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SHORT COMMUNICATION

Template free synthesis of nanoparticles of poly (1-naphthylamine): influence of alcoholic medium on polymerization

Ufana Riaz · Sharif Ahmad · S. M. Ashraf

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Abstract The present article highlights some preliminary investigations based on a convenient and inexpensive chemical method for preparing novel poly (1-naphthylamine) (PNA) nanostructures in the presence of different alcohols. The effect of alcoholic medium on the polymerization and morphology of PNA was investigated. Results revealed that nanomorphology can be controlled under appropriate preparative conditions. The particle sizes thus obtained were of 5–50 nm exhibiting a much smaller range than polyaniline nanoparticles synthesized under similar conditions.

Keywords Nanomaterials · Polymers · Template-free · Poly(1-naphthylamine) · Morphology · Alcohol

Introduction

Lately, conducting polymers have been widely investigated for applications in advanced nanotechnologies [1–4]. However, their insolubility in most solvents has delayed their extensive application. Polyaniline (PANI) in the nanofibre form is technologically useful due to its environmental stability and ease of synthesis [5–10]. A vital obstacle in processing polyaniline nanofibres is aggregation [11]. Strategies for preventing aggregation require coating nanoparticle with foreign capping agents or adding surfactants [12–13]. 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. Using a PANI derivative namely poly(1-naphthylamine) (PNA), this article mainly highlights the synthesis of an electrically conductive polymer having a nanoscale morphology 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 [14–16]. In the present study, a smaller particle size of 4–10 nm was obtained in an alcoholic medium and this finding may provide valuable guidance in the synthesis of one-dimensional nanostructures of conducting polymers which are expected to show superior processability as compared to PANI.

U. Riaz · S. Ahmad · S. M. Ashraf (✉)
Materials Research Laboratory, Department of Chemistry,
Jamia Millia Islamia,
New Delhi 110025, India
e-mail: smashraf_jmi@yahoo.co.in

Experimental

Chemicals

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

Synthesis of poly (1-naphthylamine)

1-naphthylamine monomer (0.1 M) was dissolved in a mixture of methyl alcohol (10 ml) and 1 N HCl (10 ml) at room temperature. The solution was purged in nitrogen for an hour. Ferric chloride (0.1 M) dissolved along with methyl alcohol (5 ml) was then added to a solution of 1-naphthylamine with slow stirring at 0 °C. A violet-colored dispersion appeared as the polymerization further

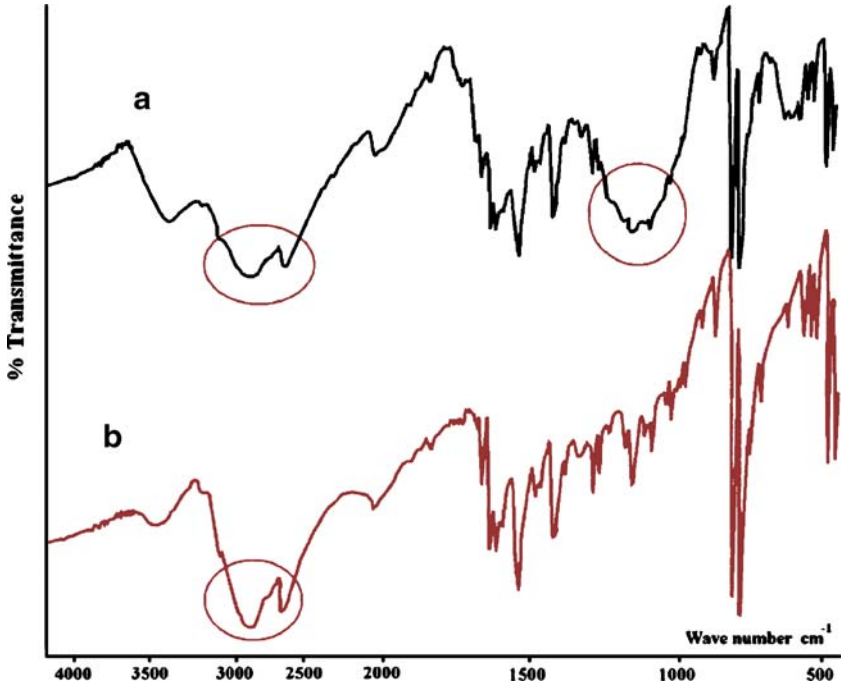

Fig. 1 FTIR spectra of PNA synthesized in **a** methanol and **b** ethanol

progressed. The purple black-colored glassy dense solid obtained turned into a suspension after holding it for a period of 12 h at room temperature. It was further purified through soxhlet extraction using methyl alcohol for a period of 16 h so that the oligomeric fractions and other impurities were eliminated. The end resulting powder was then dried under vacuum at a temp of 50 °C for a period of 72 h. A similar procedure was adopted for the synthesis of PNA in ethanol medium.

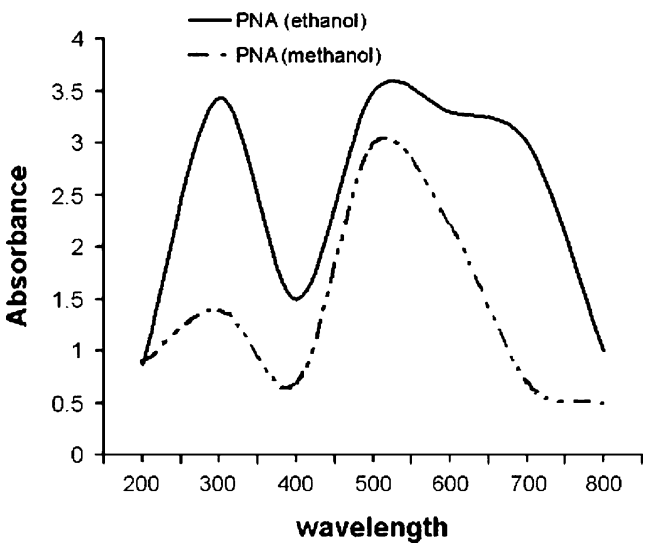

Fig. 2 UV–visible spectra of PNA synthesized in alcohol

Characterization

Fourier transform infrared (FTIR) spectra of the polymers were taken on a spectrometer model IMPACT 410, NICOLET U.S.A. A UV-visible spectra was taken on Perkin Elmer lambda EZ-221.Transmission electron micrographs were taken on Morgagni 268-D TEM, FEI, USA. Conductivity measurements were taken on Keithley Multimeter model DMM 2001 using the four probe method at 30 °C.

Results and discussion

FTIR spectra

The FTIR spectra of PNA synthesized in methanol medium (Fig. 1a) shows the characteristic absorption peaks at 3,430 cm^{-1} (broad) for NH stretching vibration. The imine stretching vibration peaks appear at 1,640 and 1,608 cm^{-1} while the quinonoid ring skeletal vibration and benzenoid ring vibration peaks appear at 1,592 and 1,512 cm^{-1}; 1,460 and 1,398 cm^{-1}, respectively, the later being larger than the former [18]. The characteristic peak of CN vibration is noticed at 1,266 cm^{-1} while the broad peak at 1,134 cm^{-1} corresponds to B–NH=Q and B–NH–B vibrations. The broadness indicates hydrogen bonding with methanol [17]. The peaks observed at 779 cm^{-1} can be correlated to N–C (5) linkage [18] while the peaks at 771 and 862 cm^{-1} correspond to N–C(4) linkage[18]. The dopant peaks appear

at 567, 540 and 519 cm^{-1}. The presence of these peaks confirmed the polymerization of 1-naphthylamine [18].

The FTIR spectra of PNA synthesized in ethanol (Fig. 1b) reveals the following characteristic peaks 3,370 cm^{-1} for NH stretching peak; 1,640 and 1,608 cm^{-1}, for imine stretching mode; 1,592 and 1,512 cm^{-1}: for quinonoid skeletal vibrations; 1,458 and 1,397 cm^{-1}: for benzenoid vibrations; 1,315 cm^{-1}: for CN vibrations; 1,139 cm^{-1}: for B–NH=Q and B–NH–B vibrations; 797 and 662 cm^{-1}; for N–C(4) linkage [18]; at 797 and 960 cm^{-1}: for N–C(5) linkage [18]; 564, 540 and 519 cm^{-1} for the dopant. Comparing the spectra of PNA synthesized in methanol and ethanol (Fig. 1a and b, respectively), the NH stretching peak centered at 3,430 cm^{-1} in case of the former is broad, likewise the peak at 1,134 cm^{-1} for B–NH–Q and B–NH–B is also broad showing that strong hydrogen bonding occurs in this case which has profound effect on the conformation of the PNA chains synthesized in methanol. It can be concluded that the rate of polymerization of PNA is lower in methanol medium owing to the intense hydrogen bonding of PNA with methanol. The benzenoid and quinonoid vibrations appear to be of lower intensity in this case. This further confirms

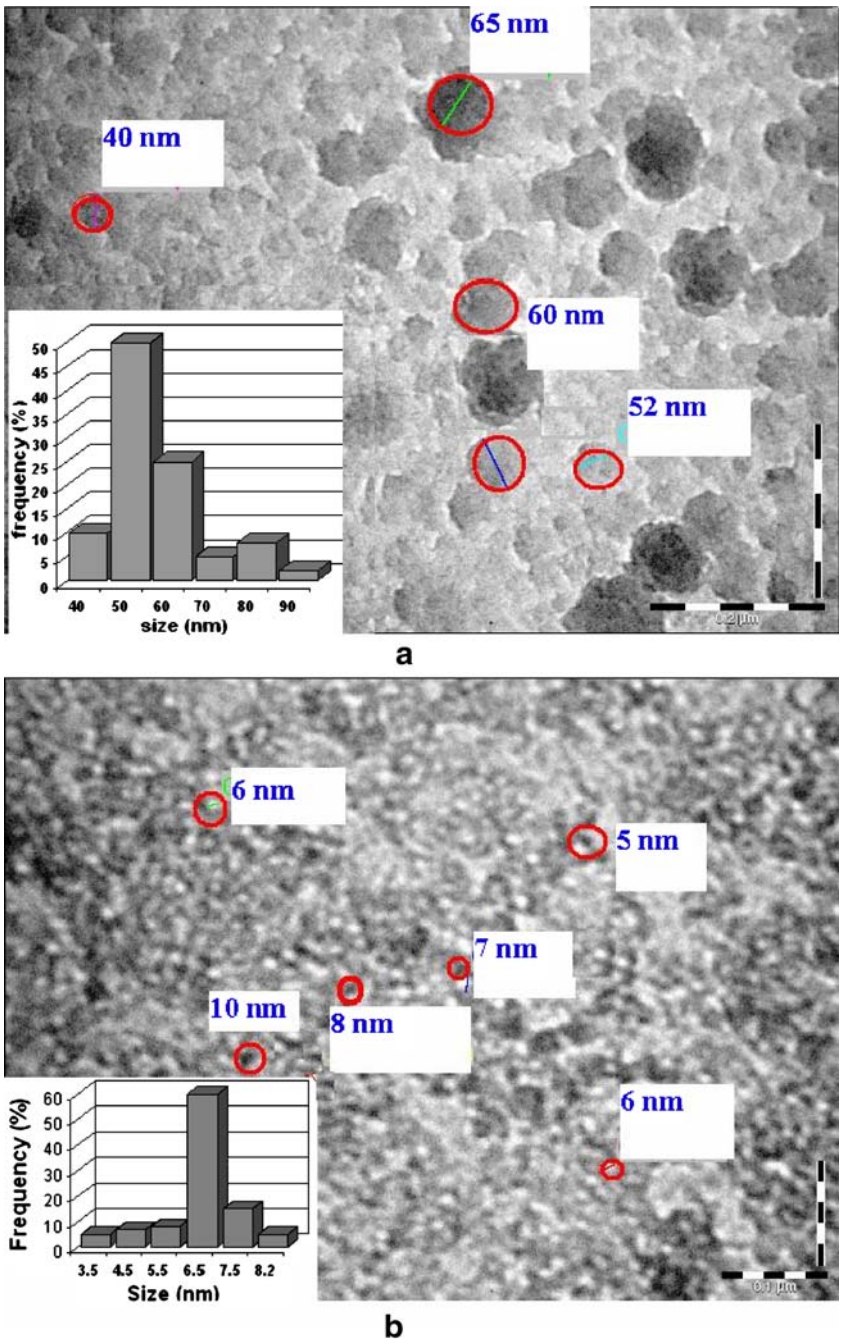

Fig. 3 TEM micrographs of PNA synthesized in **a** methanol and **b** ethanol

that the intense hydrogen bond formation of PNA with methanol retards the polymerization of PNA.

UV–visible spectra

The UV–visible spectra of PNA in *N*-methyl pyrolidone (Fig. 2) exhibits pronounced peaks at 300 nm in the UV range and at 500 and 664 nm in the visible range incase of PNA synthesized in ethanol. Peaks in the UV range can be assigned to ∏–∏* transitions in the 1-naphthylamine units whereas peaks in the visible range are assigned to the polaronic transitions. Similar transitions of electrochemically synthesized PNA were observed by Schmitz and Euler [19] 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 synthesized in methanol (Fig. 2), only peaks at 500 and 300 nm are visible. The peak at 644 nm observed when PNA was synthesized in ethanol appears to be missing. This indicates a lower conjugation in PNA synthesized using methanol. The same peak appeared to be shifted to a lower value of 500 nm in methanol having much lower intensity suggesting that the PNA has a 'compact coil' type conformation; this is attributed to the differences in the conformation as well as disposition of the PNA chains prepared in methanol and ethanol media. The conductivity of PNA synthesized in ethanol medium was found to be in the conducting range of 3.1×10^{-3} S/cm while PNA synthesized in methanol exhibits a semi-conducting value of 4.7×10^{-5} S/cm. The above results clearly explain the effect of alcoholic medium on the conjugation length and consequently on the polaronic transitions and 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, low-energy localized state at the point of crossover occurs when PNA is synthesized using ethanol. Hence, a higher value of polaronic transitions at 664 nm was obtained. Results pertaining to the case of methanol showed increased hydrogen bonding leading to the formation of aggregates. This causes a shift of the polaronic transitions by 50 nm resulting in poor conductivity.

TEM analysis

The TEM image of PNA synthesized in methanol (Fig. 3a) shows a dense distribution of aggregates of varying sizes within the range of 40–60 nm. Fairly large particles appear to be distributed randomly. The TEM image of PNA nanostructures synthesized in ethanol (Fig. 3b) 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 nanoparticles in the two cases. The contrast between the morphologies of PNA is strongly influenced by the medium of polymerization. It is interesting to note that the particle sizes obtained in both cases discussed above appear to be much smaller than the one reported by Zhou et al. [17].

Conclusion

It can be concluded that the choice of the solvent plays a significant role in deciding the morphology of the nanostructure of PNA. The aggregation of nanoparticles can be prevented by selecting alcohols which serve as an active medium for the polymerization of conducting polymers. The above-stated findings thus provide a valuable guidance in the synthesis of many other nanostructures. Further investigations on the influence of other parameters on the nanostructure of PNA such as temperature of polymerization, reaction time, and choice of the oxidants is currently under investigation in our laboratory and will be published soon.

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