactant n-butanol in the apolar continuous phase of cyclohexane. The UV-Vis studies showed the formation of polyaniline polaron structure while FTIR showed the formation of quinoid and benzenoid structure of polyaniline. Transmission electron microscopic (TEM) studies and dynamic light scattering (DLS) studies indicated the sizes of polyaniline nanoparticles in the range 20 to 50 nm and 10 to 200 nm respectively. The conductivity of polyaniline in the form of thin films was found to be in the range of 0.5688 to 0.6335 S cm⁻¹.

Keywords: Nanoparticles, Inverse microemulsion, Polyaniline, Dynamic light scattering, TEM

INTRODUCTION

Nanostructured polyaniline is one of the most important conducting polymers [1] due to its stability and interesting electrical and optical properties. Potential applications of polyaniline include organic light weight batteries [2], microelectronics [3], microelectronic displays [4], electromagnetic shielding [5] and sensors [6]. Typically, conducting polyaniline is synthesized chemically or electrochemically in acidic solutions and is not soluble in common organic solvents. The insolubility in common organic solvents creates difficulty in the processability of polyaniline. The preparation of polyaniline in colloidal form containing nanoparticles of polyaniline is an important way to improve the processability of this polymer [7]. An inverse microemulsion or a reverse micelle is a thermodynamically stable and optically transparent dispersion of water in oil. The reverse micellar route is of special importance in the synthesis of nanoparticles as it provides homogeneous and monodisperse nanoparticles without the need of specialized and expensive equipments [8]. The reverse micelles obtained at particular ratio of aqueous phase to the surfactant leads to uniform sized nanoreactors and have an aqueous core in which polymerization reaction could be carried out. This route had been extensively exploited in the synthesis of inorganic nanoparticles [9,10]. However, relatively little work has been done on the synthesis of polyaniline by the reverse micellar route. There are reports of using non-ionic surfactant Empilan NPS [11], sodium dodecyl benzene sulphonate [12] and cetyl trimethyl ammonium bromide [13] in the synthesis of nanostructured polyaniline by the reverse micellar route. In this paper we report the synthesis of polyaniline nanoparticles by the inverse microemulsion route using Tergitol as the

*Corresponding Author
nahmedjnc25[at]gmail.com

Receiving Date: August 08, 2020
Acceptance Date: August 28, 2020
Publication Date: September 04, 2020

surfactant and n-butanol as the co-surfactant. Our methodology results in the formation of highly stable dispersion of polyaniline nanoparticles. The polyaniline nanoparticles were characterized in detail by transmission electron microscopy (TEM), dynamic light scattering studies (DLS), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The conductivity of polyaniline dispersion in the form of thin film was

determined by the standard four-probe technique. Scanning electron micrographs (SEM) were obtained from a SEM instrument LEO 1430 VP, operated at 10.00 kV. The magnification was from 7.00 KX to 17.41 KX. For scanning electron microscopic investigation, slides were prepared on thin glass plates of the size of 1 cm², wrapped with the shining face of aluminium foil and smoothed as much as possible. A minute drop of the dispersion from a capillary tube was placed on the slide and dried in a vacuum desiccator. Transmission electron microscopic (TEM) studies were carried out using a JEOL–JEM 100C X II instrument operated at an accelerating voltage of 100 kV. TEM specimens were prepared by placing a small drop of the diluted (by adding cyclohexane) sample on a carbon coated copper grid and then dried carefully. The light scattering experiments were performed in a dynamic light scattering particle size analyser instrument – Zetasizer 3000 HS_A. The UV – Vis spectra of the samples were recorded in a Perkin Elmer spectrophotometer in the range 200–900 nm with a scan rate of 16 and resolution of 4.0 cm⁻¹. Partially full cuvette of polyaniline dispersion was directly taken on the photometer to record the UV–Vis spectra. The FTIR spectra of the samples were performed on a Perkin Elmer spectrophotometer using KBr disk technique in the range 4000–400 cm⁻¹ with a scan rate of 16 and resolution of 4.0 cm⁻¹. The conductivity of polyaniline nanoparticles were measured by the standard four-probe method. A thin film of the polyaniline dispersion was deposited on a glass plate, whose conductivity was then measured. At least four readings were taken at different points of the thin film, the average of which was taken to measure the conductivity value.

MATERIALS AND METHODS

For the synthesis of polyaniline nanoparticles in a Tergitol mediated reverse micellar medium, we procured Tergitol NP – 9, figure 1, from Sigma Aldrich and Aniline from Merck which was distilled twice before use. Again, n - Octanol, Cyclohexane, Ammonium Peroxysulphate (APS) and Sulphuric acid were also procured from Merck and are used as received.

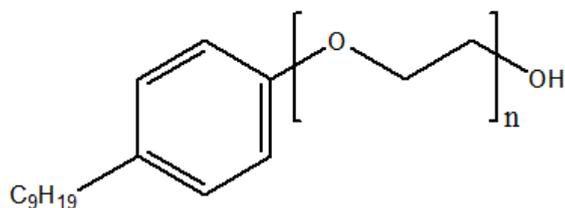


Figure 1: Tergitol NP- 9

All the synthesis was carried out by varying the volume of Tergitol from 7 mL to 4 mL with 60 mL Cyclohexane and 5.2 mL n – Octanol. Synthesis of polyaniline nanoparticles were also carried out by varying APS to Aniline molar ratio from 0.5 to 2.5 for a given volume of Tergitol (Surfactant), Cyclohexane (Apolar organic solvent) and n – Octanol (Co-surfactant). Finally, all the synthesis was also carried out in the absence of co-surfactant n - octanol.

EXPERIMENTAL DETAILS

The synthesis of polyaniline nanoparticles has been achieved using two microemulsions (I and II) as describe below. **Micro-emulsion I** is composed of Tergitol as the surfactant, n - Octanol as co-surfactant, cyclohexane as the hydrocarbon phase and aniline in 1.0 M H₂SO₄ as the aqueous phase. **Micro-emulsion II** is comprised of the same constituents as above except for ammonium per sulphate (APS) solution instead of anilinium hydrochloride as the aqueous phase. The weight fractions of various constituents in these micro-emulsions are shown in Table 1 for APS to Aniline molar concentration 1.0 and Table 2 for 1.5. The maximum weight percentage of aqueous phase up to which the transparent micro-emulsion could be formed, was ascertained by the titration method [14]. The two micro-emulsions were mixed instantaneously to avoid secondary

growth [15]. It was then stirred for 2 h and left overnight. Detailed of the synthesis were shown in the table 1 and 2.

Table 1: Synthesis of PANI in reverse micelle by varying the amount of anilinium salt and APS (maintaining APS to aniline molar ratio = 1.0) with 7 mL Tergitol, 60 mL Cyclohexane (oil), 5.2 mL Octanol (co-surfactant)

Composition	Emulsion	Aniline (mole)	APS (mole)	Remarks
Composition 1	Microemulsion I	0.0116		Dispersion
	Microemulsion II		0.0116	
Composition 2	Microemulsion I	0.0105		Dispersion
	Microemulsion II		0.0105	
Composition 3	Microemulsion I	0.0095		Dispersion
	Microemulsion II		0.0095	
Composition 4	Microemulsion I	0.0084		Unstable Dispersion
	Microemulsion II		0.0084	
Composition 5	Microemulsion I	0.0074		Unstable Dispersion
	Microemulsion II		0.0074	
Composition 6	Microemulsion I	0.0063		Unstable Dispersion
	Microemulsion II		0.0063	
Composition 7	Microemulsion I	0.0053		Precipitation
	Microemulsion II		0.0053	Precipitation

Table 2: Synthesis of PANI in reverse micelle by varying the amount of anilinium salt and APS (maintaining APS to aniline molar ratio = 1.5) with 7 mL Tergitol, 60 mL Cyclohexane (oil), 5.2 mL Octanol (co-surfactant)

Composition	Emulsion	Aniline (mole)	APS (mole)	Remarks
Composition 1	Microemulsion I	0.0116		Dispersion
	Microemulsion II		0.0174	
Composition 2	Microemulsion I	0.0105		Dispersion
	Microemulsion II		0.0158	
Composition 3	Microemulsion I	0.0095		Dispersion
	Microemulsion II		0.0143	
Composition 4	Microemulsion I	0.0084		Dispersion
	Microemulsion II		0.0126	
Composition 5	Microemulsion I	0.0074		Dispersion
	Microemulsion II		0.0111	
Composition 6	Microemulsion I	0.0063		Dispersion
	Microemulsion II		0.0095	
Composition 7	Microemulsion I	0.0053		Unstable Dispersion
	Microemulsion II		0.008	Precipitation

The process was repeated with the same composition of Tergitol, n-octanol and cyclohexane but at varying APS to aniline molar ratios like 0.5, 2.0, 2.5, etc. However the best results were obtained with APS to aniline molar ratios 1.0 and 1.5 only. Similarly, attempts were made to prepare PANI nanoparticles with varying composition of Tergitol, n-octanol and cyclohexane at APS to aniline molar ratio of 1.0 and 1.5, here, again best results were obtained with 7 mL Tergitol, 60 mL Cyclohexane (oil), 5.2 mL Octanol (co-surfactant). The synthetic strategy for the synthesis of stable microemulsion of PANI nanoparticles were outlined below in the flow chart diagram. In the flow chart diagram, Figure 2 shows the effect of surfactant concentration and the role of critical micelle concentration (CMC) in the formation of polyaniline nanoparticles or the dispersions.

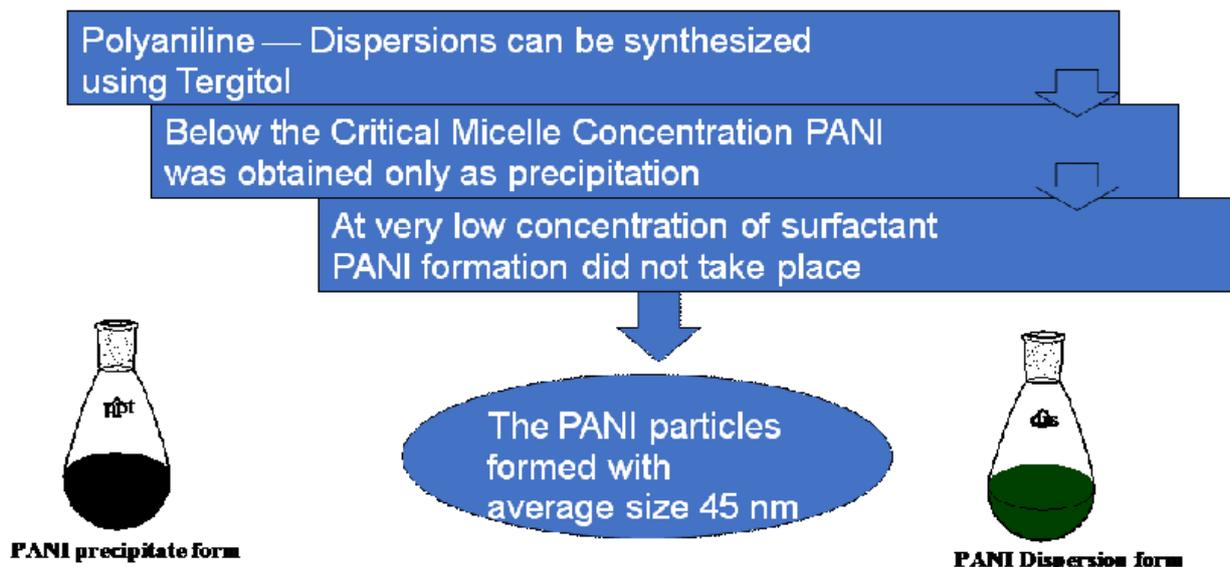


Figure 2: Role of CMC and surfactant concentration in the synthesis of PANI nanoparticles

Figure 3 shows the effect of co-surfactant n-octanol with the surfactant Tergitol in the synthesis of polyaniline nanoparticles. These effects are clearly understood both from the Table 1 and 2.

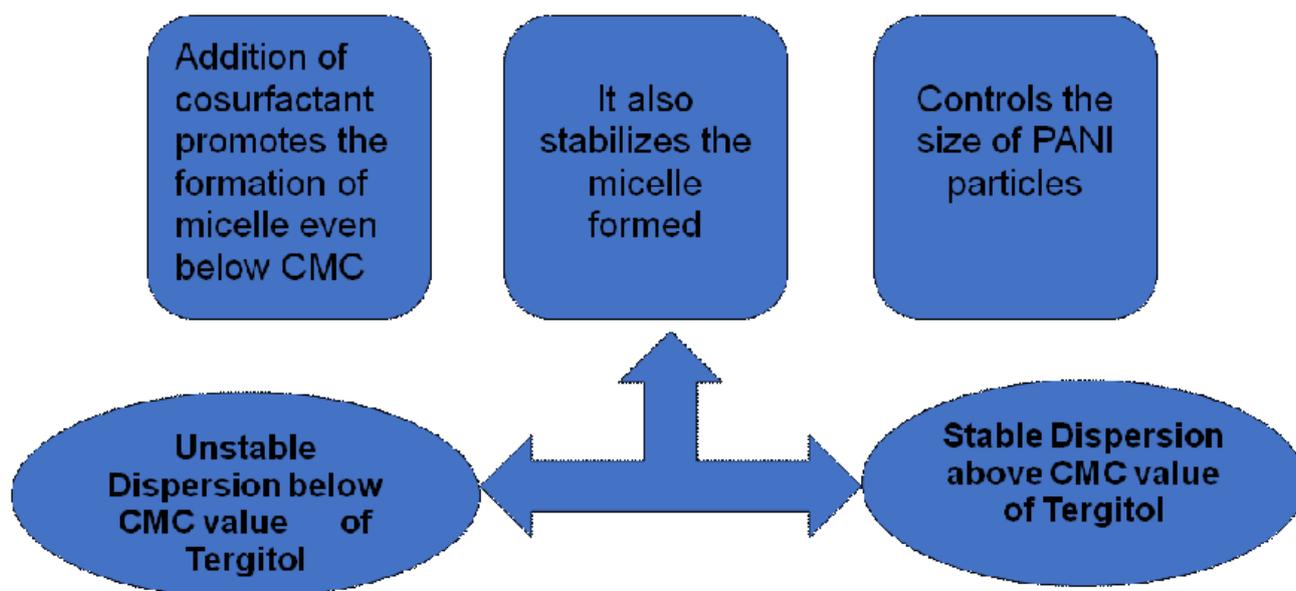


Figure 3: Tergitol mediated synthesis of PANI in the presence of co-surfactant n-Octanol

The effect of co-surfactant n-octanol with the surfactant Tergitol is to stabilize the micelle formed and thereby in the formation of stable PANI dispersions. Figure 4 given below explains the exact role of co-surfactant in synthesis of polyaniline nanoparticles.

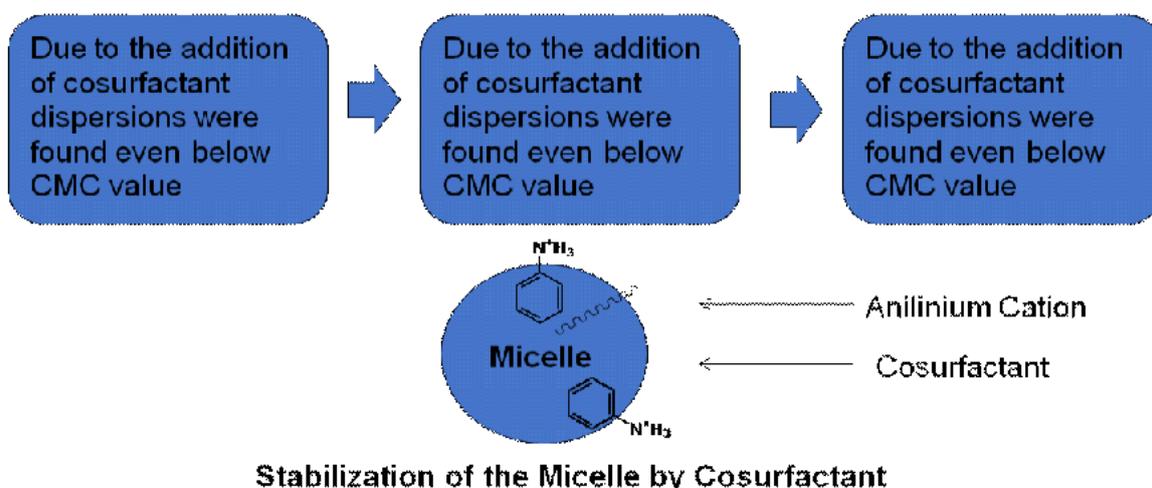


Figure 4: Effect of cosurfact in the formation of stable PANI dispersion

Polymerization of Aniline

RESULTS AD DISCUSSION

Polymerization of Aniline: Polymerization of aniline proceeded in the microemulsion under stirring to a transparent green coloured microemulsion results only up to a certain amount of aqueous solution, which was determined by titration method. When an anilinium hydrochloride or ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution were sequentially added to a certain amount of cyclohexane, Tergitol and n-octanol, transparent microemulsion results only up to a certain amount of [APS]/ [Surfactant] molar ratio which is the key factor for the formation of microemulsion. Stable microemulsions were only formed at [APS]/ [Surfactant] 1.0 and 1.5, higher [APS]/ [Surfactant]- value led to turbid formulations. The time required for the completion of reaction was 2 h. Stable dark green coloured dispersions when formed remained stable even under centrifugation at 10 000 rpm.

From the tables it is evident that PANI dispersions are best formed with APS to aniline molar ratio 1.0 and 1.5. It has been observed that at other APS to Aniline molar ratios (0.5 and 2.0) stable colloidal dispersions are not formed in majority of the cases.

Particle size and Morphology: The morphology and particle size were investigated by SEM, TEM and dynamic light scattering (DLS) methods.

SEM analysis: In order to prepare slides for Scanning Electron Microscopy (SEM) studies, thin glass plates in the size of 1 cm^2 were cut out. The glass plates were then wrapped with the shining surface of Aluminum foil. The foil was then smoothed as much as possible. After that a minute drop of the sample dispersion were put on the surface of the foil and the plate was kept in vacuum desiccators for drying. With the help of Scanning Electron Microscope LEO 1430 VP, the sizes of the polyaniline particles were analyzed in the range of 10 nm to 300 nm. The accelerating voltage was 10.00 kV. The magnification was from 7.00 KX to 17.41 KX. The scanning electron micrograph (SEM) of the polyaniline colloidal dispersion is shown in Figure 5. It shows the spherical morphology of the polyaniline particles ranging from 50 nm to 75 nm.

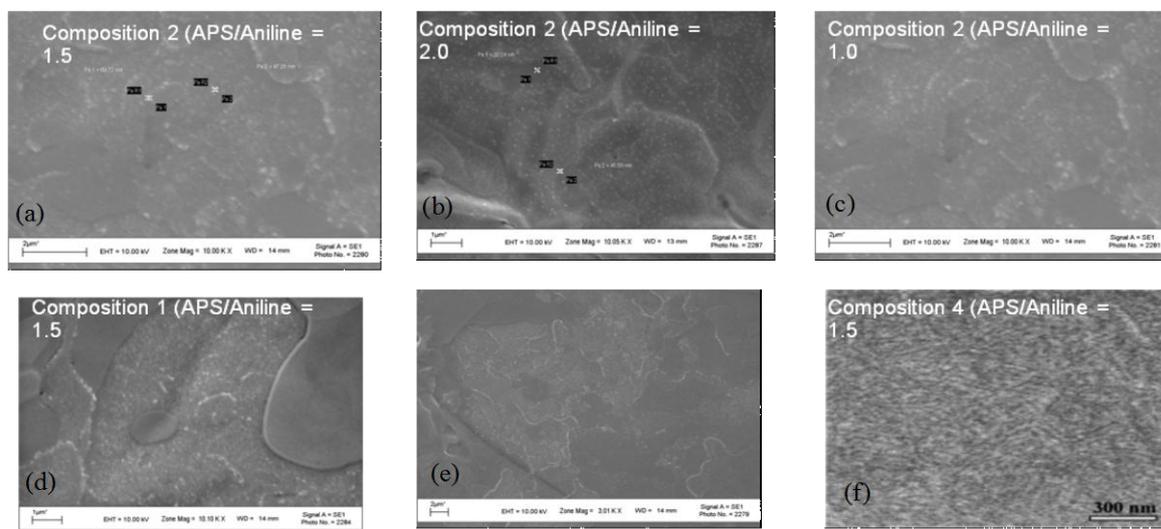


Figure 5: SEM micrographs of the polyaniline colloidal dispersion

The Scanning Electron Micrographs of PANI dispersions reveal the presence of the both cylindrical (micrographs a, c, d and e) and spherical morphology (micrographs b and f) of the PANI particles. Particle sizes of the polyaniline dispersions were found to be in the range of 50 to 75 nm.

TEM Analysis: Figure 6 shows the TEM micrographs of PANI nanoparticles in the colloidal dispersions. The spherical polymeric nanoparticles were produced and the sizes are 10 to 35 nm at [APS]/ [Surfactant] 1.0 and 1.5 respectively and these are represented in the figure 6(a), 6(b), 6(c), 6(e) and 6(f). It is observed that the rise in [APS]/ [Surfactant] value resulted in the rise in the size of PANI particles, figure 6(d). This is because the increase in the [APS]/ [Surfactant] value resulted in an increase in the size of the water pools (nanoreactors). TEM analyses were carried out in make-JEOL (model-JEM 100C X II) within the accelerating voltage 100 KV. It shows the presence of only spherical particles of sizes in the range of 40-95 nm.

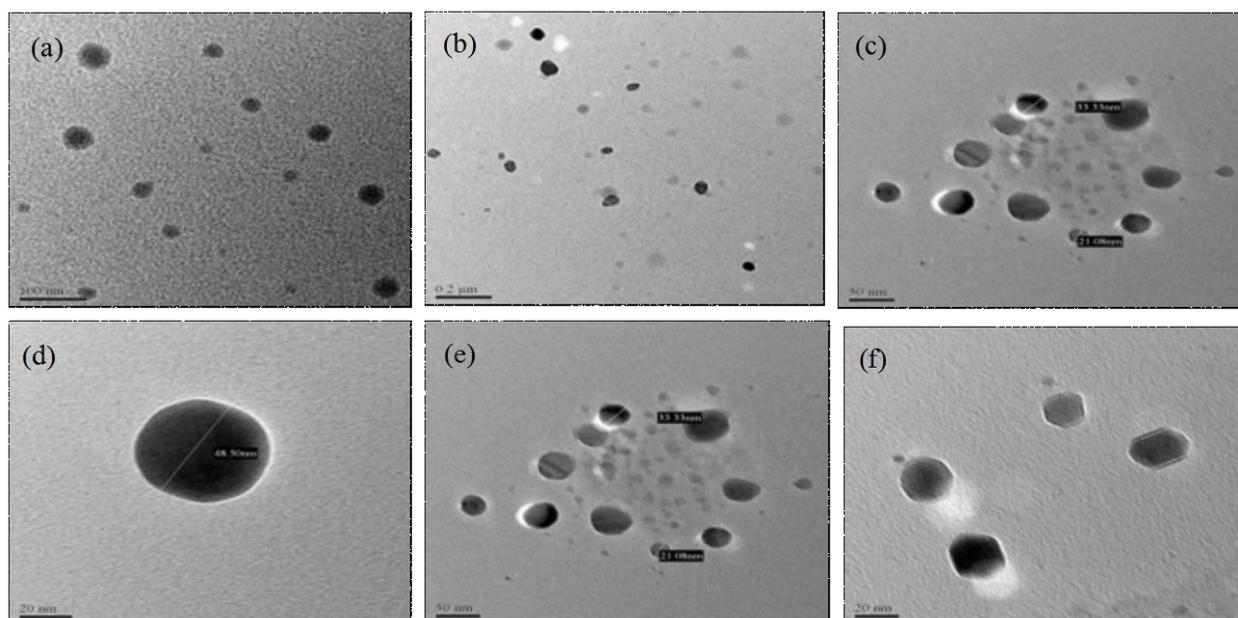


Figure 6: TEM images of polyaniline nanoparticles

Dynamic Light Scattering Studies: The particle sizes and their distribution were also investigated by the dynamic light scattering (DLS) method. The results of DLS studies are presented in Figure 7. The Particle sizes observed by dynamic light scattering are in line with the values observed by the TEM. However, a slight increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size. DLS results also showed that the particle sizes were dependent on the size of the water pools, which is controlled by the [APS]/ [Surfactant] value of the microemulsions. Dynamic light scattering particle size analysis was carried out with Zetasizer 3000 HS_A. Average size distributions of the particles synthesized in micellar medium were found to be in the range 20 to 75 nm.

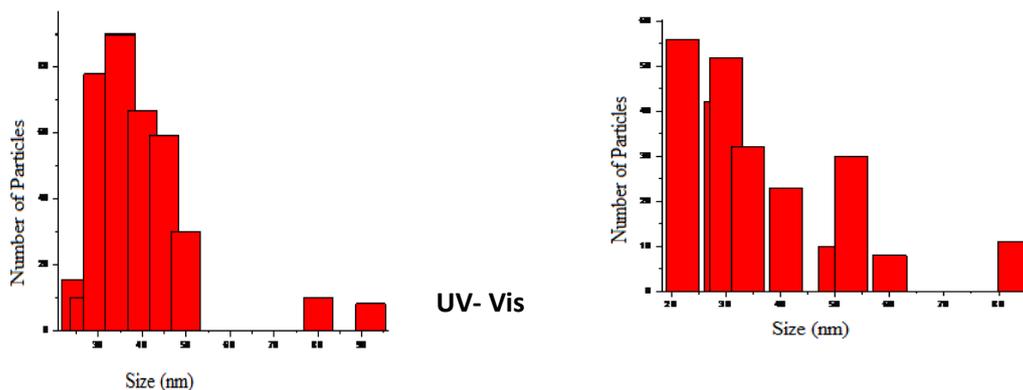


Figure 7: Distribution of particle size of polyaniline nanoparticles from dynamic light scattering

Absorption Spectra: The UV – Vis Spectra of polyaniline dispersions synthesised from composition I, II, III and IV are shown in Figure 8. The UV-Vis spectra of all the samples show similar features with very little variations. The absorption peaks in the region 307 – 396 nm are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment. The peak at 442–590 nm and 800 nm are due to polaron– π^* and π - polaron [14,15] band transition which indicates the doped status of PANI [16-18]. The band observed near or more than 800 nm is due to charge carriers, the tail of this band extends to IR region indicating that the charge carriers are bipolarons.

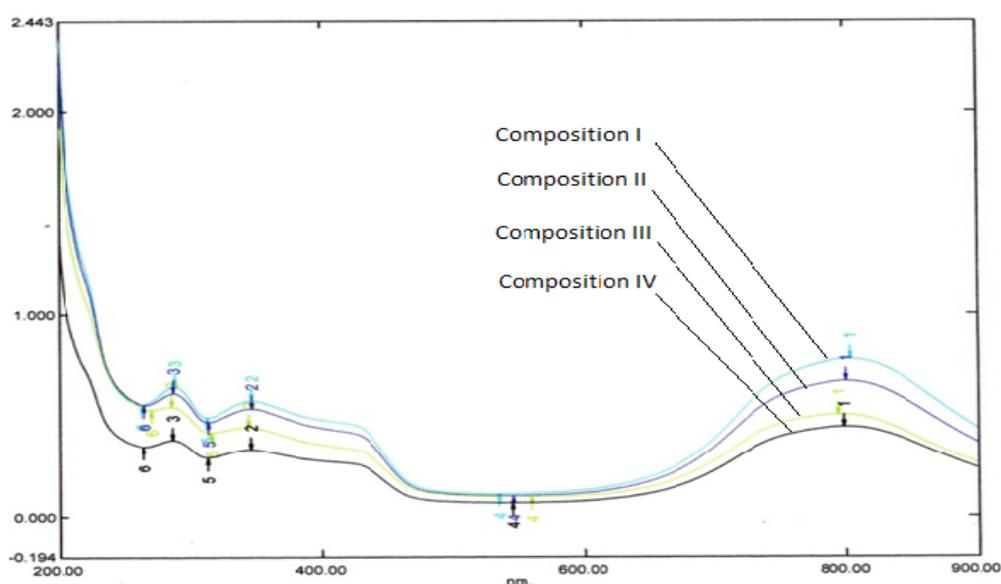
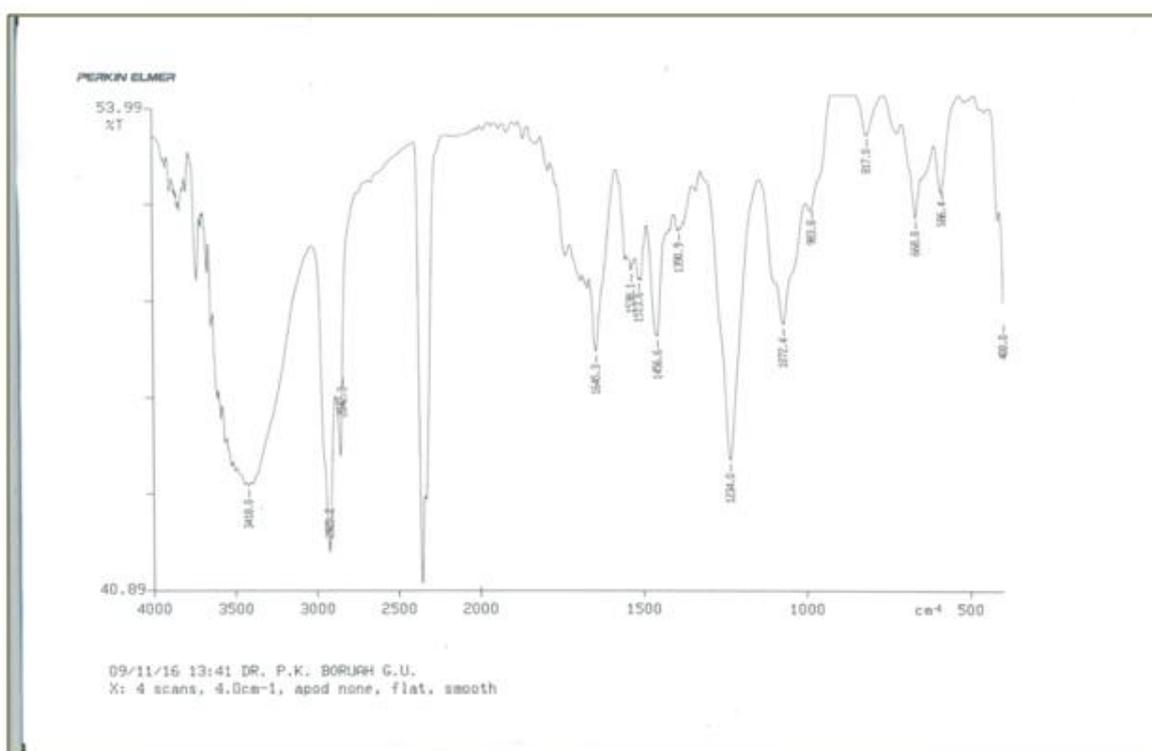


Figure 8: UV–Vis Spectra of polyaniline nanoparticles

FTIR – Spectra: The FTIR spectrum of polyaniline nanoparticles is shown in Figure 9. It shows all the characteristic bands of polyaniline. The absorption band at 1140 cm^{-1} in PANI-Tergitol system is said to be due to charge delocalization in polymer backbone because in the undoped state the intensity of this band is very weak. In the present study this band is observed at $1093\text{--}1121.5\text{ cm}^{-1}$. Bands due to aromatic ring breathing mode are observed between $1461\text{--}1481\text{ cm}^{-1}$ are characteristics bands for. Bands in between $1562\text{--}1588\text{ cm}^{-1}$ are due to nitrogen quinoid. The N — H stretching are observed in between $1295\text{--}1300\text{ cm}^{-1}$. N — H band is observed between $3431\text{--}3454\text{ cm}^{-1}$. Aromatic C-H is observed between $2838\text{--}2901$ & $2934\text{--}2967\text{ cm}^{-1}$. The bands near 1456 and 1540 cm^{-1} are assigned to C = C stretching of benzenoid and quinoid rings respectively. These bands appear at lower wave number than were observed near 1500 and 1600 cm^{-1} for undoped PANI, as was usual for well doped PANI. The peak at 1234 cm^{-1} , which is characteristic of the conducting PANI–ES form, is also seen. It has been interpreted as originated from bipolaron structure, related to C — N stretching vibration [18]. The peaks ranging from 2800 to 3000 cm^{-1} are assigned to aliphatic C — H stretching mode.

**Figure 9: FTIR Spectra of polyaniline nanoparticles [APS]/ [Tergitol] molar ratio 1.0**

Conductivity of polyaniline: All conducting polymers have intrinsic topological defects which are introduced during polymerization and their ground states are non-degenerate. Application of an external electric field makes both cation and dication mobile via the rearrangement of conjugation. Here in case of PANI the charged species are formed during the protonation of polymer which is responsible for its increase in conductivity. The conductivity in polyaniline is shown in Figure 10.

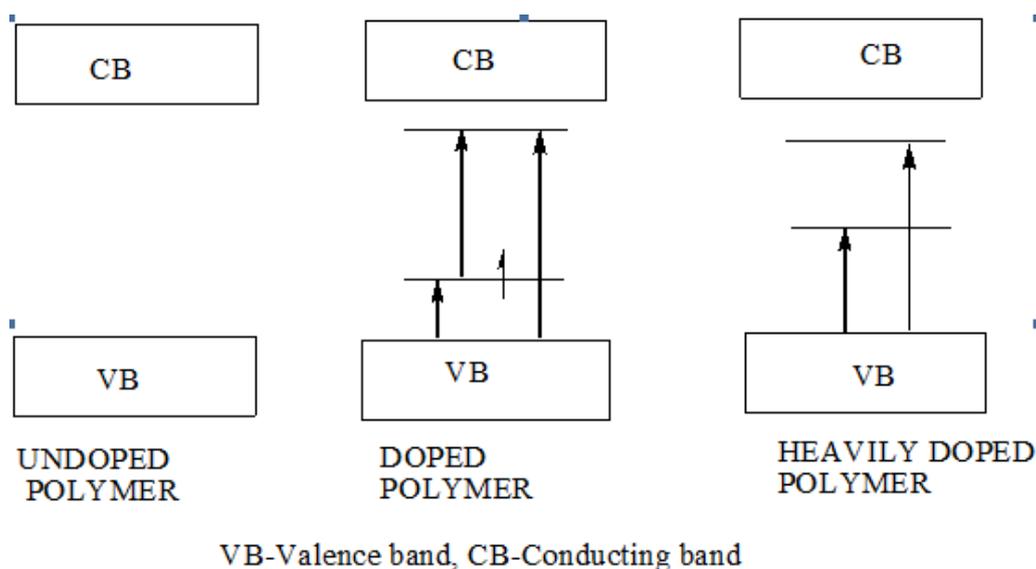


Figure 10: Conductivity of Polyaniline

The conductivity of PANI depends on the degree of doping, oxidation state, particle morphology, crystallinity, inter- or intra-chain interactions, molecular weight, etc. The particle size has an effect on the conductivity of PANI [19]. A decrease in the particle size facilitates more effective doping resulting in an increase in the conductivity value. In the present case also the conductivity is marginally increased with lowering of particle size of PANI. The variation of conductivity of polyaniline nanoparticles obtained through inverse microemulsion with the *APS to surfactant* molar ratio value is shown in the Table 3. Conductivity measurements were carried out by the standard four probe method. The conductivity was measured in the form of a film deposited on Glass slide. The conductivity of PANI dispersions was found to be dependent on the concentration of Surfactant and also on the co-surfactant.

Table 3: Conductivity of polyaniline nanoparticles

Sl. No	Sample description	Conductivity (mS cm^{-1} at room temp.)
1	Composition 1, APS/ Aniline = 1.5	0.35
2	Composition 2, APS/ Aniline = 1.5	0.723
3	Composition 3, APS/ Aniline = 1.5	0.774
4	Composition 4, APS/ Aniline = 1.5	0.401

CONCLUSION

PANI dispersions containing PANI particles in the nanometer size were successfully synthesized in a Tergitol mediated reverse micellar solution and the PANI dispersions were formed only above the CMC value of the Tergitol. Further, the PANI dispersions were formed even below the CMC value of the Tergitol in presence of isopropyl alcohol. It has been observed that the PANI dispersions were stable enough and does not coagulate even after six months and also stable under centrifugation at the rate of 10000 rpm for 10 minutes. From the sophisticated instrumental analysis, it has been observed that the PANI nanoparticles synthesised in this way are spherical in nature and the majority particle are in the range of 20 to 50 nm. Further the sizes of nanoparticles were found to be dependent on the size of the water pools in the inverse microemulsion. Finally, the conductivity of the PANI dispersions were found to be in the range of 0.785 to 0.350 mS cm^{-1} .

ACKNOWLEDGEMENT

The authors acknowledge University Grant Commission, NE- Region for the Teacher Fellowship under UGC – FDP Scheme with the reference number F.5-34/TF/2007/2007/755, date: 28.08.2015.

REFERENCES

- 1) Mac Diarmid AG. Polyaniline and polypyrrole. *Synth. Met.* 1997 (84): 27., (b)Mac Diarmid AG, Chiang JC, Richter AF, and Epstein AJ. Molecular Engineering of π - Conjugated Polymers. *Synth. Met.* 1987 (18): 285. (c) Chinn D, Dubow J, Liess M, Josowicz M, and Janata J. Understanding the Processing-Structure-Property Relationship of Water-Dispersible, conductive Polyaniline. *J. Chem. Mater.* 1995 (7): 1504.
- 2) Genies EM, Hany P and Santier CJ. A rechargeable battery of the type polyaniline/ propylene carbonate–LiClO₄/ Li–Al. *J. Appl. Electrochem.* 1995 (18): 285.
- 3) Chen SA and Fang Y. Polyaniline Schottky barrier: Effect of doping on rectification and photovoltaic characteristics. *Synth. Met.* 1993 (60): 215.
- 4) Jelle BP and Hagen GJ. Transmission Spectra of an Electrochromic Window Based on Polyaniline, Prussian blue and Tungsten Oxide. *J Electrochem Soc.* 1993 (140): 3560-3564.
- 5) Epstein AJ and Yue J. Polyaniline compositions, process for their preparation and uses thereof. 1991, US Patent No. 5237991.
- 6) (a) Sukeerthi S and Contractor AQ. Molecular Sensors and Sensor Arrays based on Polyaniline Microtubules. *Anal. Chem.* 1999 (71): 2231-2236. (b) Liu CH, Liao KT and Huang HJ. Amperometric immunosensors based on a protein – A coupled polyaniline-perfluorosulfonated ionomer composite electrodes. *Anal. Chem.* 2000 (72): 2925-2929.
- 7) Kim BJ, Oh SG, Han MG and Im SS. Preparation of Polyaniline Nanoparticles in Micellar Solutions as Polymerization Medium. *Langmuir.* 2000 (16): 5841- 5845.
- 8) Pileni MP. Reverse micelles as microreactors. *J. Phys. Chem.* 1993 (97): 6961-6973.
- 9) Ahmed T, Chopra CR, Ramanujachary KV, Lojland SE and Ganguli AK. Nanorods of copper and nickel oxalates synthesized by the reverse micellar route. *J. Nanoscience and Nanotechnology.* 2005 (5): 1840-1845.
- 10) Han MY, Huang W, Chew CH, Gan LM, Zhang XJ and Ji W. Large Nonlinear absorption in coated Ag₂S/CdS nanoparticles by Inverse Microemulsion. *J. Phys. Chem. B.* 1998 (102): 1884-1887.
- 11) Gan LM, Chew CH, Chan HSO and Ma L. Synthesis of crystalline polyaniline. *Polym. Bull.* 1993 (31): 347.
- 12) Yan F and Xue G. Synthesis and characterization of electrically conducting polyaniline in water-oil microemulsion. *J. Mater. Chem.* 1999 (9): 3035.
- 13) Xia H and Wang Q. Polyaniline/Fe₃O₄ magnetic nanocomposite prepared by ultrasonic irradiation. *J. Nanopart. Res.* 2001 (3): 401.
- 14) Menger FM and Efrington AR. Gemini-surfactants: Synthesis and properties. *J. Am. Chem. Soc.* 1991 (113):1451-1452.
- 15) Huang JX and Kaner RB. Nanofiber formation in the chemical polymerization of aniline: A mechanistic study. *Angew. Chem. Int. Ed.* 2004 (43): 5817.
- 16) Lu et al. Uniform polymer particles by dispersion polymerization in alcohol. *Journal of Polymer-Wiley online Library.* 1986.
- 17) Stafstrom et al. Transport studies of protonated emeraldine polymer: A granular polymeric metal system. *Phys. Rev. B.* 1987 (36): 3475.
- 18) Han MG et al. Preparation and characterization of polyaniline nanoparticles synthesized from DBSA micellar solution. *Synthetic Metals.* 2002 (126): 53 – 60.
- 19) Wnek GE. Porous polyaniline films with high conductivity. *Synthetic Metals.* 1986 (15): 213.