

Polyaniline Nanoparticles in Sodium Dodecyl Sulfate based Inverse Microemulsion

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ABSTRACT

Nanoparticles of polyaniline have been synthesized by an inverse microemulsion technique. Polymerization of aniline was confined to a nanoreactor 'water pool' surrounded by surfactant molecules of sodium dodecyl sulphate 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 presence of quinoid and benzenoid structures 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, transmission electron microscopy, dynamic light scattering.*

INTRODUCTION

Polyaniline is one of the most important intrinsically conducting polymer^[1] due to its stability and interesting electrical and optical properties. Potential applications of polyaniline include its use in 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. Among different methods the preparation of polyaniline in colloidal form containing nanoparticles of polyaniline is an important way to improve the processability of this polymer^[7].

J. Polym. Mater. Vol. **28**, No. 4, 2011, 561-575

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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 highly specialized and expensive equipment^[9]. 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 less amount of 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 sodium dodecyl sulfate based inverse microemulsion route. 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 (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.

EXPERIMENTAL

The synthesis of colloidal dispersion of using two

microemulsions (I and II) as described below. Microemulsion I is composed of sodium dodecyl sulfate (SDS) as the surfactant, n-butanol co-surfactant, cyclohexane the hydrocarbon phase and aniline in 1.0 M HCl' the aqueous phase.

Microemulsion II is comprised of the same constituents as above except for ammonium persulfate (APS) solution instead of anilinium hydrochloride as the aqueous phase.

The maximum weight percentage of aqueous phase up to which the transparent microemulsion could be formed, was ascertained by the titration method^[14]. The two microemulsions were mixed instantaneously to avoid secondary growth^[15]. It was then stirred for 2 h and left undisturbed for overnight. The details of the synthesis are presented in the Table 1-4.

Scanning electron micrographs (SEM) were recorded in 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 in 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. 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 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 was 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 as the conductivity value.

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 1.47g SDS (Surfactant), 3.65 mL Butanol (Cosurfactant) and 36.5 mL Cyclohexane (Oil)

Composition	Emulsion	Aniline(mol)	APS (mol)	Result
Composition I	Microemulsion I	0.0116	-	Dispersion
	Microemulsion II	-	0.0116	
Composition II	Microemulsion I	0.0105	-	Dispersion
	Microemulsion II	-	0.0105	
Composition III	Microemulsion I	0.0095	-	Dispersion
	Microemulsion II	-	0.0095	
Composition IV	Microemulsion I	0.0084	-	Dispersion
	Microemulsion II	-	0.0084	
Composition V	Microemulsion I	0.0074	-	Dispersion
	Microemulsion II	-	0.0074	
Composition VI	Microemulsion I	0.0063	-	Dispersion
	Microemulsion II	-	0.0063	
Composition VII	Microemulsion I	0.0053	-	Unstable
	Microemulsion II	-	0.0053	Dispersion
Composition VIII	Microemulsion I	0.0042	-	Ppt.
	Microemulsion II	-	0.0042	

TABLE 2. Synthesis of PANI in Reverse Micelle by varying the Amount of Anilinium Salt and APS (Maintaining APS to Aniline Molar Ratio = 0.5) with 1.47g SDS (Surfactant), 3.65 mL Butanol (Cosurfactant) and 36.5 mL Cyclohexane (Oil)

Composition	Emulsion	Aniline(mol)	APS (mol)	Result
Composition I	Microemulsion I	0.0096	-	Dispersion
	Microemulsion II	-	0.0048	
Composition II	Microemulsion I	0.0088	-	Dispersion
	Microemulsion II	-	0.0044	
Composition III	Microemulsion I	0.0078	-	Dispersion
	Microemulsion II	-	0.0039	
Composition IV	Microemulsion I	0.0070	-	Unstable
	Microemulsion II	-	0.0035	Dispersion
Composition V	Microemulsion I	0.0062	-	Unstable
	Microemulsion II	-	0.0031	Dispersion
Composition VI	Microemulsion I	0.0052	-	Cloudy
	Microemulsion II	-	0.0026	Solution
Composition VII	Microemulsion I	0.0044	-	Ppt.
	Microemulsion II	-	0.0022	
Composition VIII	Microemulsion I	0.0036	-	Ppt.
	Microemulsion II	-	0.0018	

TABLE 3. Synthesis of PANI in Reverse Micelle by Varying the Amount of Anilinium Salt and APS (maintaining APS to Aniline Molar Ratio = 1.5) with 1.47g SDS (Surfactant), 3.65 mL Butanol (Cosurfactant) and 36.5 mL Cyclohexane (Oil)

Composition	Emulsion	Aniline(mol)	APS (mol)	Result
Composition I	Microemulsion I	0.0116	-	Dispersion
	Microemulsion II	-	0.0174	
Composition II	Microemulsion I	0.0105	-	Dispersion
	Microemulsion II	-	0.0158	
Composition III	Microemulsion I	0.0095	-	Dispersion
	Microemulsion II	-	0.0143	
Composition IV	Microemulsion I	0.0084	-	Dispersion
	Microemulsion II	-	0.0126	
Composition V	Microemulsion I	0.0074	-	Dispersion
	Microemulsion II	-	0.0111	
Composition VI	Microemulsion I	0.0063	-	Unstable
	Microemulsion II	-	0.0095	Dispersion
Composition VII	Microemulsion I	0.0053	-	Unstable
	Microemulsion II	-	0.0080	Dispersion
Composition VIII	Microemulsion I	0.0042	-	Ppt.
	Microemulsion II	-	0.0063	

TABLE 4. Synthesis of PANI in Reverse Micelle by varying the Amount of Anilinium salt and APS (maintaining APS to Aniline Molar ratio = 2.0) with 1.47g SDS (Surfactant), 3.65 mL Butanol (Cosurfactant) and 36.5 mL Cyclohexane (Oil)

Composition	Emulsion	Aniline(mol)	APS (mol)	Result
Composition I	Microemulsion I	0.0096	-	Unstable
	Microemulsion II	-	0.0058	Dispersion
Composition II	Microemulsion I	0.0026	-	Unstable
	Microemulsion II	-	0.0054	Dispersion
Composition III	Microemulsion I	0.0020	-	Unstable
	Microemulsion II	-	0.0040	Dispersion
Composition IV	Microemulsion I	0.0018	-	Unstable
	Microemulsion II	-	0.0036	Dispersion
Composition V	Microemulsion I	0.0015	-	Unstable
	Microemulsion II	-	0.0030	Dispersion
Composition VI	Microemulsion I	0.0013	-	Cloudy
	Microemulsion II	-	0.0026	Solution
Composition VII	Microemulsion I	0.0011	-	Ppt.
	Microemulsion II	-	0.0022	
Composition VIII	Microemulsion I	0.0009	-	Ppt.
	Microemulsion II	-	0.0018	

RESULTS AND DISCUSSION

Polymerization of Aniline

Polymerization of aniline proceeded in the microemulsion under stirring. When an aqueous solution of anilinium hydrochloride or ammonium persulphate, was added to a certain amount of cyclohexane, SDS only up to a certain amount of aqueous solution, which was determined by titration method. [Water]/ [Surfactant] molar ratio (*w*) value is a key factor for the formation of microemulsion. The values of *w* for the various microemulsions are shown in Table 5. As evident from Table 5, microemulsion only formed at $w \leq 3.48$, higher *w*- value led to turbid formulations. When the two microemulsions were mixed the

nanoreactor water pools containing anilinium hydrochloride and ammonium persulphate coalesce and react to form polyaniline which was evident from the change in colour from light blue, blue, blue-green, green to dark green. The time required for the completion of reaction was 2 h. Stable dark green colored 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 (Table 2 and Table 4) in majority of the cases.

TABLE 5. *w* Values for Various Compositions and APS to Aniline Molar Ratios (Bold *w*-values Indicates the Formation of Stable Nanostructured PANI)

Composition ↓ APS : Aniline →	<i>w</i> - Value for Table 1 1.0	<i>w</i> - Value for Table 2 0.5	<i>w</i> - Value for Table 3 1.5	<i>w</i> - Value for Table 4 2.0
I	2.32	0.96	3.48	1.16
II	2.1	0.88	3.16	1.08
III	1.9	0.78	2.86	0.8
IV	1.68	0.7	2.52	0.72
V	1.48	0.62	2.22	0.6
VI	1.26	0.52	1.9	0.52
VII	1.06	0.44	1.6	0.44
VIII	0.84	0.36	1.26	0.36

Particle Size and Morphology

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

The scanning electron micrographs of the polyaniline colloidal dispersions are shown in Fig.1 for $w = 3.48$ and 0.96. It shows the spherical morphology of the polyaniline

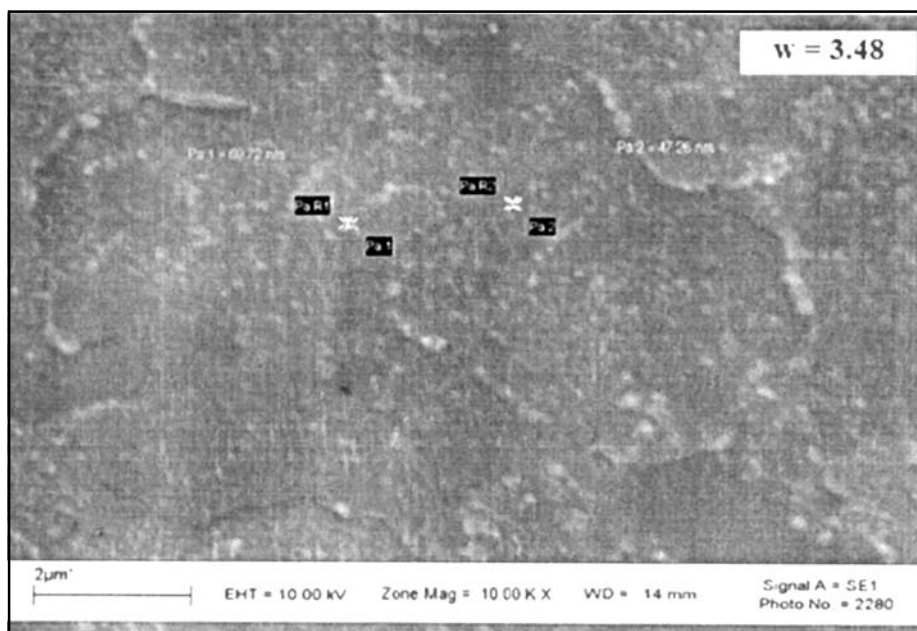
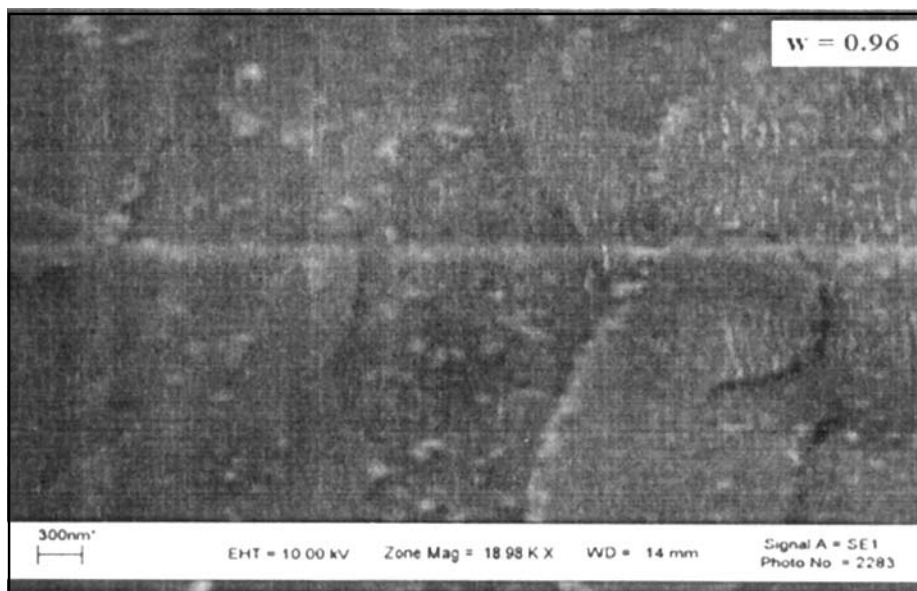


Fig. 1. SEM images of polyaniline nanoparticles

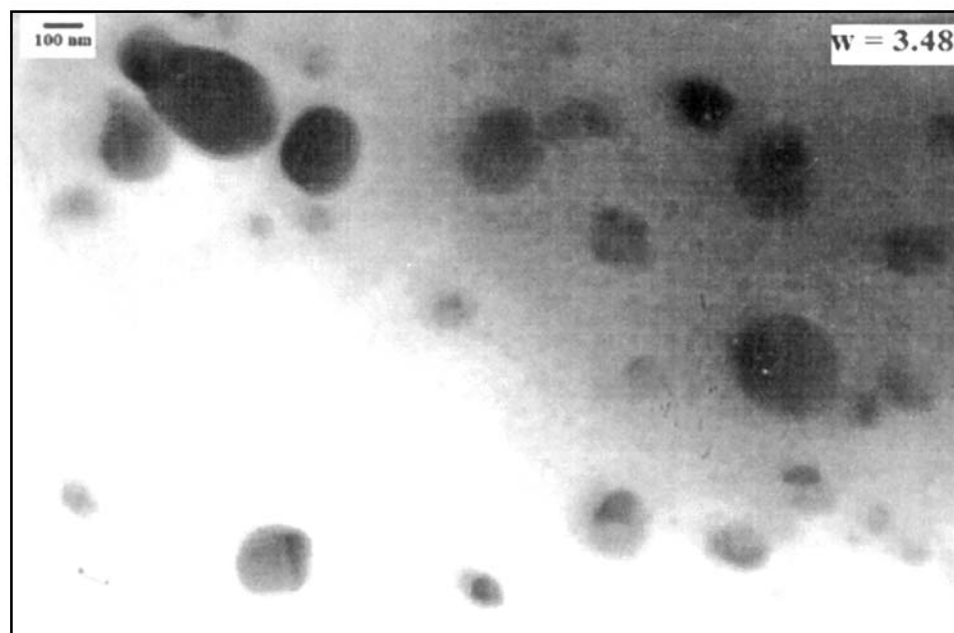
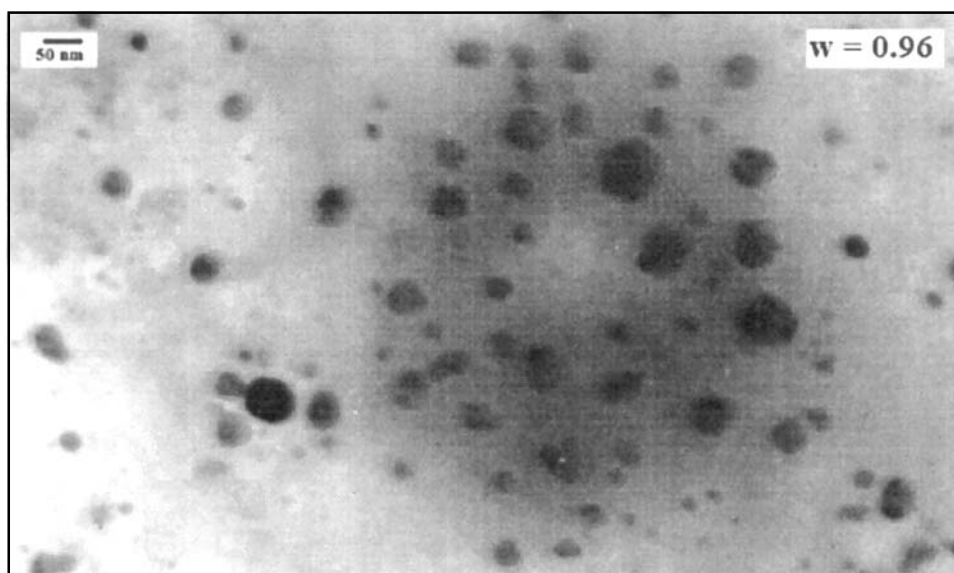
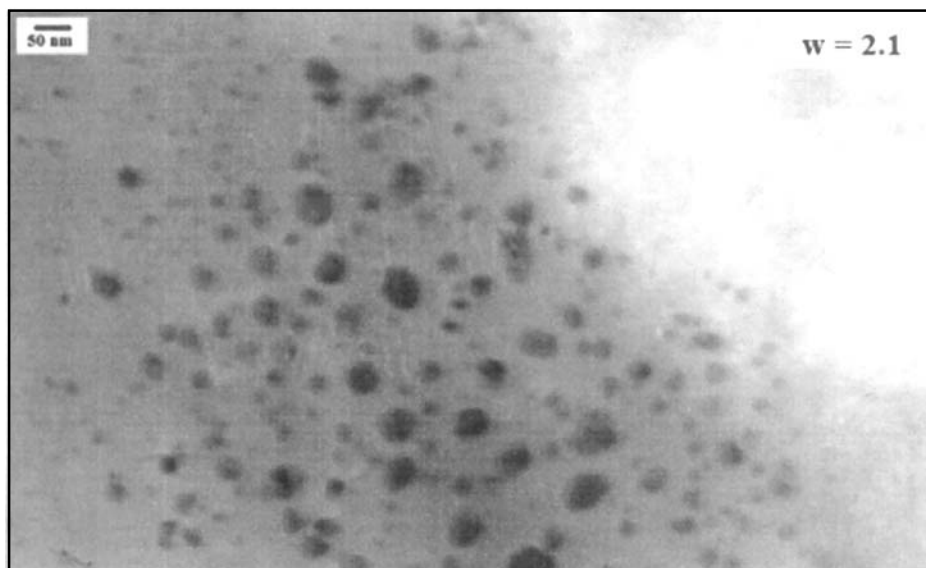
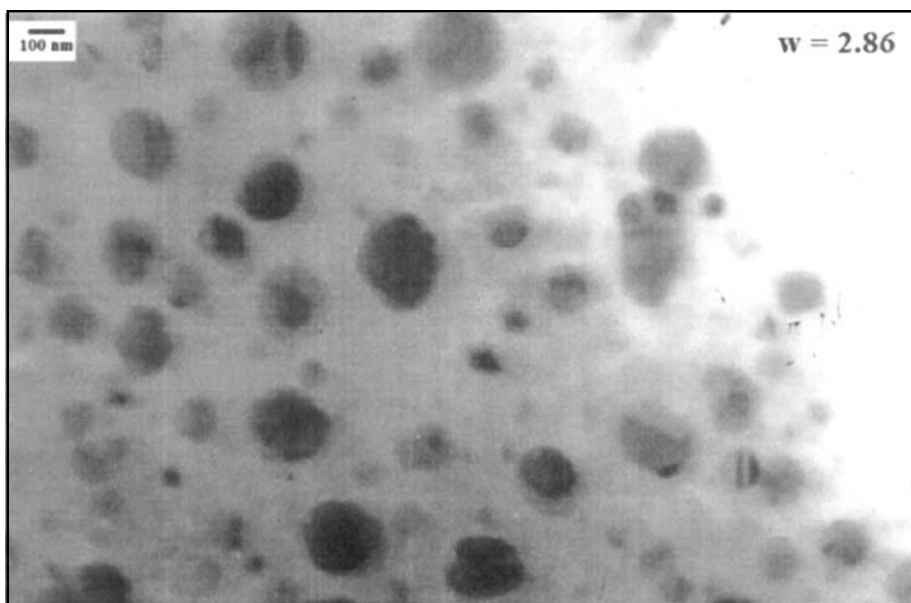


Fig. 2. TEM Images of polyaniline nanoparticles



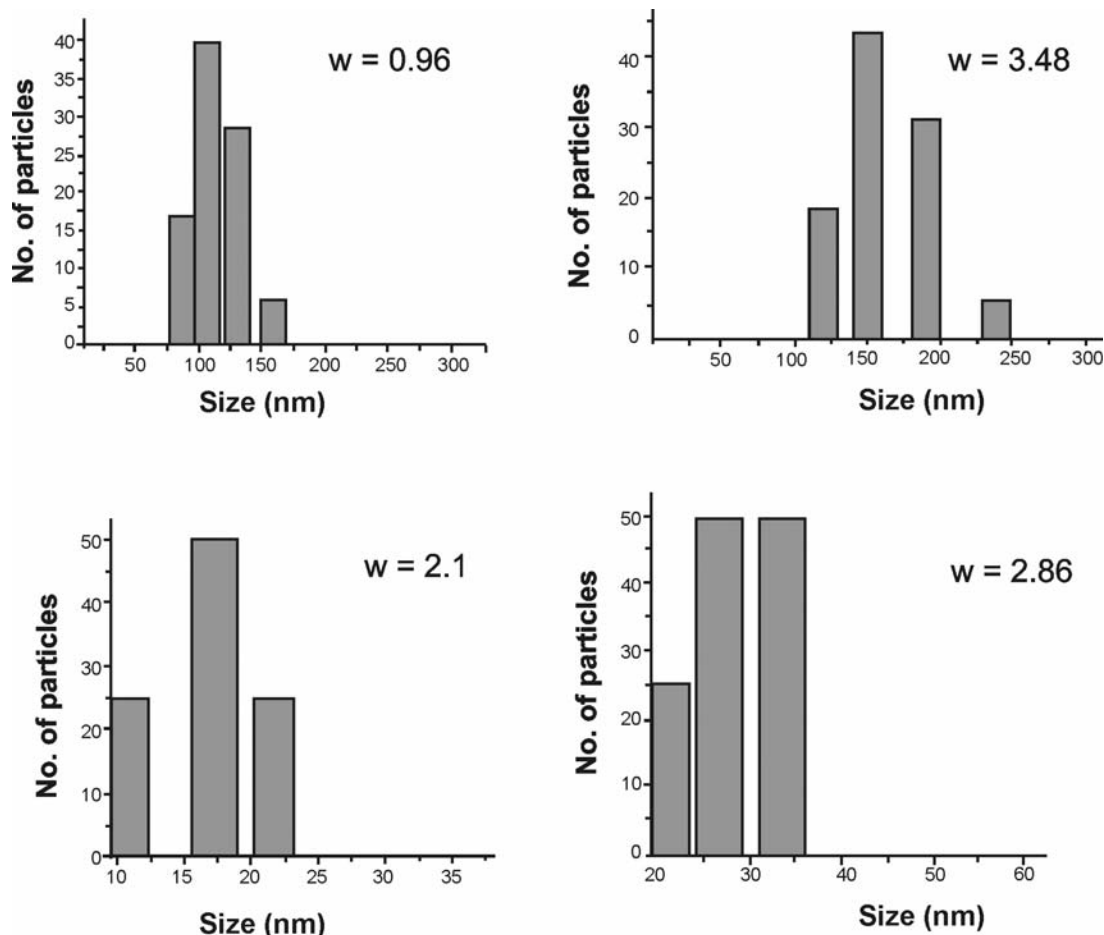


Fig. 3. Distribution of particle size of polyaniline nanoparticles from dynamic light scattering

particles. The particle size ranges from 40 nm to 80 nm when w -value was 0.96 and the corresponding values at w -value 3.48 were from 50 nm to 90 nm. As was evident, the particle sizes were dependent on the size of water pools, being controlled by the w -values. Fig. 2 shows the transmission electron micrographs of PANI nanoparticles in the colloidal dispersions for various w values. The spherical polymeric nanoparticles were produced and the

sizes are 10 to 35 nm at $w = 0.96$, 10 to 40 nm at $w = 2.1$, 10 to 45 nm at $w = 2.86$ and 20 to 50 nm at $w = 3.48$ respectively. It was observed that the rise in w -value resulted in an increase in the size of PANI particles. This is because the larger w value resulted in an increase in the size of the water pools (nanoreactors). The particle sizes at different w values are presented in Table 6.

TABLE 6: Dependence of Particle Sizes of Polyaniline Nanoparticles from TEM Studies with w - values

Composition	Table	w -Value	Particle size (nm)
I	2	0.96	10 - 35
II	1	2.1	10 - 40
III	3	2.86	10 - 45
I	3	3.48	20 - 50

The particle sizes and their distribution were also investigated by the dynamic light scattering (DLS) method. The results of DLS studies are presented in Fig.3 for various values of w . 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 w values of the micro-emulsions.

UV - Visible Absorption Spectra

The UV - Vis spectra of polyaniline dispersions synthesised for different w values are shown in Fig. 4. The UV-Vis spectra of all the samples show similar features with very little variations. The absorption peaks in the region 300 - 350 nm are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment. The peak at 400-440 nm and 800 nm are due to polaron $-\pi^*$ and π -polaron band transition which indicates the doped status of PANI.^[16-17]

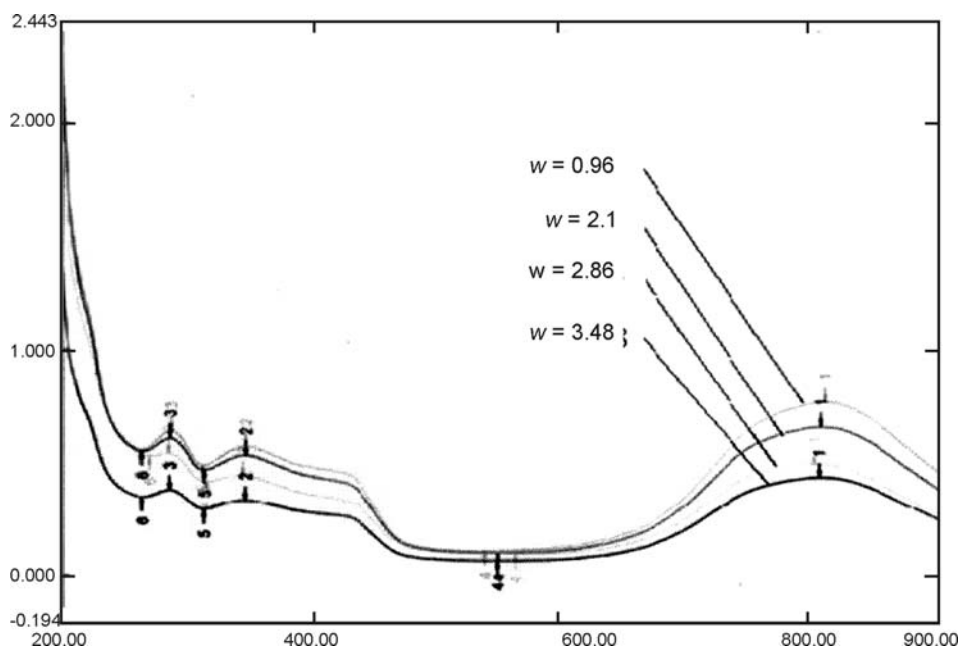


Fig. 4. UV-Vis Spectra of polyaniline nanoparticles

FTIR - Spectra

The FTIR spectrum of polyaniline nanoparticles is shown in Fig.5. It shows all the characteristic

bands of polyaniline. The N-H stretching band is observed at 3418 cm^{-1} . The bands near 1456 and 1540 cm^{-1} are assigned to C = C stretching

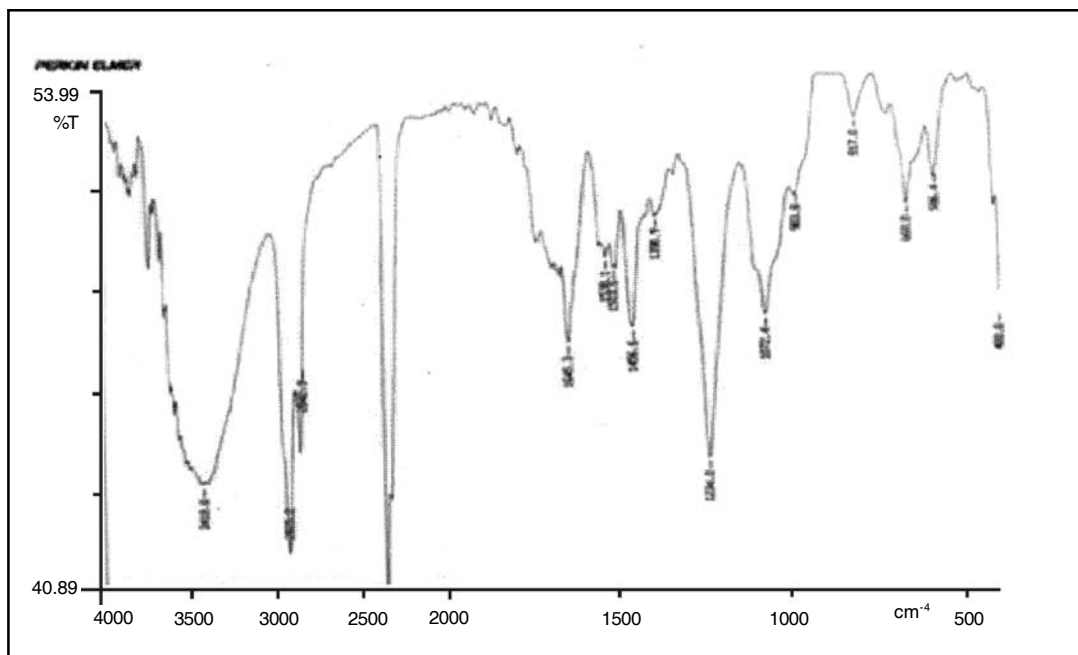


Fig. 5. FTIR Spectra of polyaniline nanoparticles

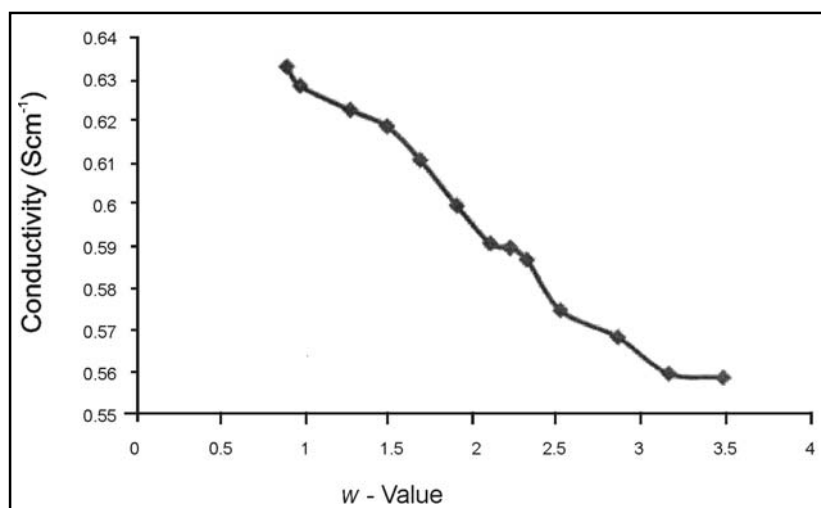


Fig. 6. The variation of conductivity of polyaniline nanoparticles with w - value

TABLE 7. Variation of conductivity with w - values

w -Value	Conductivity ($\times 10^{-3}$ S cm^{-1})
3.48	5.592
3.16	5.601
2.86	5.688
2.52	5.752
2.32	5.873
2.22	5.977
2.10	5.901
1.90	6.001
1.68	6.111
1.48	6.192
1.26	6.231
0.96	6.289
0.88	6.335

of benzenoid and quinoid rings respectively. These bands appear at lower wave number than were observed for undoped PANI near 1500 and 1600 cm^{-1} . This was usual for well doped PANI. The peak at 1234 cm^{-1} , which is characteristic of the conducting PANI-ES form, is also seen^[18]. The peaks ranging from 2800 to 3000 cm^{-1} are due to aliphatic C – H stretching vibration.

Conductivity

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 conductivity values in S cm^{-1} are presented in Table 7. The variation of conductivity of polyaniline nanoparticles obtained through inverse microemulsion with the w value is presented in Fig. 6. The conductivity values are in the same range as reported by Stejskal et al.^[20-22]

Conclusion

Polyaniline nanoparticles were successfully synthesised in a sodium dodecyl sulfate based inverse microemulsion. The PANI nanoparticles synthesised in this way are spherical in nature and the majority particle are in the range of 20 to 50 nm as was evident from the TEM-micrographs. Further the sizes of nanoparticles were found to be dependent on the size of the water pools. APS to aniline molar ratio was observed to be an important parameter which determined the stability of the colloidal dispersion. The optimum-ratio was found to be 1.0 to 1.5. The conductivity values were also dependent on the size of the PANI nanoparticles.

ACKNOWLEDGEMENT

The authors (1 & 2) acknowledge University Grant Commission, NE- Region for the Teacher Fellowship under the UGC - FDP Scheme.

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RECEIVED : 2 September, 2011

ACCEPTED : 12 September, 2011