Chapter 3

Selective Micellar Templating for Divergent Polyaniline Nanostructures
3.1. Introduction

Tuning the morphology of the nanostructures is a challenging task in conducting polymer nanomaterials research\textsuperscript{1,4}. In emulsion route for polyaniline nanomaterials the polymerization is carried out in aniline in water emulsion stabilized by surfactants or functionalized dopants\textsuperscript{5,7}. The underlying principle in emulsion route is that the micellar soft template formed by the surfactant (or dopant) directs the morphology of the resulting polymer. In interfacial route for polyaniline nanofibers, the polymerization is performed in an immiscible aqueous/organic two phase system\textsuperscript{8,9}. The polymerization occurs at the interface and the resultant polyaniline in its hydrophilic emeraldine salt form diffuses away from the reactive interface which makes more reaction sites available at the interface. The interfacial route is mostly restricted to < 1 g scale (also low yield) due to the difficulty in controlling the diffusion process at the interfaces for large scale synthesis of polyaniline nanomaterials. Interestingly, the nanofibers produced through interfacial route were thin (< 100 nm), free from agglomerates and easily dispersible in water compared to other synthetic routes\textsuperscript{10}.

Figure 3.1. Polyaniline nanostructures by interfacial, emulsion and dilution routes (Adapted from references 9,11).

A dilute polymerisation route for polyaniline nanofibers developed by Epstein group has been carried out at very low concentration of monomer and thus prevents excessive aggregation tendencies of polymer chains leading to agglomerates\textsuperscript{11,12}. In dilute polymerization the kinetics of polymerization is relatively very low so it is very advantageous to tune the morphology of the forming polymer by adjusting experimental conditions. For example, Guo and co-workers fabricated polyaniline rectangular sub-micron tubes by carrying out the polymerization of aniline in dilute
anionic surfactant solutions. Both interfacial and dilute polymerizations are important non-template routes to synthesize high quality polyaniline nanofibers. The advantage of these polymerization approaches is that the aniline monomer concentration is very low and hence the secondary growths of nanofibers leading to particulate aggregates are well prevented. However, low yield, inability to large scale synthesis and structural restriction to a few acid dopants are unsolved problems associated with these superior processes. So far there is no detailed study has been done to analyze the influence of the structural changes of templates in emulsion, dilute or interfacial route on polyaniline nanomaterials morphology. Further, a wider discrepancy was also noticed in the polyaniline nanomaterials synthesis over the selection of dopant molecules and polymerization routes: for instance, an emulsion friendly dopant failed as a good candidate for interfacial or dilution routes and vice-versa. It restricts the deep understanding of the mechanistic aspects of polymerization processes and their dependency on the formation of nanomaterials. Therefore, the development of a single amphiphilic surfactant (or dopant) based templates for the synthesis of various polyaniline nanostructures under emulsion, interfacial and dilution conditions is very much demanding.

Figure 3.2. Amphiphilic azobenzene soft-template mediated synthesis of polyaniline nanostructures—fibers, tubes, spheres and rods.

This chapter is focused on the use of the unique micellar soft template approach based on an in-built amphiphilic molecule, 4-[4-hydroxy-2((Z)-pentadec-8-
Selective Micellar Templating

3.1. Selective Micellar Templating

(25x699)phenylazo)-benzenesulfonic acid (developed in chapter-2), for tuning various types of polyaniline nano materials such as fibers, rods, spheres and tubes through selective templating process in water. This approach is very unique in the sense that all the starting materials are same (amphiphilic dopant, aniline, ammoniumpersulfate (APS) and water), but various nanomaterials were produced in a controlled way depending on how these constituents are self-organized and polymerized in water under normal conditions. During the chemical oxidative polymerization of aniline via self-assembly process, amphiphilic dopant molecules form thermodynamically stable aggregates of inherent nanoscale dimensions in solution, which act as template for the overall morphology of the resulting polyaniline. Templates formed by the dopant aniline complex in emulsion, dilute and interfacial polymerization is characterized by DLS (in solution) and TEM (in solid state). In emulsion route the dopants form either cylindrical micelles or bilayers with aniline monomer and their oxidation yields nanofibers and nanotubes respectively. Up on diluting the emulsion, it transformed into micelle aggregates of 175 nm size, which seeds for nanorods. In the interfacial route the spherical aggregates formed by the dopant-APS complex acts as template for nanospheres. The nanomaterials were characterized by SEM, TEM, absorption spectroscopy and X-ray diffraction to understand the morphology, electronic and solid state ordering. In summary, a unique amphiphilic sulfonic acid was developed to form variety of templates with aniline and APS to produce wide range of nanomaterials of fibers, rods, tubes and spheres. The idea of utilizing a single molecular dopant system in both emulsion (dilution) and interfacial routes to trace the factors which control the morphology of the nanomaterials is crucial and important for fundamental understanding of polyaniline nanomaterials.

3.2. Experimental Procedures

3.2.1. Materials: Aniline, ammonium persulfate (APS) and sulfanilic acid were purchased from Aldrich. Aniline was distilled and kept under nitrogen prior to use. The renewable dopant molecule 4-[4-hydroxy-2((Z)-pentadec-8-ethylphenylazo]-benzenesulfonic acid was synthesised by following the procedure given in chapter 2.
The polyaniline nanomaterials E-1 to E-900 synthesised by emulsion route (see chapter-2) is used for current studies also.

3.2.2. General Procedures: For SEM measurements, polymer samples were subjected to thin gold coating using JEOL JFC-1200 fine coater. The probing side was inserted into JEOL JSM-5600 LV scanning electron microscope for taking photographs. Transmission electron microscope images were recorded using a FEI Tecnai 30G^2 S Twin HRTEM instrument at 100kV. For TEM measurements, the water suspension of nanomaterials were prepared under ultrasonic stirring and deposited on Formvar coated copper grid. Wide angle X-ray diffractions of the finely powdered polymer samples were recorded by Philips Analytical diffractometer using CuK-alpha emission. Dynamic light scattering (DLS) measurements were carried out using a Nano ZS Malvern instrument employing a 4mW He-Ne laser (\(\lambda=632.8\) nm) and equipped with a thermo stated sample chamber. For all the DLS measurements HPLC quality (Merck, India) double distilled water is used. All the dopant solutions are centrifuged (2000 rpm, 5 min) prior to DLS measurements in order to remove any suspended particles, whereas the emulsions and dopant + APS complexes are not centrifuged since centrifugation may destabilize the emulsion. Infrared spectra of the polymers were recorded using a Perkin Elmer, spectrum one FTIR spectrophotometer in the range of 4000 to 400 \(\text{cm}^{-1}\). For conductivity measurements, the polymer samples were pressed into a 10 mm diameter disc and analyzed using a Keithley four probe conductivity instrument by applying a constant current. The resistivity of the samples was measured at five different positions and at least two pellets were measured for each sample: the average of 10 readings was used for conductivity calculations. The thermal stability of the polymers was determined using TGA-50 Shimadzu Thermo gravimetric Analyzer at a heating rate of 10 °C/min in nitrogen. UV-Vis spectra of the PANI in water were recorded using Perkin Elmer Lambda-35 UV-VIS Spectro Photometer. The emission studies were performed by a SPEX Fluorolog F112X spectrofluorimeter. The fluorescence quantum yields of the dopant and nanomaterials were determined in water using quinine sulfate in water (\(\phi=0.546\)) as standard by exciting at 360 nm. The concentration of polymer solution (also dopant) and standard were adjusted in such a way to obtain the absorbance equal to
0.1 at 360 nm. The quantum yields of the samples are calculated by the following equation:

\[ \phi_s = \phi_r [F_s A_r / F_r A_s] (n_r/n_s)^2 \]

Where, \( \phi_s \) is the fluorescence quantum yield of the sample, \( F \) is the area for the emission peak, \( n \) is the refractive index of solution, and \( A \) is the absorbance of the solution at the exciting wavelength. The subscripts \( r \) and \( s \) denote reference and sample respectively. The resonance Raman peak for water appeared at 420 nm, which was deconvoluted computationally from the sample spectra for the calculating the area of the emission peaks.

3.2.3. Dilute Polymerization Route to Polyaniline Nanomaterials: Typical procedure for the synthesis of polyaniline nanomaterials is described in detail for D-100a and other samples were prepared following the same procedure. The dopant (0.053 g, 0.11 mmol) was dissolved in doubly distilled water (20 mL) and stirred under ultrasonic for 1h at 30 °C. Distilled aniline (1mL, 1.02 g, 11 mmol, [aniline]/[dopant] = 100) was added to the dopant solution and stirred under ultrasonic for additional 1h at 30 °C. The resulting emulsion was diluted by adding 15 mL of water. To this ammonium persulfate (10 mL, 1.1 M solution) was added at 30 °C. The resultant green color content was allowed to stand at 30 °C for 15 h. The solid was filtered, washed with distilled water, methanol and diethyl ether for several times till the filtrate become colorless. The solid product was dried in a vacuum oven at 60 °C for 48 h (0.01 mm Hg). \(^1\)H-NMR (500 MHz, DMSO-d\(_6\)) \( \delta \): 7.81 (b, 4H, Ar-H, dopant) 7.55 (b, 2H, Ar-H), 7.52 (b, 2H, Ar-H), 7.11, 7.18, 7.29 (1/1/1 triplet, 1H, -NH+), 6.91 (b, 1H, Ar-H, dopant), 6.81 (b, 1H, Ar-H, dopant), 5.3 ppm (b, 2H, CH=CH, dopant), 0.5-3.5 (27H, aliphatic-H, dopant); FTIR (KBr, in cm\(^{-1}\)): 3013, 1561, 1486, 1304, 1251, 1153, 1103, 1029, 812, 705 and 616. In a similar way the total volume of the reaction feed is varied by adding 30 mL, 60 mL, 90 mL and 120 mL water by keeping the [aniline]/[dopant] as 100 to synthesize samples D-100b, D-100c, D-100d, and D-100e, respectively.

3.2.4. Interfacial Polymerization Route for Polyaniline Nanomaterials: The dopant (0.053 g, 0.11 mmol) and ammonium persulfate (2.5 g, 11mmol) were
dissolved in doubly distilled water (30 mL) in a 50 mL glass vial. In a separate glass vial distilled aniline (1mL, 1.02g, 11 mmol, \([\text{aniline}]/[\text{dopant}] = 100\) was dissolved in dichloromethane. To the dichloromethane solution, dopant plus oxidant in water was carefully added without disturbing the interface. The interfacial polymerization was allowed to stand at 30 °C for 15 h without disturbing. Then the polyaniline solid mass was formed in the aqueous phase which was centrifuged, washed with distilled water and methanol for several times till the filtrate become colourless. The solid product was dried in a vacuum oven at 60 °C for 48 h (0.01 mm Hg). Yield = 0.36 g (35 %).

\(^1\)H-NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 7.81 (b, 4H, Ar-H, dopant) 7.55 (b, 2H, Ar-H), 7.52 (b, 2H, Ar-H), 7.11, 7.18, 7.29 (1/1/1 triplet, 1H, -NH\(+\)), 6.91 (b, 1H, Ar-H, dopant), 6.81 (b, 1H, Ar-H, dopant), 5.3 ppm (b, 2H, CH=CH, dopant); 0.5-3.5 (27H, aliphatic-H, dopant); FTIR (in cm\(^{-1}\)): 3015, 1563, 1484, 1301, 1248, 1151, 1106, 1027, 812, 707 and 618. Similarly 1-300 and 1-450 were prepared by varying \([\text{aniline}]/[\text{dopant}]\) ratio as 300 and 450 (in moles) respectively.

3.3. Results and Discussion

3.3.1. Dilute Route Synthesis of Polyaniline Nanomaterials:

The amphiphilic azobenzene dopant molecule, 4-[4-hydroxy-2-(Z)-pentadec-8-enyl) phenylazo]-benzenesulfonicacid (see figure 3.2) was employed as structural directing dopant for polyaniline nanomaterials. From previous studies (chapter 2), it is found that renewable resource based amphiphilic azobenzenesulfonic acid is a good water soluble surfactant and exists in the form of ~ 4.3 nm spherical micelles above CMC value. These dopant micelles are efficient structure directing soft templates for polyaniline nanofibers in emulsion route for a wide range of \([\text{aniline}]/[\text{dopant}]\) ratios. Here, in order to tune the morphology of nanomaterials as well as to thoroughly understand the mechanism of formation of nanomaterials, three synthetic approaches were employed. (i) Emulsions with varied ratio of \([\text{aniline}]/[\text{dopant}]\) in the feed \([\text{from} [\text{aniline}]/[\text{dopant}] = 1 \text{ to } 900]\) as discussed in chapter 2 (ii) Dilution polymerization by the addition of water in to pre-templated emulsion \([\text{[aniline]}/[\text{dopant}] =100]\) results in the decrease in both aniline and dopant concentration (see figure 3.3) and (iii) interfacial polymerization which is carried out in an aqueous/organic bi-phasic interfacial
system by varying the [aniline]/[dopant] ratio in the feed as 100, 300 and 450 (in moles) (see figure 3.4).

Table 3.1. [Dopant], [aniline], yield, S/N ratio, dimensions, conductivity, and WXRD-data of polyaniline nanomaterials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Dopant] (M)</th>
<th>[Aniline] (M)</th>
<th>Yield (%)</th>
<th>S/N (%)</th>
<th>Diameter (nm)</th>
<th>$\sigma$ (Scm$^{-1}$)</th>
<th>$I_{(20)6.4}/I_{(20)25.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-100a</td>
<td>2.4x10$^{-3}$</td>
<td>0.24</td>
<td>76</td>
<td>29.5</td>
<td>125-210</td>
<td>7.8x10$^{-3}$</td>
<td>0.44</td>
</tr>
<tr>
<td>D-100b</td>
<td>1.8x10$^{-3}$</td>
<td>0.18</td>
<td>59</td>
<td>28.6</td>
<td>140-220</td>
<td>1.5x10$^{-2}$</td>
<td>0.68</td>
</tr>
<tr>
<td>D-100c</td>
<td>1.2x10$^{-3}$</td>
<td>0.12</td>
<td>68</td>
<td>29.1</td>
<td>130-225</td>
<td>4.6x10$^{-3}$</td>
<td>0.69</td>
</tr>
<tr>
<td>D-100d</td>
<td>9x10$^{-4}$</td>
<td>0.09</td>
<td>58</td>
<td>27.5</td>
<td>0.7-1.3 $\mu$m</td>
<td>7.3x10$^{-3}$</td>
<td>0.82</td>
</tr>
<tr>
<td>D-100e</td>
<td>7.2x10$^{-4}$</td>
<td>0.07</td>
<td>63</td>
<td>27.1</td>
<td>0.6-1.4 $\mu$m</td>
<td>2.4x10$^{-3}$</td>
<td>0.82</td>
</tr>
</tbody>
</table>

(a) Calculated for isolated product.
(b) Calculated from elemental analysis data.
(c) The values are determined from the SEM images.
(d) Values are obtained using four probe conductivity units at 30° C.
(e) From wide angle X-ray diffraction measurements at 30° C.

The amphiphilic azobenzene dopant is freely soluble in water and its complex with aniline form stable emulsion, which acts as self-assisted template for polyaniline nanomaterials. The emulsion formed is very stable for a wide range of [aniline]/[dopant] ratios and are very stable for more than one month under normal ambient conditions. This gives the opportunity to trace both the effect of composition and concentration of the reactant constituents on the formation of nanomaterials. Emulsion polymerization details were described in chapter 2.

Figure 3.3. Dilute polymerization route for polyaniline nanorods.

In dilution route by gradually adding water into the pre-formed thick emulsion transformed into a clear solution without phase separation (see figure 3.3). Unlike the
emulsion route, in the dilution route the concentration of the aniline also decreases along with dopant, which account for the homogenous solution. It suggests that the amphiphilic dopant is very versatile in nature and wide range of composition of the reactants as well as their concentration can be fine-tuned for nanomaterials synthesis. The dilution polymerization mixtures were oxidised by APS solution to obtain green polyaniline nanomaterials. Typically the polymerization was carried out by dissolving aniline and dopant in water and subsequently stirring under ultrasonic at ambient conditions for 30 minutes. The resultant milky emulsion was diluted by adding required amount of water and oxidized by adding ammonium persulfate (1.1 M solution) in water under ultrasonic for 1 h. The green solution was kept at 30 °C without any disturbance. The green polymer was filtered and purified by washing with water and methanol until the filtrate become colourless. The samples prepared by dilution method were denoted as D-100x, where x = a, b, c, d and e (see table 3.1). The concentration of the aniline and dopant are given in table 3.1. The polymer samples were dried under vacuum for 24 h (0.05 mm of Hg) at 60 °C prior to further analysis. Polyaniline nanomaterials were produced in 60-80 % yield. The yield, composition and elemental analysis data (S/N ratio) of the polyaniline nanomaterials are summarized in table 3.1.

3.3.2. Interfacial Route Synthesis of Polyaniline Nanomaterials:

Interfacial polymerization is performed in an aqueous/organic two phase system with aniline dissolved in dichloromethane as solvent and ammonium peroxydisulfate +dopant were dissolved in an aqueous solution.

Figure 3.4. Snap shot showing the progress of interfacial polymerization.
The polyaniline samples were prepared by varying the [aniline]/[dopant] ratio in the feed as 100, 300 and 450 (in moles), respectively. The polymer were denoted as
I-X (I-100, I-300 and I-450), where I and X refer the interfacial route and ratio of [aniline]/[dopant] in the feed, respectively. Ammonium persulfate and dopant-1 were dissolved in water and immediately transferred to a vial containing aniline in dichloromethane. It is observed (within two minutes) that upon adding APS solution, the aqueous dopant layer slowly transform to yellow turbid (see vials in figure 3.4). After an induction period of 10 minutes, the polymerization started and green layer of polyaniline emeraldine appears at the interface (see vials in figure 3.4). As the reaction proceeds, the green layer became thick and after 15 h the entire aqueous layer turned to a dark solid. The aqueous layer was separated carefully, centrifuged and washed well with water and methanol to remove all oligomers, excess dopant and inorganic impurities. The samples were dried under vacuum for 24 h (0.05 mm of Hg) at 60 °C prior to further analysis. Polyaniline nanomaterials were produced in 40 % yield, which is relatively much higher than that reported for other sulfonic acid dopants 8 (for example camphoresulfonic acid, 8 % yield). The polyaniline structure and doping of emeraldine salt by the sulfonic acid was confirmed by FTIR analysis and the degree of doping (S/N ratio) was determined from elemental analysis (see table 3.2).

### Table 3.2. [Dopant]/[aniline], S/N, yield, conductivity, dimensions and WXRD-data of polyaniline nanomaterials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Aniline]/[Dopant] (moles)</th>
<th>Yield a (%)</th>
<th>S/N b (%)</th>
<th>$\sigma$ c (S/cm)</th>
<th>Diameter d (nm)</th>
<th>WXRD d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-100</td>
<td>100</td>
<td>34</td>
<td>33.3</td>
<td>2x10^{-2}</td>
<td>0.4-2.1μm</td>
<td>14.4,13.6, 4.8</td>
</tr>
<tr>
<td>I-300</td>
<td>300</td>
<td>36</td>
<td>41.3</td>
<td>5x10^{-2}</td>
<td>300-400nm</td>
<td>14.5,13.6, 4.8</td>
</tr>
<tr>
<td>I-450</td>
<td>450</td>
<td>41</td>
<td>32.4</td>
<td>1x10^{-2}</td>
<td>50-120nm</td>
<td>13.6,4,4,3.4</td>
</tr>
</tbody>
</table>

a) Calculated for isolated product.
b) Calculated from elemental analysis data.
c) Values are obtained using four probe conductivity units at 30° C.
d) The values are determined from the SEM images.
3.3.3. Morphology of Nanomaterials:
The SEM and TEM images of dilute polymerization route samples are given in figure 3.5. The samples D-100a and D-100c consists of nanofibers of ~100 nm thickness, which are thin compared to that of emulsion route fibres. Largely diluted sample, D-100d mainly comprises of nanorods plus spheres instead of nanofibers. As the polymerization medium become very dilute, (as in the case of D-100e), the sample comprises of only nanorods of diameter ranging from 175 nm – 800 nm.

The TEM images of D-100d (see figure 3.5) revealed that the nanorods are formed by the aggregation of nanospheres. The contrast difference of the interior part and exterior part clearly suggests the non-cylindrical shape of the nanorods and the whiskers like growth seen in rod surface indicates the adsorption of nanospheres. It is also interesting to see from the TEM images of D-100e that the rod composed of nanofibers of diameter ~75 nm. Based on the TEM (also SEM) images, it is reasonable to believe that during the initial stages of polyaniline formation in very dilute polymerization both nanospheres and nanofibers are formed. During the course of reaction the spheres are adsorbed on nanofiber surface that leads to nanorod formation. The above assumption is supported by the fact that the SEM and TEM image of rod clearly indicates the non-cylindrical in shape mostly due to the surface adsorption of nanospheres over the initially formed nanofiber fragments.
The SEM and TEM images of the interfacial polymerized polyaniline nanomaterials are given in figure 3.6. The SEM images of interfacial samples showed an interesting observation that the morphology of the materials changing from microspheres to nanospheres plus fibres with the decreasing the amount of dopant in the feed (from [aniline]/[dopant] = 100 to 450 in moles). $\mathbf{I-100}$ consists of both micron and nanospheres whereas $\mathbf{I-300}$ predominantly has only nanospheres of $\sim 400$ nm diameter. The sample $\mathbf{I-450}$ has nanospheres ($\sim 400$ nm) and also thin nanofibers of $< 150$ nm diameter. SEM technique is inadequate to distinguish whether the nanomaterials are hollow or rigid and also poor resolution for $< 150$ nm size (see figure 3.6) Therefore, the polyaniline nanomaterials samples were subjected to TEM analysis and the TEM images of $\mathbf{I-100}$, $\mathbf{I-300}$ and $\mathbf{I-450}$ are given in figure 3.6. TEM image of $\mathbf{I-100}$ appeared as well separated nanospheres with diameter 300-400 nm, whereas $\mathbf{I-300}$ is seen as a cluster of highly aggregated nanospheres of 300 nm. In $\mathbf{I-450}$ the presence mixtures of thin nanofibers with nanospheres were clearly visible. The charged conducting nanomaterials have very strong affinity to each other and cluster together during the sample preparation (for TEM analysis) via solvent evaporation method. This leads to the TEM images of the materials ($\mathbf{I-300}$ and $\mathbf{I-450}$) looks like meso-structures$^{14}$. It is clear from the morphological analysis by SEM and TEM that the polyaniline nanomaterials prepared by interfacial method are predominantly nanospheres. In general, polyaniline nanofibers are commonly reported
for interfacial route (for HCl and CSA), but here the formation of nanospheres was observed. This suggests that the mechanism of formation of nanomaterials in interfacial route for the amphiphilic azobenzene dopant is different compared to other dopants known. Additionally, the formations of different morphologies in the emulsion dilute, and interfacial routes (fibres, rods and spheres) also indicate that same dopant molecule follows different mechanistic pathways in these three routes.

The morphological analysis of nanomaterials clearly indicates that (i) the decrease in the dopant amount in emulsion route (decrease in the aniline / dopant ratio), the nanomaterials are transformed from nanofibers to nanotubes, (ii) the decrease in the concentration of both aniline and dopant (for fixed [aniline]/[dopant] ratio = 100), results in the transformation of thin-fibres to nanorods and (iii) the interfacial route produced exclusively nanospheres rather than nanofibers. It strongly suggests that the amphiphilic dopant follows an entirely different pathway in the interfacial route to produce nanospheres compared to that of emulsion and dilution routes. It is very important to note that in all the cases the starting materials are same (aniline, dopant, APS and water) and different nanomaterials are produced depending upon their composition, concentration, combination of the constituents and types of the polymerization processes were employed.

Figure 3.7. FTIR spectra of polyaniline nanomaterials.
The FTIR spectra of polyaniline nanomaterials (fibres, tubes, spheres and rods) are given in figure 3.7 and found that almost similar to conventional polyaniline. The two peaks at 1583 and 1481 are corresponding to the quinoid and benzenoid ring C=C stretching ring deformations, respectively\textsuperscript{15,16}. The peak at 1315 and 832 are corresponding to C-N stretching and C-H out-of-plane vibrations of 1, 4-disubstituted benzene ring, respectively. The appearance of new peaks in the dopant doped samples at 1304 and ~ 632 cm\textsuperscript{-1} are attributed to symmetric and un-symmetric stretching vibrations of O=S=O and S-O groups. The peak at 1021 cm\textsuperscript{-1} is corresponding to NH\textsuperscript{+}….SO\textsuperscript{3}\textsuperscript{-} interactions between the polymers chain and the dopant \textsuperscript{17}. This analysis confirmed the doping in polyaniline nanomaterials.

Figure 3.8. TGA plots of dopant 1, polyaniline nano-fibres, spheres and rods.

The thermal properties of the polyaniline nanomaterials were measured by means of thermo gravimetric analysis (TGA). TGA curves for dopant 1 and polyaniline nanomaterials are given in figure 3.8. It is clear from the TGA of dopant that it very stable up to 250 °C and started decomposing above this temperature. The TGA curves for polyaniline nanomaterials have a typical three step weight loss behavior: the loss of water or solvent around 100 °C, dedoping and decomposition of dopant at 250 °C and decomposition of the polymer chain above 300 °C. Thermal
analysis showed that all the polyaniline nanomaterials are stable up to 300°C and so suitable for higher temperature applications.

3.3.4. Mechanism of Nanomaterials Formation:

It is very clear from morphological analysis of nanomaterials that the formations of different morphologies in the interfacial, dilution and emulsion routes (spheres, rods, tubes and fibres). At the same time it is important note that in all routes the reactants used were same (aniline, dopant 1, water and ammonium per sulphate), which indicates that the same dopant molecule follows different mechanistic pathways in different routes\textsuperscript{18,19}. In order to get more light on the templating behaviour of the amphiphilic azobenzene dopant DLS measurements were carried out for (i) aniline +dopant and (ii) APS+ dopant to trace factors which influence on the morphology of the nanomaterials in the emulsion, dilution and interfacial routes and shown in figure 3.9. Upon adding aniline into the dopant micelles in water, a thick emulsion was formed and it showed a bimodal distributions with majority of the aggregates in the range of 3- 5 µm (see figure 3.9). It confirms that the aniline can form a stable aggregated emulsion with amphiphilic dopant. As the emulsion is diluted by adding water the milky appearance vanishes and the resultant aniline-dopant complex showed a pale turbidity (see vials in figure 3.9). DLS data showed a shift in the distribution of the aggregates size and shape from micro-meter to less than 600 nm (see figure 3.9 for D-100b). At higher dilution, the aniline+dopant complex (D-100e) almost become transparent and showed narrow uniform distribution with aggregates of 175 nm (see figure 3.9). It suggests that the dilution of pre-aggregated micro-emulsion leads to small nano-aggregates (D-100e) without any phase separation. During the interfacial polymerization, it was noticed that the addition of ammonium persulfate solution into dopant in water resulted in the formation of red turbidity. The DLS profile of the turbid APS+ dopant complex indicates that the amphiphilic dopant has also tendency to form a large 3- 5 µm micrometer size aggregates with the APS. However, the nature of the distribution plot was different from that of the aniline+dopant complex. It confirms that upon adding APS to dopant in water larger aggregates of 3-5 µM in size were produced which are stable and dispersed in the aqueous phase.
Figure 3.9. DLS histograms of dopant and various polymerization templates in water.

The dopant+aniline and dopant+APS complexes were stable for more than 24 h in water, which gives us opportunity to characterize them by TEM\textsuperscript{20,21}. High resolution TEM images of the templates were recorded and shown in figure 3.10. The TEM images of dilute templates (D-100e) shows that it contains both spherical
aggregates of 200 nm size plus small number of rod type aggregates (up to micrometer size). It suggests that upon dilution, the long cylindrical aggregates (see chapter 2) are truncated into smaller spherical or rod like aggregates. These spheres + rods has template for polyaniline nanorods formation in the dilute route. Interestingly, the TEM image of dopant +APS complex (interfacial template) showed completely different trend and the templates appeared as exclusively spheres of 0.5 micrometers to 200 nm. It clearly proves that dopant +APS complex has unusual spherical templating behaviour in the interfacial route, which produces exclusively nanospheres.

Figure 3.10. Template morphology by high resolution TEM.
Based on the SEM and TEM morphology of the synthesized samples and template characterization by TEM and DLS, the formation of various types of nanomaterials from amphiphilic dopant is proposed in figure 3.11. The studies from chapter 2 showed that the dopant molecules exist in the form of 4.3 nm micelles or layer-like assemblies depending upon its concentration in water. The addition of aniline produces long micrometer range cylindrical aggregates for [aniline]/[dopant] < 600, which template for polyaniline nanofibers. At lower dopant concentration ([aniline]/[dopant] > 600), the aniline molecule trapped in the layer assemblies of dopant, which template for the polyaniline nanotubes. The dilution of emulsion template (for fixed [aniline]/[dopant] = 100) produces micron range spheres plus rods, which aggregated together to template for polyaniline nanorods. It suggests that the effect of composition ([aniline]/[dopant] ratio) in the dopant + aniline varies the morphology from fibres to tubes whereas the concentration gradient transforms from fibres to nanorods. In the interfacial route, the dopant forms spherical aggregates with APS. During the course of polymerization aniline monomers will diffuse from organic layer and adsorbed over the spherical template surface. The subsequent oxidation of these aggregates will lead to formation of nanospheres. The SEM pictures of interfacial samples indicate that the morphology of the materials in this route was more sensitive to the [aniline]/[dopant] ratio in feed. The samples 1-100 and 1-300 were predominantly spheres, however, the decreasing the amount of dopant changes the morphology from spheres to fibres in 1-450. In 1-100 and 1-300 relatively higher dopant amount in aqueous layer results in homogeneous aggregates, this produces more uniform nanospheres. Further dilution of dopant in the APS+ dopant mixture in the aqueous layer; disturb the aggregates formation and results in the formation of fiber plus spheres in 1-450. Here, conducting polyaniline nanomaterials with variety of nanostructures are produced from same reaction constituents through selective polymerization in water at ambient conditions. The renewable amphiphilic dopant is very unique and it can form stable and aggregated micelles of cylindrical and layered shape for wider range of concentrations and compositions in reaction medium to tune polyaniline nanomaterials in a single system.
3.3.5. Optical and Solid-state Properties of Nanospheres and Nanorods:

The polyaniline nanomaterials were freely suspendable in water and other organic solvents by simple mixing under ultrasonic stirring at room temperature. UV-vis spectra of the nanospheres and nanorod samples are recorded in water are shown in figure 3.12. It is clear from the figure that the absorption spectra of polyaniline nanomaterials are free from quinoid ring (at 650 nm), which confirm the efficient doping of dopant. Generally, the absorption spectra of polyaniline show three characteristic absorption at 360, 450 and 800 nm, which are assigned as the transitions from $\pi-\pi^*$ band, polaron band to $\pi^*$ band, $\pi$ band to polaron band, respectively$^{22,23}$. Whereas in nanospheres the peak at 360nm is absent and the near-IR region absorption was completely different (above 850nm).
MacDiarmid and co-workers studied the secondary doping of simple polyaniline-CSA doped materials (not nanomaterials) by m-cresol solvent\textsuperscript{23,24}. They found that the more coil-like conformation in polyaniline chains produce peak characteristics at 800 nm whereas expanded chain conformation showed a free carrier tail commencing at 950-1000 nm in near IR-region\textsuperscript{22,25}. The absorption spectra of the nanospheres showed the disappearance of peak at 360 nm and free carrier tail-characteristics in the near-IR region above 850 nm which confirms the delocalization of polaron band with respect to more expanded chain conformation in the polyaniline nanospheres (prepared via interfacial route). It is important to note that the presence of spheres plus fibres in I-450 (see figure 3.12a) partially disturb the expanded conformation of the polymer chains, which is further reflected on the absorbance spectra. The samples I-100 and I-300 (see figure 3.12a) predominantly have only nanospheres and their absorbance spectra confirmed that they are in expanded
polymer chain confirmation. In the same time the polyaniline nanorods (or fibers) produced via dilution route (or emulsion) showed a characteristic peak at 800 nm corresponding to more coil-like chain conformation (see figure 3.12b). The conformational changes in the polyaniline nanomaterials actually arise from their difference in the mode of chemical reactions in the polymerization processes. The interfacial polymerization is mainly driven by the selective solubility of the polymer chains specifically in one of the solvent medium at the interface for driving the equilibrium to form of higher molecular weight chains. In interfacial polymerization route, the resultant hydrophilic (also charged) polyaniline emeraldine salt has more affinity towards water rather than the organic phase. The higher water affinity of the charged chains drives the polymerization equilibrium towards the aqueous phase for the formation of higher molecular weight chains. Since the polymer chains have more tendencies to adopt expanded conformation in good solvents, the diffused charged chains in their expanded confirmation in water behave as a nucleating site for subsequent growth of polymer chains. On the other hand, in the dilute route (or emulsion route) such a solvent-driven uni-directional growth is not possible, and therefore, the nanorods were obtained in entangled coil-like conformation compared to that of the interfacial route. The four probe conductivity of nanospheres were obtained in the range of \(~10^{-2}\) S/cm, which is one ordered higher than that of nanofibers and nanorods \(~10^{-3}\) S/cm) (see table 3.1 and 3.2). The conductivity of the polyaniline nanomaterials matched with that of the reported values. It suggest that the expanded confirmation of polyaniline chains in spheres increase the delocalization of charge carriers (evident by UV-Vis spectra, see figure 3.12a) and produced conductivity one order higher than that of nanofibers. Since the degree of doping (S/N ratio see table 3.1 and 3.2) in both fibres and spheres are comparable, so it is concluded that the more expanded confirmation chains increase the electrical conductivity of the polyaniline nanomaterials.
Figure 3.13. *UV-Vis spectra of polyaniline nano-spheres and rods in various solvents.*

In general, polyaniline nanomaterials are not soluble due to the highly aromatic nature of the polymer back bone. This is one of the major disadvantages of this versatile material that hampers its uses. In the present case, the amphiphilic surfactant molecule makes these conducting nanostructures easily dispersible in almost all organic solvents and results a transparent suspension which behaves like a solution. The presence of hydrophobic tail in the amphiphilic dopant increases the solubility of both polyaniline nanospheres and nanorods in common organic solvents. The materials can be easily suspended in chloroform, n-butanol, chlorobenzene, xylene and m-cresol, etc. To study the effect of solvents on the expanded chain to coil-like conformation, the UV-vis spectra of the **I-300** (spheres) and **D-100d** (rods)
were recorded in various solvents and shown in figure 3.13. In organic solvents also the nanomaterials showed all the characteristic absorptions of polyaniline. It is clear from the spectra that optical density of the polaron transition is affected by the organic solvents, however, the conformations of the polymer nanomaterials are retained and less influenced by the solvent in which they were suspended. The absorption of polaron peaks at the lower wavelength region (~400 nm) was blue shifted for samples recorded in organic solvents (except m-cresol) compared to that of water. The optical density of the absorption band corresponding to the polaron of polyaniline rods and spheres (above 950 nm) were more susceptible in organic solvents, however the chain conformations were not affected. It confirms that the conformations of the polymer chains in the nanomaterials are predominately controlled during the chemical polymerization techniques and not affected by the solvents in which they were dispersed. Since the conformation of polymer chains in polyaniline nanomaterials (both nanospheres and nanofibers) are almost unaltered by the various solvent, it can be assumed that once the polymer chains are confined to particular topology at nanometre level they are less influenced by the external stimuli such as solvent nature and its polarity.

Figure 3.14. WXRD polts of polyaniline nano-fibres, spheres and rods.
To further confirm the conformational changes in the polyaniline chains (nanofibers, nanorods and nanospheres) and also to study the solid state behaviour of the dopant molecule with polyaniline nanomaterials, the finely powdered samples were subjected for wide angle X-ray diffraction analysis at 30 °C. It is reasonable to expect that the expanded chain conformation of the polymer chains in nanospheres will show further increase in the solid state ordering (or crystalline) than nanofiber and nanorods, which possess a coil-like polymer chain conformation. WXRD patterns of I-100, E-100 and D-100d are given in figure 3.14. All the three samples are semi-crystalline with characteristic peaks. The WXRD patterns of nanofibers and nanorods (E-100 and D-100d) showed three distinct peaks at $2\theta = 6.4$, 20.1 and 25.5 (d-spacing =13.6, 4.4 and 3.5 Å, respectively). The two peaks at 20.1 and 25.5, which is mostly superimposed with amorphous background scattering, are generally observed in doped polyaniline, but the peak at $2\theta = 6.4$ is only observed for highly ordered samples in which the polyaniline chain distance increased by effective interdigitations of dopant molecules. In the case of nanospheres (I-100), a new intense peak at $2\theta = 6.05$ (d-spacing 14.3 Å) is observed in addition to a peak at $2\theta = 6.4$ (d-spacing 13.6 Å, as observed in fibres and rods). The presence of new peak at $2\theta = 6.05$ indicates that the polymer chains in nanospheres possesses more expanded chain conformation for increased solid state ordering compared to that of the nanofibers or nanorods. It was also noted that in nanospheres the amorphous region at higher angles ($2\theta = 15$ to 35°) very much suppressed and peaks become well resolved and sharp. This is due to the more expanded nature of the polymer chains in this sample which can pack in a more ordered fashion to increase the solid state ordering. The WXRD analysis of polyaniline nanomaterials demonstrated that nanospheres (interfacial route) have a high degree of ordering due to more expanded like polymer chain conformation compared to nanofibers and nanorods (emulsion or dilute route) possessing coil-like chain conformation. This suggests that the polymerization routes as well as corresponding soft-template have significant effect on the crystallinity of polyaniline nanomaterials.
Figure 3.15. WXRD plots of polyaniline nanomaterials synthesised by interfacial and dilution routes.

Among interfacial samples there are some noticeable differences in solid state packing between samples. Samples 1-100 and 1-300 the peak at $2\theta = 6.05$ (d-spacing 14.3 Å) is observed in addition to a peak at $2\theta = 6.4$ (d-spacing 13.6 Å). The lower angle peak at $2\theta = 6.05$ is more intense for uniformly distributed nanospheres 1-300 compared to broadly distributed sample 1-100 (see figure 3.15). 1-450 has mixture of nanospheres+ fibres, and therefore, the expanded conformation of polymer chains were disturbed, which account for the vanishing of the low angle peak at $2\theta = 6.05$. 
Lunzy et al. studied various kinds of polyaniline materials and shown that the ratio of the intensities of the peaks at $2\theta = 6.4^\circ$ and $26^\circ$ is directly related to crystallinity of polyaniline samples. The ratio of the intensities of the peaks at $2\theta = 6.4^\circ$ and $25.9^\circ$ of both emulsion and dilute route polyaniline nanomaterials and fiber thickness (from SEM images) are plotted against the concentration of dopant present in the reaction feed and are shown in figure 3.16. In the case of emulsion route sample the peak intensity ratio initially increases up on decreasing dopant concentration and reaches a maximum value for sample E-450 (see chapter-2) and then gradually decreases for low concentration of dopant. But in the case of dilution route, the peak intensity ratio increases as the volume of added water increases and finally attained the maxima at nanorods. Similarly the average fiber thickness of the emulsion route samples ranges 150-200 nm, whereas the thickness of the dilute route nanofibers is lower than 150 nm. This clearly indicates that upon dilution, the aggregated templates break in to smaller templates which lead to the formation of thinner fibers. From XRD studies it is clear that in the case of nanorods the polymer chains are more ordered compared with nanofibers. The reason for the enhanced ordering in the dilute route may be correlated to the effective penetration ability of the dopant in to the polymer.
matrix because of the availability of isolated polymer chains. Therefore, besides the amount of dopant in the reaction mixture, the type of the polymerization routes also play a major role in controlling the solid state properties of nanomaterials. The WXRD investigations of various polyaniline nanomaterials clearly demonstrate that the polymerization routes have significant effect on the crystallinity of polyaniline nanomaterials.

3.3.6. Luminescence Properties of the Polyaniline Nanomaterials:

The dopant possesses an integral photo-responsive azobenzene chromophore, which gives an opportunity to study the photo-physical behaviour of dopant and nanomaterials in solution by spectroscopic methods. Azobenzene molecule has lone pair of electrons on the nitrogen atoms, and therefore, the absorption spectra shows n-\(\pi^*\) \((S_0\rightarrow S_1)\) transition in additions to the \(\pi-\pi^*\) \((S_0\rightarrow S_2)\) transition. The absorbance spectrum of dopant 1 has three characteristic peaks at 245, 360 and 460 nm corresponding to \(\pi-\pi^*\) (cis), \(\pi-\pi^*\) (trans) and n-\(\pi^*\) (cis), respectively (see figure 3.17).

![Figure 3.17. UV-Vis spectra of dopant 1 in water.](image)

The photoisomerization of azobenzene molecules are highly dependent on the excitation wavelength: the n-\(\pi^*\) excitation induces the isomerization via inversion mechanism whereas the cis-trans isomerization proceeds via rotation mechanism for
the \( \pi^* \) excitation (see figure 3.18a)\(^{30,32} \). The \( n^* \) state \( (S_1) \) of trans-azobenzene is generally non-fluorescent because of the forbidden transition and isomerization in the \( S_1 \) manifold\(^{30} \). Researchers had found that the \( S_2 \rightarrow S_0 \) of trans azo-benzene chromophores showed enhanced fluorescence for self-organized supramolecular aggregates such as bi-layers or micelles in water (see figure 3.18b)\(^{32,33} \). Similar observations were also known for fluorescence enhancement from self-assembled amphiphilic trans-azobenzene chromophores in organic solutions under UV-radiations\(^{34-36} \). Basically in these self-assembled structures the photoisomerization is more or less prevented and so the excitation energy is used for emission instead of isomerisation\(^{37} \). Interestingly the renewable resource amphiphilic dopant is found to be luminescent for excitation at 360 nm.

(a) Photoisomerization

(b) Prevention of Photoisomerization

Figure 3.18. Emission from azobenzene chromophore-photoisomerization of azobenzene (a) restricted photoisomerization in bi-layer aggregates (b).
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The fluorescence spectra of the dopant at different concentrations in water exited at 360 nm is given in figure 3.19. It is very clearly evident from the plots that the fluorescent intensity of the dopant is highly dependent on its concentration in water. The emission spectra of dopant has a shoulder at 420 nm corresponding to the resonance Raman of water and, as expected, it vanished completely for the increased dopant concentration in water. The emission maximum of azobenzene chromophore is centered at 450 nm and it is not disturbed by the resonance Raman of water for further analysis. It is understood in the literature that in restricted azo-benzene chromophores, the photoisomerization (via rotation mechanism) for $S_2$ excitation is normally restricted due to steric hindrance. It suggests that the luminescent behavior of dopant-1 could arise by the prevention of the cis-trans photo-isomerization at the excited state by steric hindrance induced by the long alkyl chain in dopant 1, which facilitate the radiative decay from $S_2 \rightarrow S_0$. The formation of the supramolecular aggregates like layers and micelles in water by the amphiphilic dopant is also accountable for enhancement of emission (see chapter 2).

Figure 3.19. Fluorescent spectra of dopant 1 at various concentration in water.

In general, at low concentration, the amphiphilic azobenzene molecules (like dopant 1) are known to form weak aggregates like layers through head-to-tail packing of chromophores in water and increase in concentration leads to higher order supramolecular aggregates (evident from DLS study, chapter 2). The fluorescence
intensity of the dopant in water was plotted for various concentrations and shown in figure 3.20. The emission intensity of the dopant increases with the increase in the dopant concentration (1x10^6 to 1x10^5 M) and attained maxima at 1x10^-5 to 7x10^-5 M. Further increase in the dopant concentration (6x10^-5 to 6x10^-4 M) decreases the emission intensity and the fluorescence nature is completely lost above 1x10^-3 M. This non-linear trend suggests that the dopant 1 exist in more than one form in water depending up on its concentration. At low concentration, the dopant 1 may exist as isolated molecules and with increase in concentration they tend to aggregate to form a layer structure. At still higher concentration, the layer structure of the dopant is disturbed by the formation of micelles, which known to quench the luminescent intensity. At concentrations higher than 10^-3 M, both the higher concentration of dopant and also the existence of micelles are accountable for quenching the luminescent intensity. This is also further supported by the shift in the emission maxima of the dopant 1 (see figure 3.19, in set).

![Figure 3.20. Plot of fluorescent intensity versus of dopant 1 concentration in water.](image)

The emission maximum was not affected at very low concentration; however at very high concentration (expanded emission spectra were provided as in-set) there is a red shift of more than 100 nm. This large red shift reveals that luminescent azobenzene chromophore transformed from layer structures to aggregated micelles, which rapidly quenches the luminescent intensity. This transformation from layer-like to spherical micelle is also supported by DLS studies (see chapter 2).
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Figure 3.21. **Fluorescent spectra of dopant and polyaniline fibers in water.**

Polyaniline nanofibers doped by luminescent azobenzene dopant were expected to exhibit emission properties. The emission properties nanomaterials were studied in water and the spectra were recorded followed by exciting at 360 nm corresponding to the $\pi-\pi^*$ (trans) of the azobenzene part in the renewable resource dopant. The emission spectra for dopant 1, and few representative nanofibers E-1, E-15, E-70 and E-150 are shown in figure 3.21. The optical densities of all the solutions were maintained as 0.1. The resonance Raman peak for water at 420 nm is very intense because of the low concentration of the molecules in water (similarly observed in figures 3.21), however, the nanomaterials showed a broad peak at 450 nm corresponding to the luminescence of azo- groups. The HCl-doped polyaniline nanomaterials did not show any peak at 450 nm, which confirm that the luminescent behavior of E-1.5 to E-150 is mainly arising from the dopant 1 and not arise from the polyaniline backbone. The luminescence intensity of the nanomaterials drastically decreases with the decrease in dopant concentration in the feed. The quantum yield of the nanofibers were obtained using quinine sulfate as reference in water and shown in figure 3.21 (see in-set). The quantum yield of dopant is $2.6 \times 10^{-3}$, which is in the same range for azobenzene amphiphilic chromophores$^{40}$. 

![Figure 3.21. Fluorescent spectra of dopant and polyaniline fibers in water.](image-url)
Figure 3.22. Fluorescent spectra of the nanosphers in water.

The emission spectra for interfacially synthesised nanomaterials I-100, I-300 and I-450 were shown in figure 3.22. All the nanomaterials showed a broad peak at 450 nm corresponding to the luminescence of azo-group. The luminescence intensity of the nanospheres (azo-groups) is relatively higher than that of polyaniline nanofibers produced by emulsion route. The quantum yield of the nanospheres in water is shown in figure 3.22 (see in-set). This relatively higher quantum yield for nanospheres than nanofibers is correlated to the more expanded chain conformation, which will help the effective packing of azo chromophore in nanospheres. The nanorods obtained by dilute route are found to be very weakly luminescent since the dilute reaction conditions will make the dopant well dispersed in polymer matrix and prevent chromophore-chromophore interactions in resulting sample. In the present case, a single molecular dopant approach was utilized to tune the morphology and other properties of polyaniline nanomaterials via selective self-organization in the interfacial, dilution and emulsion routes. Therefore, it may be assumed that the pre-templating behaviour of the dopant complex and also the types of the polymerization determine the luminescent property of polyaniline nanomaterials.
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3.4. Conclusion

The self-organization properties of the renewable resource based amphiphilic azobenzene sulfonic acid dopant have been utilized to template various polyaniline nanomaterials like nanofibers, nanotubes, nanospheres and nanorods. The amphiphilic molecule is efficient structure directing dopant for polyaniline nanomaterials and has template selectivity depending upon the [dopant]/[aniline] ratio as well as concentration of dopant and aniline. DLS and TEM techniques have been successfully utilized to trace the nature and shape of polymerization templates to understand the mechanism the nanomaterials formation. The present investigation brought the following outcomes: (i) the dopant micelles have shape selective self-organization with aniline and APS, (ii) at concentration higher than CMC of the dopant, well defined micrometer sized cylindrical micelles filled with aniline acts as templates for the growth of long nanofibers, (iii) as the concentration of the dopant below CMC, the layers filled with aniline are acting as templates for the growth of nanotubes, (iv) in the dilute polymerization, the size of the aggregates become 175 nm and consists of spherical plus short cylindrical micelle aggregates, which upon chemical oxidation yields nanorods, (v) in interfacial route, the dopant micelles form spherical aggregates with APS in the aqueous layer and the diffusion of aniline (through interfacial layer) into these spherical aggregates and get oxidized to form polyaniline spheres of 200-400 nm, (vi) the structure of the cylindrical and spherical micelle templates were characterized by DLS and TEM, (vii) absorption spectra of the nanomaterials revealed that the nanospheres possesses expanded confirmation and the fibres, rods and tubes were found to have coil-like confirmation and (viii) wide angle X-ray diffraction showed that the nanomaterials exhibit good solid state ordering because of the high penetrating power of amphiphilic dopant in to polymer matrix (ix) the polyaniline nanomaterials exclusively doped with fluorescing azobenzene sulfonic acid dopant showed enhanced emission in water and the amount of the dopant in the nanomaterial and chain conformation plays a crucial role in luminescent intensity and quantum yields. In summary, it is shown that divergent polyaniline nanomaterials such as fibres, rods, tubes and spheres can be synthesized from identical reactant ingredients by carefully choosing the amphiphilic dopant templates under emulsion, dilution and interfacial polymerizations.
3.5. References:

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