

# Preparation and Characterization of Polynaphthyl Amine (PNA) as a Novel Conducting Polymer

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Received 2 June 1999; accepted 3 December 1999

**ABSTRACT:** A series of polynaphthyl amine (PNA) were prepared in acetone/water mixture (v/v) using different concentrations of potassium persulfate as an initiator in presence and in absence of polyvinyl alcohol (PVA) as a surface active agent. Polymers of various physical properties were prepared. The physical properties of PNA using different concentrations of potassium persulfate in presence and in absence of PVA were given. The specific conductance of the prepared polymers was found to be 0.055 ohm cm, 0.145 ohm<sup>-1</sup> cm<sup>-1</sup> and 0.083 ohm<sup>-1</sup> cm<sup>-1</sup>, at 3, 1.5, and 0.75% of potassium persulfate, respectively. X-ray diffraction analysis was carried out to the sample having the highest specific conductance. The confirmation of the prepared PNA was carried out using UV and IR spectrophotometry. Finally PNA showed good air stability and excellent solubility in organic solvents differing from that of polyaniline. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 988–992, 2000

**Key words:** Novel polymer; polynaphthyl amine; conducting polymer; conjugated polymer

## INTRODUCTION

Polyaniline is the oldest<sup>1</sup> and one of the most studied conjugated polymers<sup>2</sup> due to its unusual electrical and optical properties.<sup>3</sup> Polyaniline is still one of the most commonly used electroactive polymers; it is easily prepared and moreover the substituents in polyaniline derivatives give increase in the functionality. The applications of polyanilines in batteries,<sup>4,5</sup> microelectronic devices,<sup>6</sup> ion exchangers,<sup>7</sup> electronic displays,<sup>8</sup> and as analytical sensors<sup>9</sup> have been demonstrated by the workers in this field. In 1983 polyaniline was “rediscovered” as a conducting polymer by MacDiarmid and coworkers,<sup>10–12</sup> after nonoxidative proton doping process results in a highly environmentally stable material with specific conductance in the range of 1–10 ohm<sup>-1</sup> cm<sup>-1</sup>. Although its air stability is attractive, polyaniline suffers of

poor processibility in being only slightly soluble in polar solvents such as dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO).<sup>13</sup> The preparation of polyaniline<sup>14–19</sup> offers a route to improve polymer processibility. In this study polynaphthyl amine (PNA) is carried out to solve this problem because it has an excellent solubility in common organic solvents and its processibility is a quite easy process.

## EXPERIMENTAL

### Materials

The potassium persulfate, aniline, and  $\alpha$ -naphthyl amine were delivered from Aldrich company (USA). Polyvinyl alcohol of low molecular weight (water soluble) was delivered from Hoechst company.

### Method and Preparation

The samples of PNA were prepared in presence and in absence of PVA at 0°C in an ice bath while

**Table I Physical Properties of Polynaphthylamine**

	Weight of K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /100 g water	In Absence of PVA			In Presence of PVA
		3 g	1.5 g	0.75 g	3 g
I	Color	Light purple	Bright violet	Dark brown	Brilliant violet
II	State at room temperature	Solid	Solid	Viscous liquid	Solid
III	Crystallinity	Amorphous	Crystalline	—	Amorphous
IV	Solubility	Fractionally soluble in acetone	Highly soluble in acetone	Highly soluble in acetone	
V	Specific conductance	0.055 Ω <sup>-1</sup> cm	0.145 Ω <sup>-1</sup> cm	0.083 Ω <sup>-1</sup> cm	—

stirring for 3 h by adding different amounts of potassium persulfate as an initiator.

The samples were washed with distilled water and dried in an electric oven and used for measuring the conductivity, X-ray diffraction, UV analysis and IR spectrophotometry.

The conductivity was measured using Nuve conductometer model 2100, the measurements were carried out at room temperature, and the conductivity was calculated by the following relationship:

$$\rho = \text{resistivity} = \frac{RA}{L} \Omega$$

$$A = \text{area} = \pi r^2 \quad (r = 0.5 \text{ cm})$$

$$L = \text{thickness}$$

$$\sigma = \text{specific Conductivity} = \frac{1}{\rho} = \frac{L}{RA} \Omega^{-1} \text{ cm}^{-1}$$

#### X-ray Analysis

The PNA sample prepared using 1.5% potassium persulfate was measured using Philips PW 1373 diffractometer.

#### UV-Visible Spectrophotometry

The UV-visible absorption spectra of PNA was performed using Beckman model DB spectrophotometer.

#### Fourier Transform IR Analysis

IR analysis for PNA was carried out using Shimadzu Fourier transform infrared (FTIR) spectrophotometer at Cairo University.

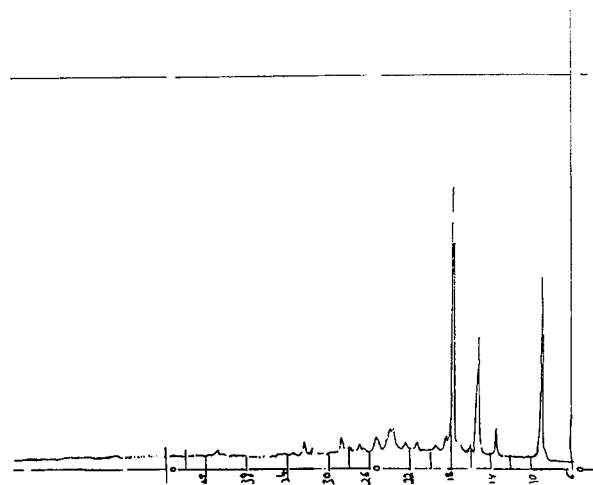
## RESULTS AND DISCUSSION

PNA was prepared by the use of potassium persulfate initiator as an oxidizing agent. Various

concentrations of potassium persulfate (0.75, 1.5, and 3% ) were used. The reaction was carried out in an ice bath with continuous stirring for 3 h.

Table I demonstrates the relationship between the method of preparation of PNA and the corresponding physical properties of the samples produced. The values of conductivity for PNA prepared at different concentrations of potassium persulfate are also given in Table I.

The sample prepared at 1.5% potassium persulfate seemed to be crystalline, although the other samples were not. X-ray analysis is shown in Figure 1 and Table II, which shows the d-values and the relative intensities of X-ray diffraction (XRD) pattern for PNA. From Figure 1 and Table II it is clear that the sample is crystalline. Also, by correlating the value of conductivity of PNA at 1.5% potassium persulfate to the crystallinity of that sample, which is clearly obvious from Figure 1 and Table II, it can be deduced that



**Figure 1** X-ray analysis for PNA prepared at 1.5% pot. Persulfate.

**Table II X-ray Diffraction Data for PNA**

$2\theta$	d Å	I/I <sub>0</sub>
9.2	11.16	66
13.6	7.56	9.6
15.2	6.76	43.5
18	5.72	100

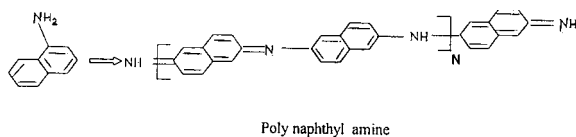
the crystallinity of that sample produces the greatest value of conductivity.

The physical properties of the produced PNA is related to the concentration of potassium persulfate; the color of the produced PNA was changed from dark brown when using 0.75% potassium persulfate up to light purple when 3% potassium persulfate was used. This could be attributed to the difference in the molecular weight and consequently to the amount of conjugation in each polymer produced. In addition, Table I shows change in the physical state of PNA from viscous liquid up to solid at 3% potassium persulfate. This is also due to the difference in the molecular weight of the produced polymers when using different concentrations of potassium persulfate.

### Characterization and Structure Confirmation of the Prepared PNA

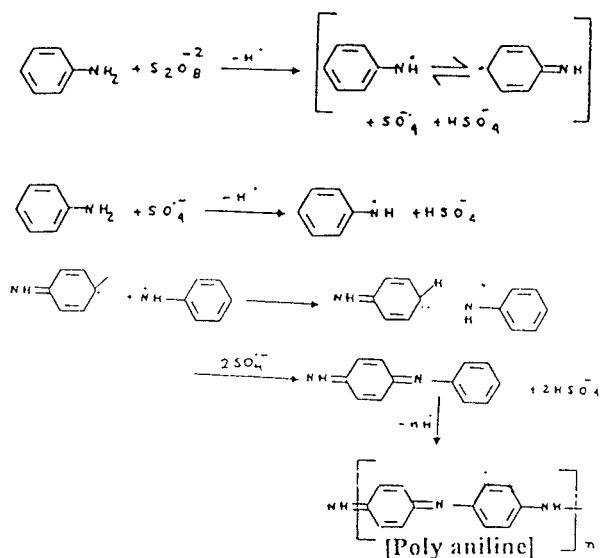
The UV visible data of the prepared polymer is illustrated in Table III. From the data given, it is clear that the ( $\lambda$  max) for the prepared polymers appears in the range of 229–395 nm in the UV region and in the range of 470–939 nm in the visible region.

### Proposed Mechanism for Polymerization of Naphthyl Amine

**Table III Data of UV Visible Spectra of PNA**

Polymer	Max (ABS)
Polynaphthyl amine	229(0.268), 254(0.206), 316(1.657), 395(0.843), 470(1.33), 869(-0.285), 916(-0.276), 939(-0.281)

### Mechanism of Polymerization of Anilin<sup>20</sup>



### IR Measurements

Analysis of the FTIR spectra of the synthesized PNA gives good information about the structure of this polymer. Table IV shows the vibration assignments of the prepared polymers. The most important features are:

1. A characteristic NH stretching of secondary amines at  $3381\text{cm}^{-1}$
2. A stretching vibration of C-N of secondary amines at the range of  $1269\text{--}1303\text{ cm}^{-1}$
3. Bending of N-H in secondary amines in the range of  $1550\text{--}1600\text{cm}^{-1}$

### Mechanism of Conductivity of Electroactive Polymers

An initial reading of the literature concerning electroactive polymers gives indication to different mechanisms responsible for conductivity for each material studied. One way to begin to understand the abundance of data reported on conduction in polymeric systems is to classify materials according to the carriers responsible for con-

**Table IV** Data of IR Spectra of the Prepared PNA

PNA	Vibration Assignment
619	Out of plane (C—H) deformation in benzene ring
707–794	(C—H) out of plane deformation in benzene ring
1498–1514	(C=C) stretching vibration in aromatic rings
1076–1122	(C—H) in plane deformation in aromatic rings
2609–3053	(C—H) stretching in benzene ring
1269–1303	(C—N) stretching in secondary amines
1550–1600	(N—H) bending vibration in secondary amines
3381	(N—H) stretching in secondary amines

duction. The first species are ionic carriers. These are distinct ionically charged chemical entities: hydrogen or hydronium ions, acids, bases, salts, metallic impurities due to residual catalyst, or species intended to be electronic dopants but end up as mobile ionic species. Ionic conduction occurs throughout the entire structural ranges, from polycrystalline to amorphous, and requires actual mass transport.

The second species is localized electronic excited states<sup>21</sup>; the electrons are localized in a single molecular residue and hence can't participate in conduction.

The third most energetic species is the intramolecular exciton.<sup>22</sup> An exciton is a neutral excitation consisting of an electron and the positive species it leaves behind. Transport of this particle (coupled positive and negative charges) in itself does not lead to conduction. The transport occurs with the concerted cooperative polarization of the lattice found in organic single crystals.

Both inter- and intramolecular excitons are possible in molecular lattices, requiring increasingly cooperative lattice polarization. This neutral particle contributes to bulk conduction when the species is separated or ionized by an applied electric field.

The fourth species are migratory localized ionic states,<sup>23</sup> particularly anion. Anions may be formed through electron transfer that is either photoinitiated, chemically derived as a donor/acceptor complex, or perhaps caused by an electrochemical/redox reaction. The transport occurs through random hopping mechanisms.

A fifth and relatively new carrier is the solution. The name is taken from a hypothetical particle associated with the solution of complex sets of differential equations.<sup>24</sup> In polymers that can be molded as one dimensional, the solution is a defect or kind in the phase of the alternating car-

bon-carbon double bonds along the chain backbone.<sup>25</sup>

The sixth and final carrier species is the electron or hole carrier associated with the band theory.

These mechanisms, their dependence on external variables, and the relation to the mechanism responsible for charge transport are summarized in terms of structural order as follows:

$$\delta = \sum_i \mu_i q_i n_i$$

Where  $\delta$  is the conductivity and equals the summation of the product of carrier mobility,  $\mu$ , its charge  $q$ , and the number of carriers,  $n$  and  $i$ , represents more than one type of charge.<sup>26</sup>

From the previous discussion it could be concluded that the fifth type of conduction in the previous scheme is the type that coincides with our case in this research (PNA) due to the presence of alternating carbon-carbon double bonds along the chain backbone of the PNA.

## CONCLUSION

In this work PNA has been prepared as a novel conducting polymer. PNA is readily soluble in acetone and common organic solvents, which facilitates the processibility of this conducting polymer in different applications. This property is not present in polyaniline, which has poor processibility. In addition, the structure of the prepared PNA has been confirmed, and it seems that the crystalline PNA produce greater conductivity than amorphous PNA. Physical properties of the produced PNA are quite dependent on the initiator concentration. Finally, the mechanism of po-

lymerization of PNA and its conductivity have already been discussed.

## REFERENCES

1. Lemerl, J.; Nejen, L.; Lefebure, J. *J Inorg Chem* 1980, 42, 17.
2. Hanack, S.; Scier, H. *Synth Met* 1991, 41, 601.
3. Nouji, A. J.; White, H. *J Electrochem Soc* 1982, 129, 2261.
4. Itaya, K.; Akahoshi, H.; Toshima, S. *J Electrochem Soc* 1982, 129, 765.
5. Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Patel, C. *Appl Phys Lett* 1980, 36, 422.
6. Paul, F. W.; Rizzo, A. J.; Wrighton, M. S. *J Phys Chem* 1985, 89, 1441.
7. Oyama, N.; Ohsaka, T.; Shimizu, T. *Anal Chem* 1985, 57, 1526.
8. Gottesfeld, S.; Rendendo, A.; Feldberg, S. W. *J Electrochem Soc* 1987, 134, 279.
9. Woltgen, H. *J Anal Chem* 1984, 56, 87.
10. MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yauiger, S. I. *Mol Cryst Liq Cryst* 1985, 121, 173.
11. Chiang, J. C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
12. Huang, W. S.; MacDiarmid, A. G.; Epstein, A. P. *J Chem Soc Chemical Commun* 1987, 93, 1123.
13. Li, S.; Cao, Y.; Xue, Z. *Synth Met* 1987, 20, 147.
14. Parmes, S.; Aldissi, M. *J Chem, Soc, Chem Commun* 1989, 88.
15. Armes, S. P.; Aldissi, M.; Agnew, S.; Gottesfeld, S. *Mol Cryst Liq Cryst* 1990, 63, 190.
16. Armes, S. P.; Aldissi, M. *Mater Res Soc Proc* 1990, 311, 173.
17. Armes, S. P.; Aldissi, M.; Howley, M.; Beery, J. G.; Gottesfeld, S. *Langmuir* 1991, 7, 1447.
18. Bay, R. F. C.; Armes, S. P.; Pickett, C. J.; Ryder, K. S. *Polymer* 1991, 32, 2456.
19. Tadros, P.; Armes, S. P.; Luk, S. Y. *J Mater Chem Commun* 1992, 2, 125.
20. Caro, N. *Angew Chem* 1986, 11, 845.
21. Vartanyan, A. T., *Zh FizKhim* 1984, 22769.
22. Nalwa, H. S.; Sinra, J. M.; Vasudevan, N. J. *Makromol Chem* 1981, 182, 811.
23. Abd El Ghani, N. T.; Issa, R. M.; Kchild, M. A. *Thermochem Acta* 1988, 125, 163.
24. Naarman, H. *Brite Report RIIB olog-DB* 1989.
25. ElShereafy, E.; ElGhafar, M. A. *Thermochem Acta* 1991, 178, 254.
26. Whorl, D. *Adv Polym Sci* 1983, 50, 105.