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Synthesis and characterization of conducting poly (1-aminonaphthalene), poly (2-aminonaphthalene) and poly (aniline-co-1-aminonaphthalene)

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Abstract. Poly (1&2)-aminonaphthalene and poly (aniline-co-1-aminonaphthalene) have been synthesized in high yields by chemical oxidative polymerization method. The polymers are soluble in polar solvents such as DMSO, NMP etc. In PNA-2 as head-to-tail coupling cannot occur, the electrical conductivity is lower than PNA-1. The copolymer exhibits distinct morphology, higher viscosity, characteristic exciton peak, appreciable thermal stability and electrical conductivity compared to PNA-1.

Keywords. Aminonaphthalene; conductivity; thermal stability; co-polymer.

1. Introduction

Conjugated aromatic organic polymers e.g. polyphenylene, polyaniline, polythiophene (Sanechika *et al* 1979; Sorillon and Garnier 1982; MacDiarmid *et al* 1987a,b), have attracted a great deal of attention as electrically conducting materials. Among these organic polymers, polyaniline has attracted special attention due to its high stability towards air and moisture, high electrical conductivity (MacDiarmid *et al* 1985) and unique redox properties (Moon *et al* 1993). However, polyaniline is almost insoluble in common organic solvents especially in doped form, which causes difficulties in determination of molecular structure and restricts them to practical use. The soluble polyanilines (Angelopoulos *et al* 1988; Inoue *et al* 1989, 1991) have great advantage for characterization and preparation for the casting film (Watanabe *et al* 1987; Pandey *et al* 1993; Zheng *et al* 1994) which are suitable materials for practical use (Yue *et al* 1991). This technique has been applied in more diverse fields of research to get better applicable materials. Poly (*N*-phenyl-1-naphthaleneamine) (Wei *et al* 1995), poly (1-aminonaphthalene) and poly (1-aminoanthracene) (Chen and Hwang 1995) are new significant members in this field. These polynuclear aromatic amines are a new class of conducting materials, those showing good electrical conductivity without any doping due to small intrinsic band gap. Such a scenario may possibly be utilized to avoid the process of doping which is cumbersome and involves the use of corrosive materials. It is observed that in the undoped state some of these polymers have significant electrical current carrying capability, five to six orders more than PAN base. Poly nuclear aromatic amine homopolymers have been prepared electrochemically and by oxidative methods, using H_2O_2–Fe catalyst. In the present work, we prepared poly (1-aminonaphthalene) (PNA-1), poly (2-aminonaphthalene) (PNA-2), and its co-polymer (PANA).

2. Experimental

Aniline (99·5% Aldrich) was distilled twice under reduced pressure. Reagent grade ammonium persulfate (99% E. Merck) was used as received. 1-Aminonaphthalene (Fluka) and 2-aminonaphthalene (Fluka) were used as received. 1-Aminonaphthalene and 2-aminonaphthalene were dissolved in aqueous 1 M HCl solution followed by addition of $(NH_4)_2S_2O_8$ solution dropwise with vigorous stirring over a period of 20–30 min, at 30–35°C (Ray *et al* 1989; MacDiarmid *et al* 1991). The resultant mixture was further stirred for about 6 h at 30°C. The obtained polymer was filtered, washed successively with 1 M HCl and ethanol until the filtrate became colourless. Schematic representation of polyaniline and its derivatives are given in figure 1.

Co-polymer of aniline and 1-aminonaphthalene was prepared by using different mole ratios of two components in the feed. 1-Aminonaphthalene/aniline co-monomer solution was prepared by dissolving aniline and 1-aminonaphthalene in 200 ml 1 M HCl. $(NH_4)_2S_2O_8$ solution was added dropwise with constant stirring over a period of 6 h at 25–27°C. The blue polymers were filtered, successively washed with 1 M HCl and ethanol and dried in vacuum over P_2O_5. The percentage yields for PNA-1, PNA-2 and *a*-A were 77, 75 and 70, respectively.

The finely ground polymer powder was used for IR spectra in KBr pellets by Perkin Elmer spectroscope

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Table 1. Experimental details of conductivity and viscosity of polymer.

Sample	Mole ratio	Reaction temp.	Yield	Conductivity	h_{int} (dl/g) in H_2SO_4
Poly (1-aminonaphthalene) (*a*-PNA)	–	30–35	70	$1·9 \times 10^{-4}$	0·109
Poly (2-aminonaphthalene) (*b*-PNA)	–	35–40	60	$6·5 \times 10^{-6}$	0·070
Poly (aniline-co-1-aminonaphthalene) (PANA-20)	0·20	25–27	80	$7·9 \times 10^{-7}$	0·273
Poly (aniline-co-1-aminonaphthalene) (PANA-35)	0·35	25–27	78	$3·5 \times 10^{-2}$	–
Poly (aniline-co-1-aminonaphthalene) (PANA-50)	0·50	25–27	72	$2·9 \times 10^{-2}$	–
Poly (aniline-co-1-aminonaphthalene) (PANA-70)	0·70	25–27	65	$3·2 \times 10^{-3}$	–

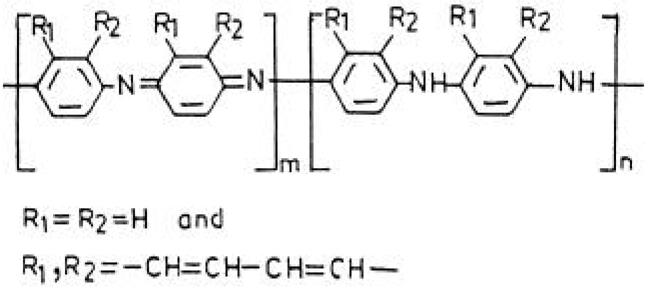

Figure 1. Structure of polymer.

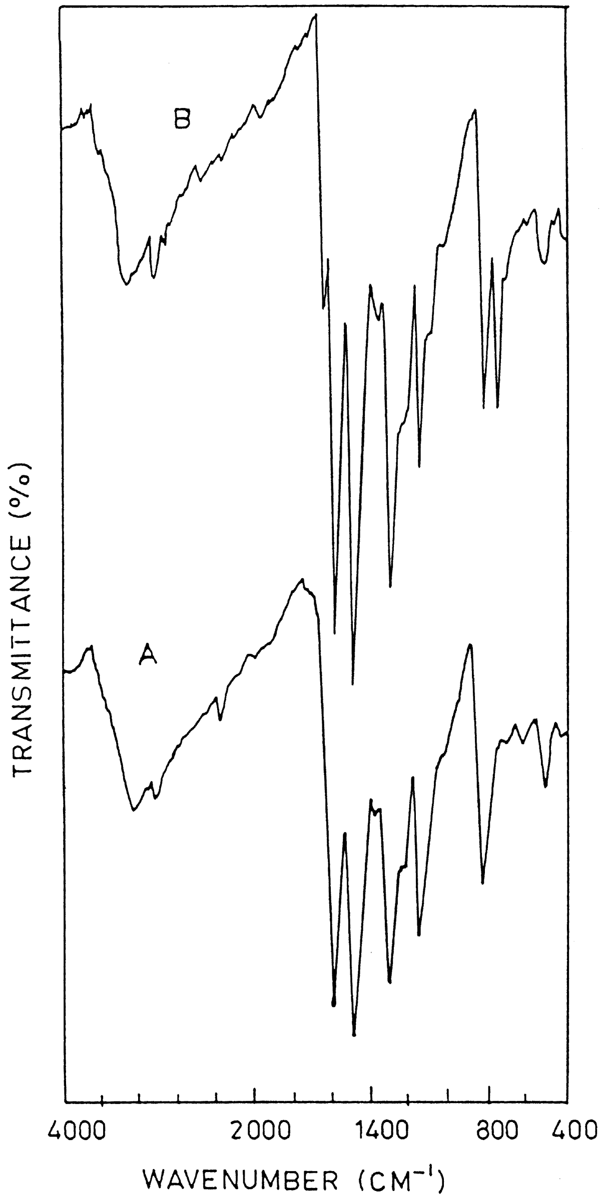

Figure 2. Infrared spectroscopy of A. PNA-1 and B. PNA-2.

(Model 883). The UV-vis spectra of polymer solution in DMSO was recorded by using Shimadzu UV-3100 spectrometer. The thermal analysis (TG, DTA) was done by a Shimadzu DT-40 unit, in air, with a heating rate of 10°C min^{-1}. Conductivity of HCl doped polymers by using pellet was measured by two-probe technique employing the Philips PR 9500 unit at room temperature. Scanning electron micrographs were taken on a cam scan2 DV unit. All the measurements except conductivity were performed on base form of the polymers.

3. Results and discussion

Polymerization of 1&2-aminonaphthalene and co-polymerization of aniline with 1-aminonaphthalene were performed with ammonium persulfate as oxidant to get high yields. The polymers are soluble in common polar solvents such as DMSO and NMP, moderately in DMF, THF and completely soluble in H_2SO_4 (96%). The intrinsic viscosity (in 96% H_2SO_4) qualitatively indicates that the prepared polymers have rather low molecular weight, especially poly (2-aminonaphthalene) compared to polyaniline (0·57 dl/g), which shows much higher viscosity.

The infrared spectra are shown in figures 2 and 3. The characteristic skeletal vibration at 1586 and 1496 cm^{-1} of polyaniline was due to quinoid and benzoid ring stretch. Above-mentioned stretching appears at 1586 and 1503 cm^{-1} for PNA-1, 1618 and 1503 cm^{-1} for PNA-2 and 1585 and 1498 cm^{-1} for PANA (Chain and MacDiarmid 1986; MacDiarmid *et al* 1987a,b; Wei *et al* 1995). The IR spectra of (table 2) PANA and PNA-1 show a mixed feature with side chain oxidation peak at 1651 and 1653 cm^{-1} having relatively lesser intensity, whereas benzoid peak is relatively stronger. The distinct character of the polymer is also indicated by the almost equal intensity of the out of plane aromatic C–H bond vibration at 814–847 cm^{-1}and

Table 2. Characteristic IR stretching frequency of polymers.

Polymer	Quinoid [Q] (cm^{-1})	Benzenoid [B] (cm^{-1})	[Q]/[B]	C–N (cm^{-1})	C–H (cm^{-1})	Other
Poly (1-aminonaphthalene)	1585	1498	0·93	1289	847/763	1653
Poly (2-aminonaphthalene)	1618	1503	1·11	1345	814/750	–
Poly (aniline-co-1-aminonaphthalene) (PANA-20)	1589	1500	0·96	1301	829/761	1651

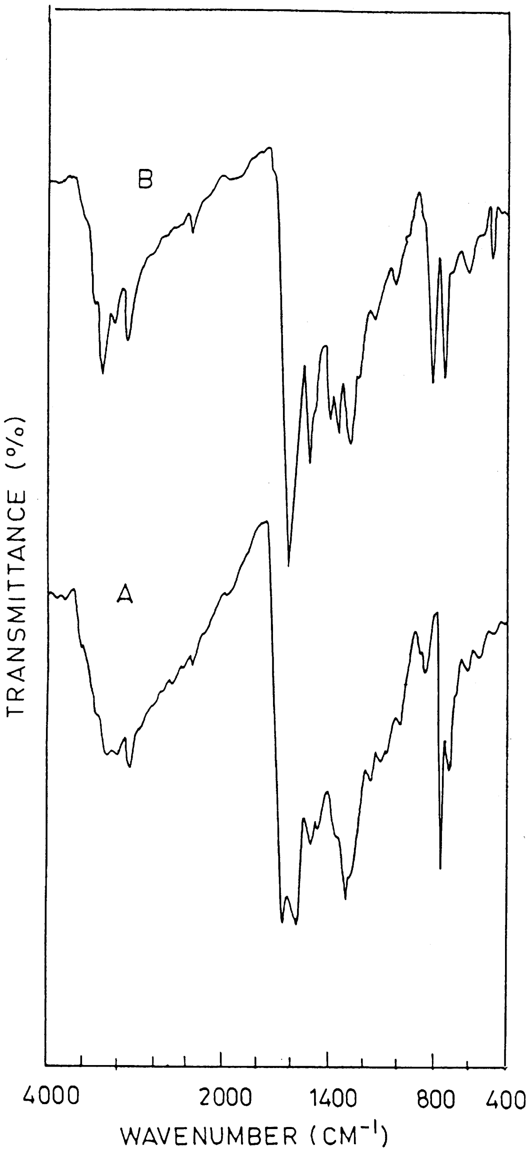

Figure 3. Infrared spectroscopy of A. PANA-20 and B. PANA-35.

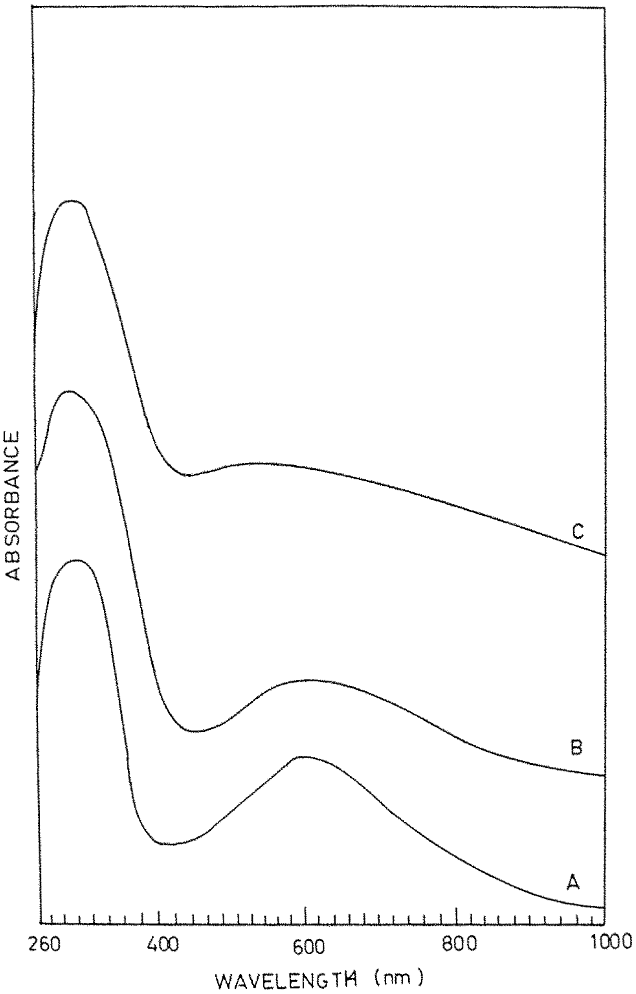

Figure 4. UV-vis absorption spectra of A. PNA-1, B. PNA-2 and C. PANA.

750–768 cm^{-1} for two and four adjacent hydrogen (2H and 4H) atoms. Several authors have suggested different coupling mechanisms. In the electrochemical polymerization of 1-aminonaphthalene, C–C (tail to tail), N–N (head to head) and N–C (head to tail coupling) modes have been envisaged. However, it is found that in aqueous medium head to tail coupling was more dominant. In *b*-PNA, head to tail coupling cannot occur, the out of plane aromatic C–H bond absorption for adjacent hydrogen (4H) (Chan *et al* 1993; Nguyen *et al* 1994) is rather reduced compared to 2H peak, indicating polymerization in 2 : 5 or 2 : 8 position in addition to 1 : 2 position, too much steric strain being associated with the latter.

The UV-vis absorption spectra of the polymers are shown in figure 4. PNA-1, PNA-2 and PANA display major absorption bands in DMSO at 314, 297 and 307 nm, respectively due to Π–Π* transition. Bands at 495 nm

Table 3. Thermal analysis of naphthalene based polymer.

Samples	Mass loss (%) 200°C	400°C	600°C	Range of decomposition (°C)
Poly (1-aminonaphthalene) base	0	7–8	80	320–630
Poly (2-aminonaphthalene) base	11–12	22–23	78	300–700
Poly (aniline-co-1-amino-naphthalene) base	0	2–3	34	250–920

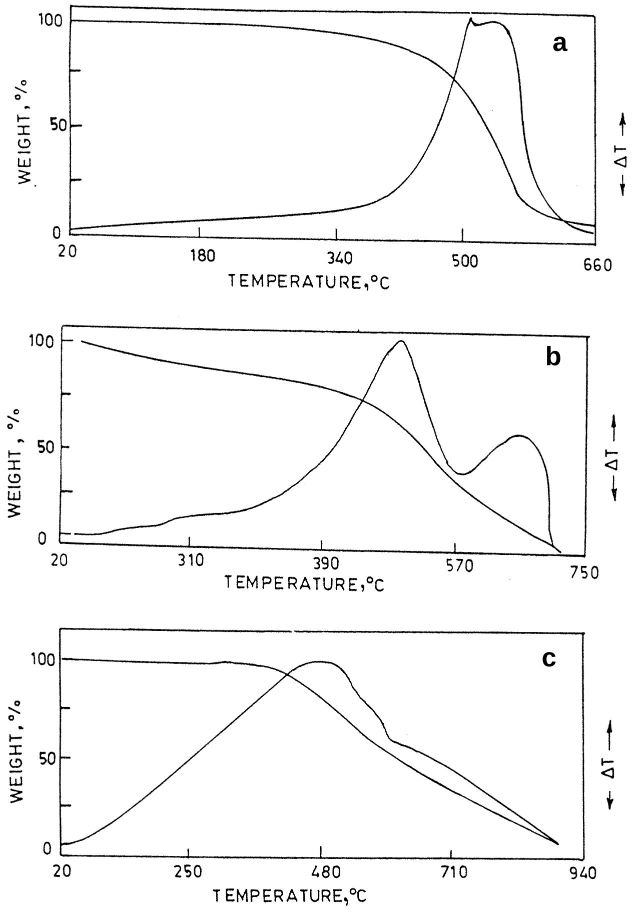

Figure 5. TG–DTA thermograms of **a.** PNA-1, **b.** PNA-2 and **c.** PANA.

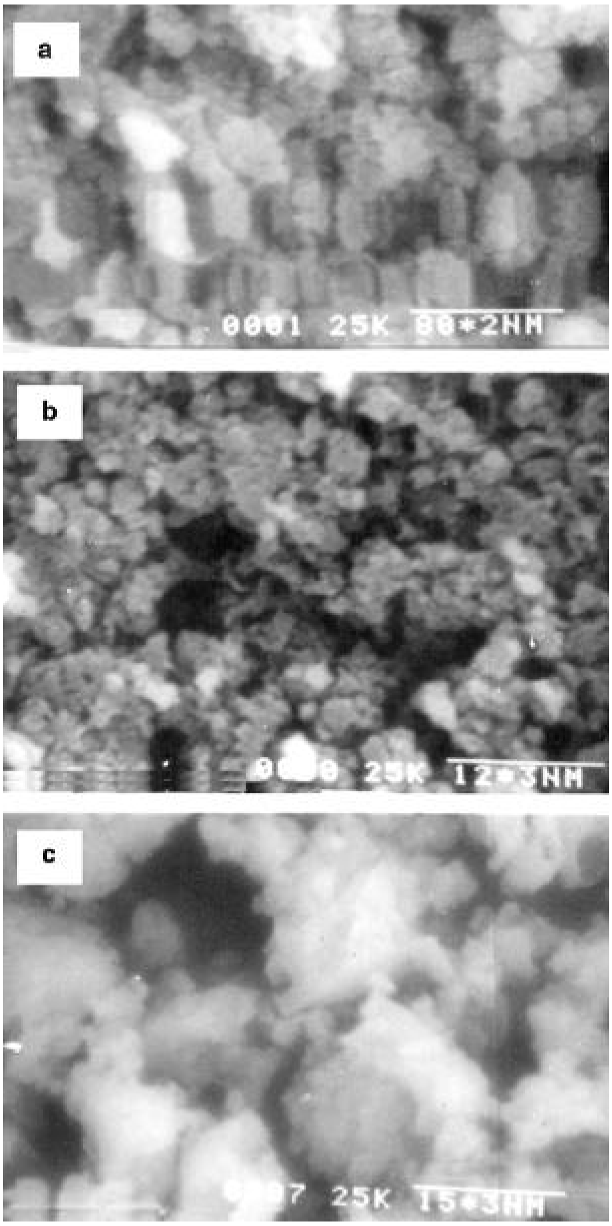

Figure 6. SEM showing **a.** poly (1-aminonaphthalene), **b.** poly (2-aminonaphthalene) and **c.** poly (aniline-co-1-aminonaphthalene).

and 575 nm for exciton transition appeared for PNA-1, PANA, respectively, the latter one is taken as a measure of extended conjugation in the polymer backbone. The blue shift increases with increasing proportion of 1-aminonaphthalene in the feed.

TG–DTA analysis of polymer is shown in figure 5. Thermal data suggest that PANA is the most thermally stable polymer. *a*-PNA shows about 7–8% mass loss at 400°C and then begin to undergo oxidative degradation, which is fast completed (600°C). The exothermic change taking place in the copolymer without any accompanying mass loss up to 400°C is due to interchanged cross-linking reaction. An exothermic behaviour occurs above 200°C supporting interchain cross-linking. This cross-linking can be attributed to the coupling of two neighbouring N=Q=N groups (Chen and Lee 1995). The final thermal oxidative degradation in *b*-PNA takes place in two stages at 495°C and 663°C, assuming coupling occurs in 2 : 5 or 2 : 8 position apart from the 1 : 2 position. First degradation may be assigned to the polymer unit with coupling in 1 : 2 positions. Energy expulsion again indicates those with 2 : 5 and 2 : 8 coupling to be of relatively low population.

The scanning electron micrographs (figure 6) of polymers, PAN and a-PNA, show the surface as made up of an aggregate of many small granules. The copolymer has a distinct criss-cross canal like feature, evidently absent in PAN and a-PNA. b-PNA shows partly a more regular canal like feature, the rest being irregular, indicating more than one phase.

Conductivity measurements (table 1) show that the polymer hydrochlorides are much less conducting than polyaniline. The co-polymer exhibits appreciably higher electrical conductivity ($7{\cdot}9 \times 10^{-2} - 3{\cdot}2 \times 10^{-3}$ S/cm) compared to PNA-1 ($1{\cdot}1 \times 10^{-4}$ S/cm). Low electrical conductivity of PNA-2 indicates considerable steric strain and absence of usual head to tail coupling pattern, prevailing in PNA-1.

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