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Influence of polymerization conditions on the template free synthesis of nanoparticles of poly (1-naphthylamine)

Ufana Riaz, Sharif Ahmad and S.M. Ashraf (✉)

Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi, 110025, India
E-mail: smashraf_jmi@yahoo.co.in

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Summary

The present article highlights some preliminary investigations on the role of oxidant and medium on the nanostructured morphology of poly (1-naphthylamine) (PNA) prepared via chemical oxidative polymerization. Results revealed that the nano morphology can be controlled under appropriate preparative conditions. The particle sizes were obtained in the range of 5-50 nm exhibiting a much smaller range than polyaniline (PANI) nanoparticles synthesized under similar conditions.

Introduction

Aromatic amine polymers have exhibited wide technological applications, such as in rechargeable batteries [1], electrocatalysts [2], smart electrochromic devices [3] sensors and actuators [4-5] due to their novel multifunctionality, redox reversibility [6] variable conductivity [6-7] strong electro-activity [2] and high environmental stability [8-9]. Increasing research interest has been focused on the electrically conductive nature of the aromatic polymer family such as polyaniline (PANI) [10], polyaminopyridine and its copolymers [11-12], polyaminoquinoline [13], polymethylquinoline [14], polypyrrole(PPY) and its copolymers [15-16]. PANI has been successfully prepared by several techniques including chemically oxidative polymerization [17] electrochemically oxidative polymerization [18] plasma polymerization [19] and photo induced electron-transfer photo oxidative polymerization [20]. Although these techniques reflect considerable environmental and economic advantages, simpler methods are still being explored to achieve agglomerate free, controlled particle size nanostructures having a one-dimensional morphology. Some problems such as low molecular weight, low solubility in common organic solvents and poor mechanical property restrict these materials to wide practical applications [3, 8]. Hence conducting polymer nanomaterials in the form of nanoparticles, nanowires, nanofilms, and nanocomposites have gained momentum owing to the advantages of improved processibility and commercial viability [21]. One of the latest advances in conducting polymers is the creation of aromatic diamine polymers by oxidative polymerization [22-23]. It is believed that investigations on the

aromatic diamine polymers are more attractive since they exhibit more novel multifunctionality than PAN and PPY [24].
This article highlights the synthesis of a seldom investigated aromatic amine polymer-poly (1-naphthylamine) (PNA), via chemical oxidative polymerization in an alcoholic medium. Despite scarce literature being available on the chemical synthesis of the same, none of the studies have reported the nanoscale synthesis of PNA [25-26]. In the present study, the effect of polymerization conditions (medium and oxidant) on the nanostructured morphology of this polymer have been explored. The findings are expected to provide valuable information on the synthesis of one-dimensional nanostructures of conducting polymers which may exhibit superior processibility as compared to the conventional conducting polymers.

Experimental

Chemicals: 1-Napthylamine (Loba Chemie, India) was purified, prior to its use. The monomer was sublimed at 120°C and recrystallized using ethyl alcohol. Methyl alcohol, ethyl alcohol, cupric chloride and ferric chloride (Qualigen, India) were of analytical grade and were used without any further purification.

Synthesis of poly (1-naphthylamine)

1-naphthylamine monomer (0.1M) was dissolved in a mixture of methyl alcohol (10 ml) and 1N HCl (10ml) at room temperature. The solution was purged in nitrogen for an hour. Oxidant (Ferric chloride, Cupric chloride) (0.1M) dissolved along with methyl alcohol (5 ml) was then added to the solution of 1-naphthylamine with slow stirring at 0°C. A violet - colored dispersion appeared as the polymerization further progressed. The purple black - colored glassy dense solid obtained turned into a suspension after holding it for a period of 12 hrs at room temperature. The resulting material was separated by centrifugation, washed several times with distilled water. It was further dried under vacuum oven at a temp of 50°C over a period of 72 hours. A similar procedure was adopted for the synthesis of PNA in ethanol medium. PNA synthesized in presence of different oxidants was designated as PNA-Fe and PNA-Cu according to the oxidant used.

Characterization

FT-IR spectra of the powdered polymers were taken in the form of KBr pellets on spectrometer model Perkin Elmer 1750 FT-IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT, USA). UV-visible spectra were taken on Perkin Elmer lambda EZ-221 of the solutions of polymers prepared in NMP,HCl (pH=3) and NaOH (pH=8.5). Transmission electron micrographs were taken on Morgagni 268-D TEM, FEI, USA. The samples were prepared by depositing a drop of well-diluted polymer and copolymer suspension onto a carbon (1 0 0)-coated copper grid and dried in an oven at 55°C for two hours. Conductivity measurements were performed by standard four-probe method using Keithley DMM 2001 and EG&G Princeton Applied Research potentiostat model 362 as current source. Pressed pellets of polymers were obtained by subjecting the powder to a pressure of 50 kN. The error in resistance measurements under these conditions was less than 2%.

Results and Discussion

FT-IR spectra

The FT-IR spectra of PNA-Fe synthesized in methanol medium, Figure.1(a), showed the following characteristic absorption peaks: 3430 cm^{-1}(broad) for: NH stretching vibration, 1640 cm^{-1} and 1608 cm^{-1}: for imine stretching vibration; 1592 cm^{-1} and 1512 cm^{-1}: for quinonoid ring skeletal vibration; 1460 cm^{-1} and 1398 cm^{-1}: for benzenoid ring [27], the later being larger than the former; 1266 cm^{-1}: for CN vibration; 1134 cm^{-1} (broad): for B-NH=Q and B-NH-B vibrations, broadness indicates hydrogen bonding with methanol [28]; 779 cm^{-1}: for N-C(5) linkage [28]; 771 cm^{-1} and 862 cm^{-1}: for N-C(4) linkage [28]. Presence of such peaks further confirmed the polymerization of 1-naphthylamine. In case of PNA-Cu synthesized in methanol, Fig.1(d), the following characteristic peaks were observed: 3100 cm^{-1}: for NH stretching peak (broad); 1569 cm^{-1} and 1532 cm^{-1}: for quinonoid skeletal vibrations; 1401 cm^{-1}: for benzenoid vibrations; and 1261 cm^{-1}: for CN vibrations 1096 cm^{-1}: for B-NH=Q and B-NH-B vibrations; 791 cm^{-1} and 765 cm^{-1}; for N-C(4) linkage [28].

The characteristic peaks of imine stretching mode and CN vibration appear to be absent. The benzenoid and quinonoid vibrations also appear to be of lower intensity revealing the formation of oligomeric PNA in this case. The FT-IR spectra of PNA-Fe synthesized in ethanol Fig.1(b) showed the following characteristic peaks 3370 cm^{-1}: for NH stretching peak; 1640 cm^{-1} and 1608 cm^{-1}: for imine stretching mode; 1592 cm^{-1} and 1512 cm^{-1}: for quinonoid skeletal vibrations; 1458 cm^{-1} and1397 cm^{-1}: for benzenoid vibrations; 1315cm^{-1}: for CN vibrations; 1139 cm^{-1}: for B-NH=Q and B-NH-B vibrations; 797 cm^{-1} and 662 cm^{-1}; for N-C(4) linkage [28]; 797 cm^{-1} and

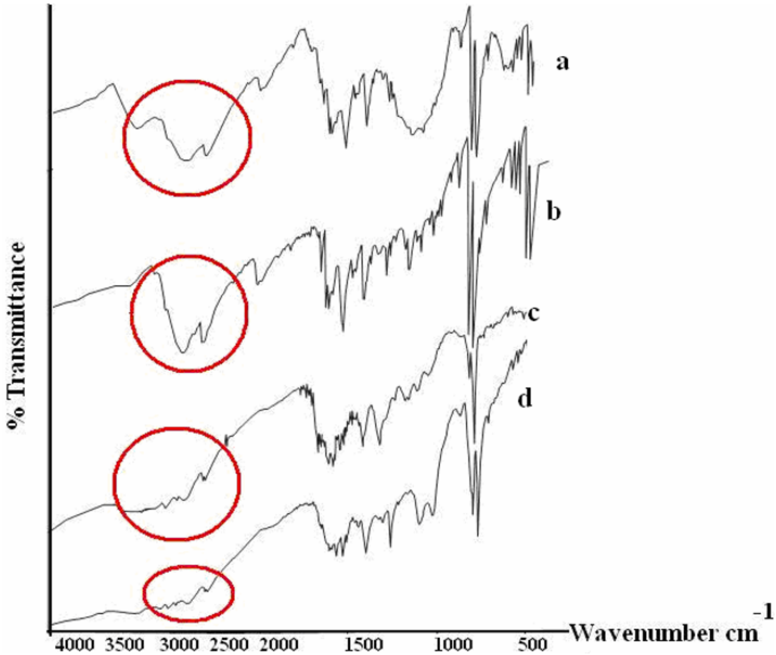


Figure.1 FT-IR spectra of (a) PNA-Fe in methanol (b) PNA-Fe in ethanol, (c) PNA-Cu in ethanol, (d) PNA-Cu in methanol

960 cm^{-1}: for N-C(5) linkage [28]. Similar peaks were observed for PNA-Cu synthesized in ethanol, Fig.1(c) but of lower intensity. Comparing the spectra of PNA synthesized in methanol and ethanol, Figure.1 (a)(b) and (c) and (d) respectively, the NH stretching peak centered at 3430 cm^{-1} in case of the former is broad, likewise the peak at 1134 cm^{-1} for B-NH-Q and B-NH-B is also broad showing that intense strong hydrogen bonding occurs during polymerization occurs in this case which has profound effect on the conformation of the PNA chains synthesized in methanol. It can be concluded that polymerization is retarded in methanol medium in case of PNA-Fe as well as PNA-Cu owing to the intense hydrogen bonding of the polymer with methanol. The benzenoid and quinonoid vibrations also appear to be of lower intensity. This further confirms the slower rate of polymerization of PNA in methanol medium. In ethanol medium pronounced peaks are observed for PNA-Fe while diminished peaks are observed for PNA-Cu. This can be correlated to the difference in the reduction potentials (RP) of the of the two oxidants, $FeCl_3$ with 0.77 V and $CuCl_2$ with 0.34V.

The UV- visible spectra of PNA-Fe synthesized in ethanol medium, Figure.2 (a), shows pronounced peaks at 300 nm in the UV range and at 500 nm and 664 nm in the visible range. Peaks in the UV range can be assigned to Π-Π* transitions in the 1-naphthylamine units whereas the two peaks in the visible range are assigned to the excitonic and polaronic transitions respectively. Similar transitions of electrochemically synthesized PNA were observed by Schmidt et al [27] at 500 nm. In case of PNA synthesized in ethanol, the polaronic transition peak observed around 664 nm appears to be intense and broad. However, in case of PNA-Fe synthesized in methanol, Figure.2, only peaks at 580 nm and 300 nm are visible. The peak at 664 nm observed when PNA was synthesized in ethanol appears to be shifted to 580 nm. This shows lower conjugation in PNA-Fe synthesized in methanol. The spectra of PNA-Cu synthesized in methanol as well as ethanol exhibits absorption bands at 300 nm and 500 nm. The indicates a lower conjugation in PNA-Cu polymers synthesized in both the alcohols and a "compact coil" type conformation which can be attributed to the differences in the conformation as well as disposition of the PNA chains prepared in presence of different oxidants.

The conductivity of PNA-Fe synthesized in ethanol medium was found to be in the conducting range of 3.1X 10^{-3} S/cm while PNA synthesized in methanol exhibits a semi conducting value of 4.7X 10^{-5} S/cm. The conductivity of PNA-Cu synthesized in ethanol medium was found to be 5.1X 10^{-4} S/cm while in methanol it exhibits a value of

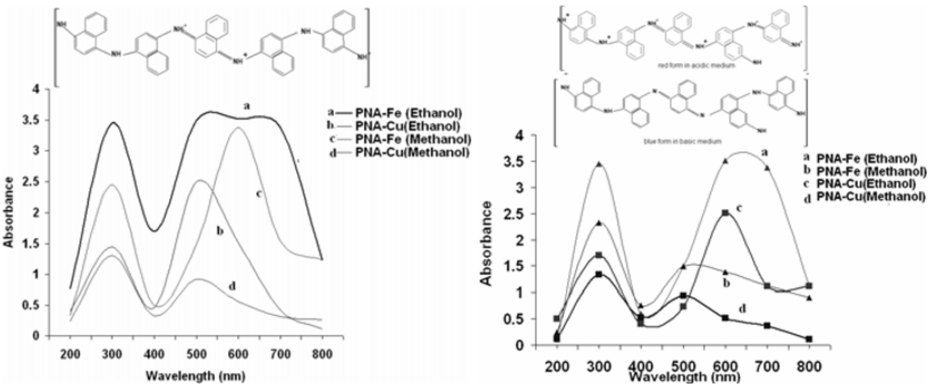
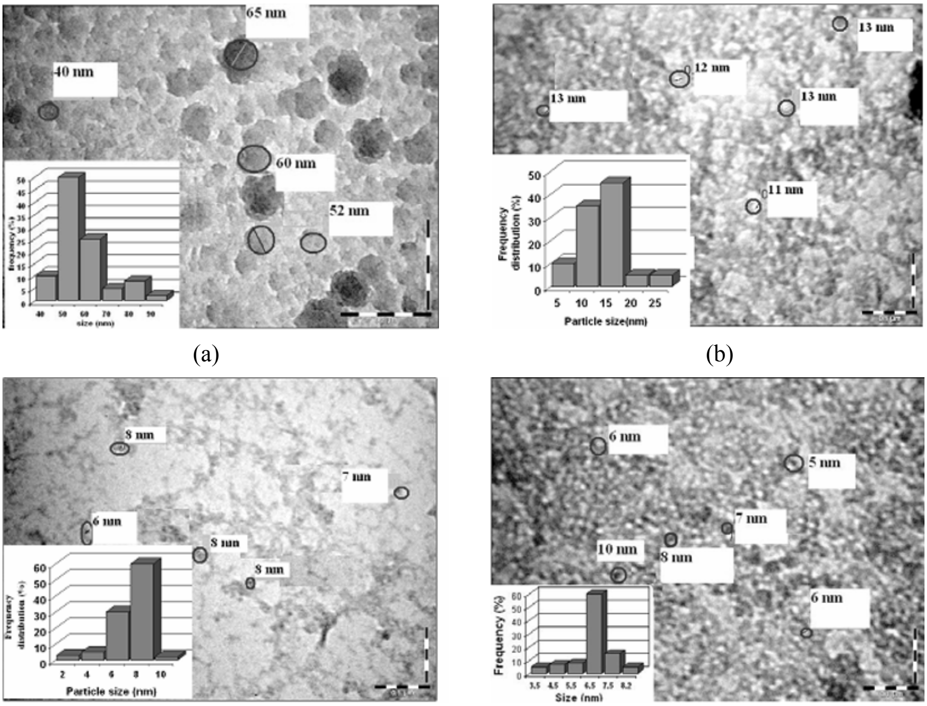


Figure.2 UV–visible spectra of PNA synthesized in (a) different alcohol a (b) in different pH

8.1 X 10^{-7} S/nm. The above results clearly explain the effect of oxidant as well as alcoholic media on the conjugation length, polaronic transitions and consequently on the conductivity of PNA. Furthermore, the decrease in the energy of the electronic degrees of freedom is primarily due to the creation of a low-energy localized state at the crossing point of the two chains. Due to lower hydrogen bonding, less energy of the localized state occurs at the point of crossover when PNA is synthesized in ethanol. Hence, a higher value of polaronic transition at 664 nm is obtained. Results pertaining to the case of methanol showed that intense hydrogen bonding leads to the formation of aggregates that shifts the polaronic electronic transitions by 50 nm resulting in lower conductivity. The UV-visible spectra of PNA-Fe and PNA-Cu in presence of acidic medium, Figure.2 (b), reveals absorption peaks at 300 nm and 650 nm in the former and at 300 nm and 600 nm in the later. In presence of basic medium, the polaronic transition peaks disappear and only excitonic peaks show up at 525 nm and 500 nm for PNA-Fe and PNA-Cu respectively; ∏ to ∏* transition peaks are observed in both cases. These observations can be correlated to the structural changes in PNA on variation of pH of the medium. The intensity of the peaks appears to be lower in case of PNA-Cu in both alcohols as observed in case of FT-IR spectra of the same.

TEM Analysis

The TEM image of PNA-Fe synthesized in methanol, Figure.3 (a), shows a dense distribution of aggregates of varying sizes within the range of 40-60 nm. Fairly large



(a) (b)

(c) (d)

Figure.3 TEM micrographs of (a) PNA-Fe synthesized in methanol (b) PNA-Fe synthesized in ethanol, (c) PNA-Cu synthesized in methanol, (d) PNA-Cu synthesized in ethanol particles appear to be distributed randomly. The TEM image of PNA-Fe nanostructures synthesized in ethanol, Figure.3(b), reveals interconnected self assembled particles of globular and elongated shapes with a diameter ranging from 5-10 nm. The resulting particles appear to be interconnected and more or less of the same size. The accompanying histograms give the size distribution of the nano particles in the two cases. Likewise the TEM image of PNA-Cu synthesized in methanol, Figure.3(c), reveals fairly small particles in the range of 6-10 nm while the micrograph of PNA-Cu synthesized in ethanol, Figure.3 (d), exhibits particle size in the range of the 10-15 nm. Aggregation of particles occurs in these cases. The contrast between the morphologies of PNA is strongly influenced by the medium and oxidant. Interestingly, the particle sizes obtained in these cases appear to be much smaller than the one reported by Kan et al [29] for polyaniline.

Conclusion

Finally, it can be concluded that the choice of the solvent as well as oxidant plays a significant role in deciding the nanostructured morphology of PNA. The aggregation of nanoparticles can be prevented by selecting alcohols which serve as an active medium for the polymerization of conducting polymers. It is also observed that cupric chloride which has lower redox potential and yields polymer with poor characteristics. The above findings thus provide a valuable guidance in the synthesis of many other nanostructures. Further investigation on the influence of other parameters on the nanostructure of PNA such as temperature of polymerization, reaction time, and choice of the dopants is currently under investigation in our laboratory and will be published soon.

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