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# Studies on Morphology and Conductivity of Poly(*N*-methyl aniline) Nanoparticles Prepared in Nonstirred Reaction Medium

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**Summary:** Polyaniline has elicited the most interest due to its wide range of applications in many fields. However insolubility and infusibility are the main factors that affect the application of polyaniline. We have studied and worked on the synthesis of dispersible polyaniline and the results are described here. Poly(*N*-methyl aniline) PNMANI nanoparticles with controllable morphology and sizes were prepared by removing a routine operation stirring from the conventional method of synthesis and using acrylic acid as a soft template. It is found that polymer formed in the non-stirring experiment predominantly produces highly dispersible, smooth nanoparticles with controllable morphology and sizes. These nanoparticles have large surface area and thereby high conductivity. Mechanism for generation of well dispersed and smooth nanoparticles is supported by homogeneous nucleation of polymer nanoparticles in non stirred experiments and the use of acrylic acid as a soft template. In the case of the experiment where the reaction mixture was stirred at 1000 RPM comparatively coral-like, granular and uncontrolled polymer particles were formed. These coral like granular particles were having comparatively small surface area and less conductivity. Conductivity measurements, UV- visible, XRD, FTIR spectroscopy and SEM were performed to characterize the product. This method can be used to synthesize highly conductive polymers in minimum time and bulk quantity.

**Keywords:** chemical synthesis; conductivity; morphology; nanoparticles; poly(*N*-methyl aniline)

## Introduction

Conducting polymers have been a popular topic of investigation, Intrinsically conducting polymers including polyacetylene, polyaniline (PANI), polypyrrole, polythiophene, poly (p-phenylene-vinylene) etc. are termed organic polymers that possess electrical, electronic, magnetic and optical properties quasi similar to what expected for a metal while retaining the mechanical properties, processability etc commonly associated with a conventional polymer. [1–7] Out of these polyaniline (PANI) is one of the most investigated conducting polymer due to its relatively easy synthesis, environmental stability, tunable conductivity, unique doping/dedoping chemistry [5,6] and low cost. Its conducting mechanism was discovered in the 1980s and this electro active polymer has been extensively investigated for many applications including lightweight batteries, electrodes, electromagnetic shielding devices, anticorrosion coating and sensors.[7–10] The major potential application of PANI is for electrorheological (ER) application by dispersing the synthesized PANI derivative particles into

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non-conducting oil.[11] It is considered that the simplest method for synthesis bulk polyaniline is the chemical polymerization of aniline with an oxidant with an acidic aqueous solution at low temperature with one reactant slowly added into the other under vigorous stirring.[10–15] But the resulting PANI product was highly aggregated and therefore not useful for much application.[15–17] Aggregation of particles in the synthesis of PANI makes it difficult to explore the properties and applications of nanostructured material. In many synthetic processes, especially template free chemical reactions, aggregation occurs immediately as particles are generated. It should be noted that this highly aggregated PANI has intractability i.e. infusibility and insolubility factors that hamper the application of PANI. Therefore dispersing of the polymer is one of the most effective approaches to solve this problem. Nanostructured and well dispersed PANI offers the possibility of enhanced performance wherever high interfacial area between PANI and its environment is important. For example in sensor applications nanostructured and dispersed PANI has greater sensitivity and faster time-response relative to its conventional counterpart because of higher effective surface area and shorter penetration depth for target molecules.[18] Due to lack of easy and reliable methods for making high quality conducting nanostructures many potential applications in sensors and other devices are limited. Despite the different present synthetic methods to make PANI nanostructures, there is a need of practical synthetic method to achieve well dispersed PANI nanoparticles of small diameters in bulk quantity. Here we report a facile chemical route to prepare high quality well dispersed PANI nanoparticles by just removing routine stirring from synthetic procedure and using acrylic acid as soft template in reaction.[19] The classical chemical synthesis involves N-methyl aniline as the monomer, ammonium per sulfate as oxidant, DL-tartaric acid as dopant and acrylic acid as soft template. The conducting behavior of PNMANI was attained by doping with DL-Tartaric Acid. Doping gives remarkable enhancement in electric conductivity by enhancing electron mobility.[13] Experiments were carried out with and without stirring reaction mass and observations were recorded.

## Mechanism

In the absence of stirring nuclei of PNMANI forms homogeneously in the parent phase after super saturation level.[20] Homogeneous nucleation [21] gives nanofibres with smooth surfaces and uniform size. Due to stirring nuclei, grow heterogeneously on other species like reactor surface or other particles in solution.[22] Heterogeneous nucleation gives granular particles. Regarding the formation mechanism of well dispersed nanoparticles by using acrylic acid as soft template it is proposed that acrylic acid be assembled with or without aniline salts into nano or micro structured intermediates.[23,24] The hydrophobic property of aniline and the hydrophilic property of the soft template played an important role in forming nano-structured PNMANI.[25,26]

## Experimental Part

All chemicals were analytical grade. N-methyl aniline was doubly distilled. And other chemicals were used as received from S.D. Fine Company. Deionized water was used for all experiments. Typically 4.6 mmol of N-methyl aniline, 13.8 mmol of DL-tartaric acid and 9.2 mmol of acrylic acid were taken in appropriate amounts of water. The mixture was cooled to 0 °C. In a separate vial, 0.46 mm of ammonium per sulfate was taken in 10 ml of water. Precooled solution of APS was added slowly 1ml/min by addition funnel [13] to above reaction mixture at 0 °C. Reaction mixture was kept without stirring for 2 hours at 0 °C. The green precipitate obtained was filtered and washed with water, the product isolated and dried at

50 °C in vacuum oven to get the desired PNMANI nanoparticles. The experiment was repeated by stirring the reaction mixture at 1000 RPM keeping all the reagents concentrations and reaction conditions exactly identical. Resulting products were used for further studies.

## Characterization

The UV-VIS. spectra of the polymer solution in m-Cresol and NMP were recorded within one hour by using Perkin-Elmer λ-20 double beam spectrophotometer in the range of 300–1000 nm.The IR spectra of the polymer were taken within 24 hours on a Perkins Elmer 1600A FT-IR spectrophotometer between the ranges of 400–4000 cm$^{-1}$. For recording IR spectra, KBr pellets of the polymer were prepared in the ratio of 150:1 mg. X-Ray diffractogram of the samples were taken on a Bruker AD-CuKα radiation source (α = 1.542 nm) X-Ray diffractogram. Surface morphologies of the polymer were observed by SUPRA 35 Scanning Electron Microscope (SEM). Synthesized polymer was made in pellet from (diameter 12 mm, thickness 3).[27] The two probe method was used for conducting measurements.[13]

## Results and Discussion

### UV-VIS Spectra

The electronic absorption spectra of the PNMANI prepared, were recorded by using the aqueous reaction mass and dissolving the polymer in benzyl alcohol[28] and is depicted in Figure 1. Polymer solubility was also checked in m-cresol and acetone.UV- Vis spectrum of PNMANI of aqueous reaction mass (1a and 1b) shows that the peak at 409 nm can be assigned to localized polarons [29] which are characteristic of the protonated poly (N-methyl aniline).

A sharp peak is observed at 780 nm for 1b in which PNMANI is prepared without stirring. Reaction mass is absent in 1a in which PNMANI is synthesized by conventional stirring method. UV-Visible spectrum of PNMANI in benzyl alcohol shows absorbance peak at 1000–1200 for the polymer prepared without stirring reaction mass (1d) and the same peak is absent in polymer prepared by stirring

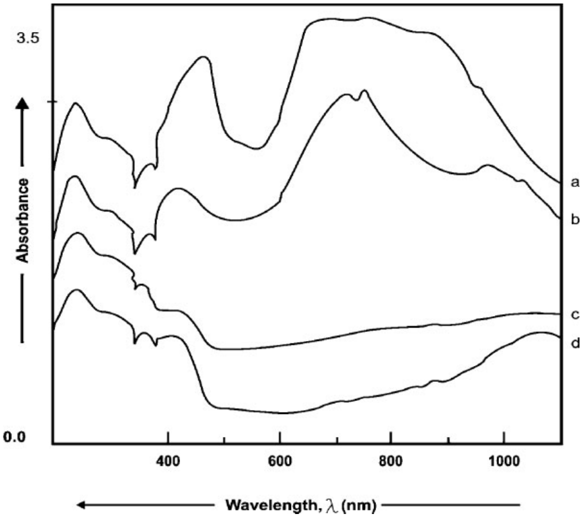

***Figure 1.***

a- PNMANI prepared by stirring reaction mass at 1000 RPM – Spectra of Aq. reaction mass. b- PNMANI prepared without stirring reaction mass- Spectra of Aq. Reaction mass. c- PNMANI prepared by stirring reaction mass at 1000 RPM –UV in Benzyl alcohol. d- PNMANI prepared without stirring reaction mass- UV in benzyl alcohol.

reaction mass (1c). The optical properties of conducting polymers are important to the development and understanding of the basic structures of the material. The conjugation in the polymers implies by their electronic spectra, thus spectroscopy is powerful probe for characterization of the electronic transitions that occurs in the conducting polymers.

## IR Spectra

The FTIR spectrum of poly(N-methyl aniline) (Figure 2 and Table 1) is in good agreement with previously reported results. For instance the large descending base line in the spectral region 400–2000 $cm^{-1}$ has been attributed to free electron conductance in PNMANI prepared without stirring reaction mass (2b) but it is absent in polymer prepared by of stirring (2a).

The IR data confirms the formation of polyaniline.[30] This is consistant with the previous data.[30] The position of the 820–870 $cm^{-1}$ peak is characteristic of paradisubstituted aromatic rings that indicate the polymer formation. The bands ~1220 and 620–680 $cm^{-1}$ are assigned to the in plane and out of plane bending motions of the aromatic ring. A band appearing near about 1260 $cm^{-1}$ represents the C–N stretching vibration. A major contribution of the quinoid ring units is represented by the band ~1470 $cm^{-1}$.[31] Band ~ 1480 $cm^{-1}$ and 1560 $cm^{-1}$ correspond to aromatic benzenoid and quinoid stretching frequencies. Broadband~ 2500–3300 $cm^{-1}$ indicates the frequency of NH stretching. Peaks at 1200 $cm^{-1}$ and 1322 $cm^{-1}$ correspond to $COO^-$ and aromatic C–N stretching frequencies. The broad and intense band at 3400–3000 $cm^{-1}$ accounts for the higher degree of doping and protonation of aniline and imine nitrogen's.

## XRD

Crystallinity and orientation of conductive polymer are of much interest because the more highly ordered systems could display a metallic like conductive state.[32]

X ray Diffraction measurement exhibited that the pattern of PNMANI prepared without stirring reaction mass is typical. Figure 3b [PNMANI prepared without stirring reaction mass] shows that intense peaks at $2\theta = 19$ and $2\theta = 25^o$ $2\theta$ clearly indicates that PNMANI prepared without stirring reaction mass is having better crystalline structure [33] as compare to PNMANI prepared by stirring reaction mass at 1000 RPM. The presence of various peaks between 19 to 25° $2\theta$ values in both the samples reveal the partial crystalline

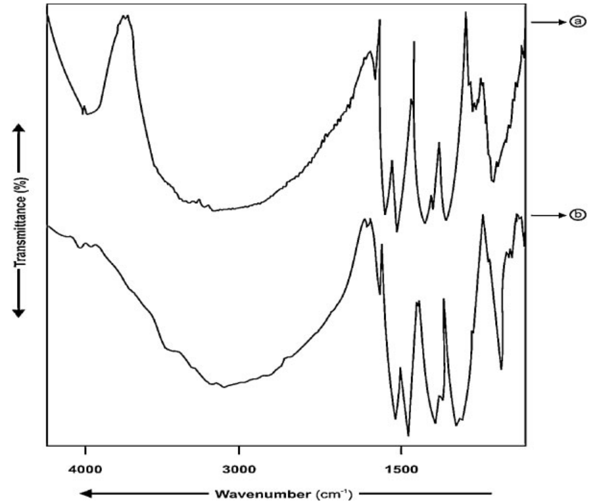

*Figure 2.*

a- PNMANI prepared by stirring reaction mass at 1000 RPM. b- PNMANI prepared without stirring reaction mass.

***Table 1.***
FTIR spectral data of PNMANI with and without stirring medium.

| Sr. No. | PNMANI-With stirring medium (Figure a) | PNMANI-Without stirring medium (Figure b) | Band Characteristics |
|---|---|---|---|
| 1 | 1745 | 1750 | Broad carbonyl ($-C{=}O$) stretching band. |
| 2 | 1576 | 1576 | Quinoid ring and ($-COO^-$) stretching band. |
| 3 | 1487 | 1504 | Benzenoid ring stretching band |
| 4 | 1305 | 1315 | Aromatic ($C-N$) stretching band |
| 5 | 1249 | 1257 | ($-COO^-$) stretching band |
| 6 | 1141 | 1167, 1122 | $B-N-B$ stretching vibration |
| 7 | 1041 | 1020–1040 | Vibration band of dopant anion |
| 8 | 823 | 821 | *Para*-disubstituted benzene ring |
| 9 | 790 | 800 | Terminal phenyl group |
| 10 | 707–620 | 725–617 | Out of plane $C-H$ bending vibration. |
| 11 | 707–620 | 725–617 | Out of plane $C-H$ bending vibration. |

nature of the polymer. The XRD pattern showing $2\theta = 19$ and $2\theta = 25$ which are ascribed to the periodicity parallel and perpendicular to the polymer chain.[34–36]

## Morphology

The effect of stirring on morphology of polymer has been studied.[4] Figure 4a gives the morphological evolution by scanning electron microscopy (SEM) images of PNMANI particles synthesized via conventional method in which reaction mass was stirred at 1000 rpm. A close look at the powder with SEM indicate that PNMANI consist of coral like granular particulates.[4] It is clear to see that the surface is smooth and few PNMANI pillars are formed. If intense stirring is kept up during the entire polymerization process the nanoparticles obtained are highly aggregated large in size and the number of granular particles increases as a function of the stirring speed.[15]

Mechanical stirring induces heterogeneous nucleation and forced particles to collide on each other and triggers aggregation of particles.[11] These coral like granular particles have comparatively large size, small surface area and less conductivity. It is well supported by SEM images Figure 4a clearly showing granular and coral polymer particles which are

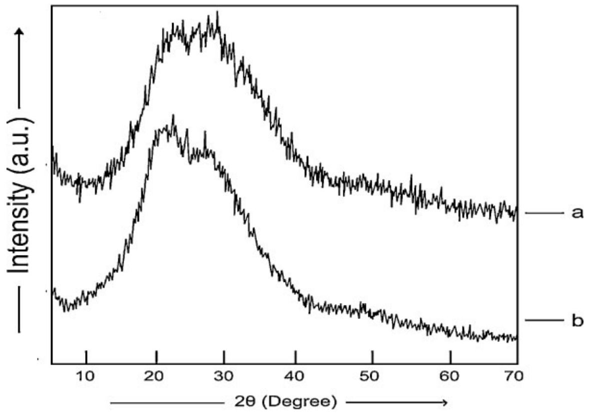

***Figure 3.***
a- PNMANI prepared by stirring reaction mass at 1000 RPM. b- PNMANI prepared without stirring reaction medium.

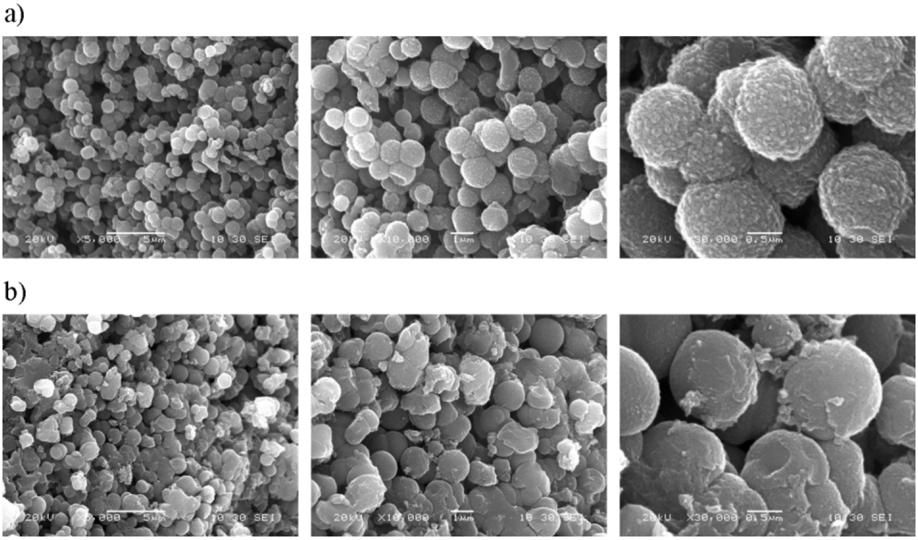

***Figure 4.***
4a-SEM images of PNMANI particles prepared with stirring reaction medium at 1000 RPM. 4b-SEM images of PNMANI particles prepared without stirring reaction medium.

bigger in sizes. It is found that the polymer formed in the non stirring experiment predominantly produces highly dispersible, smooth nanoparticles with controllable morphology [8,9] and sizes.[10] These nanoparticles have large surface area and thereby high conductivity of polymer. Mechanism for generation of well dispersed and smooth nanoparticles is supported by homogeneous nucleation of polymer nanoparticles in non stirred experiment and role of acrylic acid as a soft template. We find that when no stirring is applied to the polymerization process the resulting product clearly shows smooth and comparatively smaller nanoparticles .The morphology of the polymer synthesized without stirring the reaction mixture shows better texture and homogeneosity with smooth surface (Figure 4b). This polymer has good conductivity.

## Conductivity

The results are well supported by the conductivity data obtained for the both PNMANI depicted in Table 2. Chemically synthesized polymer was made in pellet form (diameter 12 mm, thickness 3mm) and used for measurement of conductivity.[27] PNMANI polymer synthesized without stirring reaction medium shows better conductivity [38] ($3.4 \times 10^{-2}$ S/cm) than that of stirring medium ($2.7 \times 10^{-3}$ S/cm). The results are well supported by SEM and XRD data which reveal that the highly ordered PNMANI chains produce in non stirred reaction medium.

PNMANI prepared without stirring reaction medium having good diffusion property, greater exposure area, and better penetration depth for gas molecules than that prepared using stirred reaction

***Table 2.***
Conductivity values of PNMANI prepared with stirring and without stirring.

| Polymer | Conductivity (S/cm) |
|---|---|
| PNMANI prepared by stirring reaction mass at 1000 RPM | $2.7 \times 10^{-3}$ S/cm |
| PNMANI prepared without stirring reaction mass | $3.4 \times 10^{-2}$ S/cm |

conditions which has poor diffusion. This direct correlation for the PNMANI with solid state ordering has clearly seen in the case of the non-stirred reaction medium. Thus, the high solid state ordering of polymer PNMANI contributing to their higher conductivity compared to PNMANI prepared by stirring reaction medium is evident. It suggests that morphology as well as the solid state ordering of PNMANI plays a major role in increasing the conductivity rather than the extent of doping.[5] This can also be attributed to the presence of a large concentration of $COO^-$ ions serving as a functional dopant[5] along with acrylic acid doped sites in the polymer matrix of polymer prepared without stirring the reaction medium with greater surface area capable of enhancing conductivity.[39–41]

## Conclusion

Although different synthesizing methods have been established for preparation of polyaniline it is still a major challenge to prepare well dispersed, polyaniline nanoparticles with controllable morphologies on a bulk scale.[8,9] Intractability i.e. insolubility and infusibility are the factors that affect the applications of PANI. We have overcome these problems by removing routine operation stirring from conventional synthesis of PNMANI and using acrylic acid as soft template which increases the solubility of polymer in organic solvent such as benzyl alcohol, m-cresol etc.[6] In the absence of stirring PNMANI nanoparticles formed by homogeneous nucleation produces smooth and well dispersed nanoparticles. Acrylic acid assembled with aniline salts into nano or micro structured intermediates gives polymers with controlled morphology.[8,9] This newly prepared nanostructured and well dispersed PNMANI offers the enhanced performance because of large surface area and thereby high conductivity.[40,41] For example in sensor applications nanostructured and dispersed PNMANI has greater sensitivity and faster time response relative to its conventional counterpart because of higher effective surface area and shorter penetration depth for target molecules.[13] We believe that this new method can be used to synthesize highly conductive polymers in minimum time and bulk quantity. Solubility problem of conducting polymers in common organic solvents can be solved by using this technique.

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