Synthesis of Poly(1-aminonaphthalene) and Poly(1-aminoanthracene) by Chemical Oxidative Polymerization and Characterization of the Polymers

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ABSTRACT: Poly(1-aminonaphthalene) and poly(1-aminoanthracene) have been synthesized in high yields (90–96%) by chemical oxidative polymerization of 1-aminonaphthalene and 1-aminoanthracene using H_2O_2 in the presence of Fe catalyst. The oxidative polymerization of 1-aminonaphthalene and 1-aminoanthracene proceeds *via* successive coupling that gives the polymer structure similar to polyaniline. The polymers are brown powders and soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), H_2SO_4, and HCOOH. The obtained poly(1-aminonaphthalene) and poly(1-aminoanthracene) show electrical conductivities of 1.7×10^{-6} and 1.6×10^{-4} S cm^{-1}, respectively, which increase to 3.8×10^{-4}–1.5×10^{-3} S cm^{-1} on doping with HCl or I_2. Light scattering measurement of the polymers in NMP shows a large degree of depolarization ($\rho_v = 0.33$), indicating that the polymers have a linear and stiff structure. The number-average molecular weights (M_n) of poly(1-aminonaphthalene) and poly(1-aminoanthracene) obtained are determined as 4300 and 4500, respectively, with narrow molecular weight distribution by gel permeation chromatography (*vs* polystyrene). The weight-average molecular weight (M_w) of poly(1-aminoanthracene) determined by the light scattering method is 7000. ^1H NMR spectra of PNA and PAA in DMSO-d_6 give rise to the absorption of the NH hydrogen in the region of δ 5–6 ppm, and the NH hydrogen of PNA is exchangeable with the water hydrogen contained in DMSO-d_6 on the NMR time scale with an activation energy of 27 kJ mol^{-1}. PNA and PAA do not show a distinct absorption peak in the visible region.

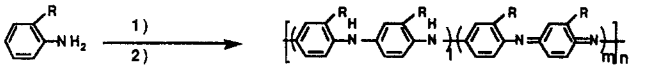
Introduction

Recently, π-conjugated organic polymers having benzenoid or heterocyclic units (e.g., poly(*p*-phenylene),[1] polyaniline,[2] polythiophene,[3] and polypyrrole[4]) have attracted a great deal of attention as electrical conducting materials.[5]

Among these organic polymers, polyaniline has attracted special attention due to its high stability toward air and moisture, high electrical conductivity,[6a] and unique redox properties.[6b–e] Recent studies on polyaniline revealed several molecular structures of the polymer depending on the oxidation state and on the degree of protonation.[7–11] The soluble polyaniline is of great advantage for characterization[12–17] and for preparation of the casting films which are suited as materials for practical use.[18]

Recently, we have reported that oxidation of aniline with H_2O_2 in the presence of Fe(II) catalyst gives polyaniline having a higher solubility toward organic solvents compared with polyaniline prepared by conventional oxidation polymerization of aniline using persulfate salts (Scheme I).[19] The method is also applicable to oxidative polymerization of 2-ethylaniline and 2-propylaniline to give the corresponding poly(2-alkylaniline)s which are not easily obtained by the other methods. On the other hand, poly(1-aminonaphthalene) and poly(1-aminoanthracene) are expected to have smaller band gaps than polyaniline, similar to poly(isothianaphthene) having a smaller band gap than polythiophene.[20] These polymers of polynuclear aromatic amines can be classified as a promising electrically conductive material that would show electrical conductivity without doping due to a small intrinsic band gap. However, there have been no good procedures to prepare the polymers other than electrochemical polymerization.[21] This situation prompted us to examine oxidation polymerization of 1-aminonaphthalene and 1-aminoanthracene using the H_2O_2–Fe catalyst system.

Scheme I



(R = H, C_2H_5, *n*-C_3H_7)

1) H_2O_2 and Fe^{2+}, at 30 °C in an aqueous H_2SO_4 solution
2) NH_4OH

In this paper, we report successful chemical oxidative polymerization of 1-aminonaphthalene and 1-aminoanthracene using H_2O_2 in the presence of Fe catalyst. The obtained polymers have been characterized by IR, NMR, and electronic spectroscopy.

Experimental Section

Materials. 1-Aminonaphthalene was purchased from Aldrich Chemical Co. Inc. and used after sublimation. 1-Aminoanthracene from Aldrich was used without further purification. $FeSO_4 \cdot 7H_2O$ and H_2O_2 (31%, aqueous) were purchased from Koso Chemical Co. Ltd. and Mitsubishi Gas Chemical Co. Inc., respectively.

Chemical Oxidative Polymerization of 1-Aminonaphthalene. To a mixture of CH_3CN (15 mL) and 1-aminonaphthalene (0.54 g, 3.8 mmol) in a 350-mL round-bottom flask was added dropwise distilled water (60 mL) and sulfuric acid (2.9 mL, 50 mmol). Acetonitrile (15 mL) was then added to make the purple reaction mixture homogeneous. With the resulting solution remaining at 30 °C, powdery $FeSO_4 \cdot 7H_2O$ (30 mg, 0.1 mmol) was added with vigorous stirring, and then 31% H_2O_2 (0.85 mL, 8.5 mmol) was slowly added to the solution. The reaction mixture was agitated continuously for 40 h under air at 30 °C to cause precipitation of a brown solid. The product was quenched with ice water, and the solid was collected on a glass filter and washed with methanol, with 28% aqueous ammonia,

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and then with methanol several times. Finally, it was dried in dynamic vacuum at room temperature to give poly(1-aminonaphthalene) (PNA) as a brown solid in 80% yield. Modified polymerization was also carried out by adding CH_3OH to the polymerization system.

Chemical Oxidative Polymerization of 1-Aminoanthracene. To a mixture of CH_3CN (80 mL) and 1-aminoanthracene (0.27 g, 1.4 mmol) in a 350-mL round-bottom flask was added dropwise distilled water (80 mL) and sulfuric acid (0.68 mL, 12 mmol). With the resulting solution remaining at 30 °C, powdery $FeSO_4 \cdot 7H_2O$ (10 mg, 0.036 mmol) was added with vigorous stirring, and then 31% H_2O_2 (0.5 mL, 4.5 mmol) was slowly added to the solution. The reaction mixture was agitated continuously for 22 h under air at 30 °C to cause precipitation of a brown solid. The product was treated with the same method described above. Finally, it was dried in dynamic vacuum at room temperature to give poly(1-aminoanthracene) (PAA) as a brown solid in 90% yield.

Reduction of Poly(1-aminonaphthalene) and Poly(1-aminoanthracene) by Hydrazine Monohydrate. Reduction of poly(1-aminonaphthalene) and poly(1-aminoanthracene) was carried out by treatment with excess hydrazine monohydrate under reduced pressure according to the methods of Green and Woodhead.[19,22]

Doping of PNA and PAA with Iodine. Powdery PNA was placed in a Schlenk flask with a glass joint connected to a small flask containing I_2. After evacuation of the system to 10^{-2} Torr, the joint was opened to expose the sample to I_2 vapor at room temperature. After 4 days of exposure, excess I_2 was removed under vacuum for 20 h. The doped sample was pressed at 200 kg cm^{-2} to make a pellet with a diameter of 1.3 cm and 0.2–0.4-mm thickness. A bar was made by cutting the pellet and the electric conductivity was measured by a two-probe method using the bar. Doping of PAA was carried out analogously. The electrical conductivity of nondoped PNA and PAA was measured analogously by using bars obtained from pressed pellets.

Doping of PNA and PAA with Hydrochloric Acid. To PNA (100 mg) in a flask was added 0.2 M HCl (100 mL), and the resulting mixture was stirred at room temperature overnight. The HCl-doped PNA was obtained as a black-brown powder which was filtered out and dried. Doping of PAA was carried out analogously. Electrical conductivity of the doped polymers was measured by a two-probe method, as described above.

Polymer Characterization. IR spectra were measured on a Jasco IR-810 spectrophotometer in KBr. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TG-30 under nitrogen atmosphere at a constant heating rate of 10 °C min^{-1}. UV–vis spectra in solutions were recorded on a Hitachi 200-20 spectrophotometer at room temperature. UV–vis spectra of a cast film were measured by Dr. Miyagi of Tosoh Co. Ltd. Near infrared spectra were recorded on a U-3400 spectrophotometer. NMR spectra in solution were taken using a JEOL JNM-GX-500 spectrophotometer. Gel permeation chromatograms (GPC) were recorded on a Toso HLC-810 apparatus at 25 °C using 0.01 mol L^{-1} LiBr/DMF as eluent. The number-average (M_n) and weight-average (M_w) molecular weights were determined by standard procedures using polystyrene standards. The light scattering of NMP solutions of PNA and PAA was measured as previously reported.[23] The electrical conductivity of doped and nondoped samples (σ) was measured with bars prepared from pressed pellets of the sample (*vide ante*) using a two-probe method with a Takeda Riken TR-8651 electrometer at room temperature (ca. 25 °C).

Results and Discussion

Synthesis of Poly(1-aminonaphthalene) and Poly(1-aminoanthracene). Chemical oxidative polymerization of 1-aminonaphthalene and 1-aminoanthracene with H_2O_2 in the presence of the Fe catalysts gives poly(1-aminonaphthalene) and poly(1-aminoanthracene) as shown in Scheme II.

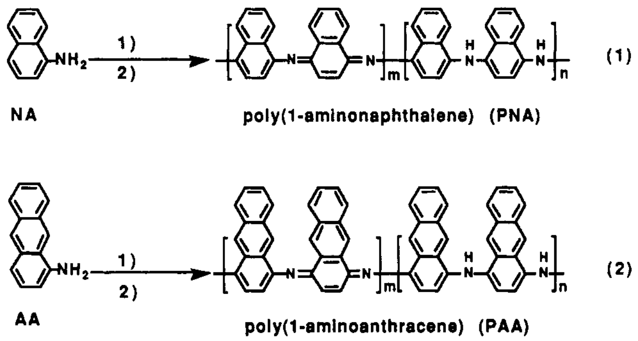
Table I summarizes results of the preparation of poly(1-aminonaphthalene) and poly(1-aminoanthracene) under various conditions. Acetonitrile was added to dissolve the monomers and to make the reaction system homogeneous. Polymerization proceeded smoothly on addition of H_2O_2 in the presence of a catalytic amount of $FeSO_4$. Polymerization did not occur in the absence of Fe^{2+}, similarly to the case of the preparation of polyaniline.[19] The polymerization gives PNA in high yield when a sufficient (2.4 mol/monomer) amount of H_2O_2 is added (nos. 1–3 in Table I). However, addition of a smaller amount (1.6 mol/monomer) causes a decrease in the yield (no. 4).

Table I. Oxidative Polymerization of 1-Aminonaphthalene and 1-Aminoanthracene with H_2O_2 and Iron(II) Sulfate Catalyst

monomer	no.	amt of solvent/mL CH_3CN/	H_2O/	CH_3OH	amt of H_2SO_4/mmol	amt of H_2O_2/mmol	time/h	temp/°C	yield/%
1-NA[a]	1	30	60		50	8.5	40	30	80
	2	30	76	15	25	8.5	48	30	90
	3	45	76		5	8.5	48	30	80
	4	45	76		50	5.7	48	35	40
	5	15	76	30	50	5.7	48	35	35
	6	15	76	30	50	5.7	56	25	19
1-AA[b]	7	80	80		3	2.2	39	30	74
	8	80	80		12	2.2	22	30	90
	9	80	80		20	2.2	21	30	96
	10	80	80		3	2.2	19	30	70

[a] 1-NA: 1-aminonaphthalene (0.54 g, 3.6 mmol). Polymerization was carried out using H_2O_2 (31%) in the presence of 0.1 mmol of $FeSO_4$. The monomer was dissolved in CH_3CN, and then H_2O was added in the reaction vessel except for nos. 5 and 6, in which H_2O was initially added followed by addition of CH_3CN. [b] 1-AA: 1-aminoanthracene (0.27 g, 1.4 mmol). Polymerizations were carried out using H_2O_2 (31%) in the presence of 0.036 mmol of $FeSO_4$. The monomer was dissolved in CH_3CN, and then H_2O was added in the reaction vessel.

Scheme II



1) H_2O_2 and Fe^{2+}, at 30 °C
2) NH_4OH

The addition procedure of CH_3CN to dissolve the monomer is important to increase the yield and to decrease the reaction time. In nos. 5 and 6, H_2O was initially added to the reaction mixture followed by addition of CH_3CN and CH_3OH. It took about 24 h to make the mixture homogeneous, and the yield was low.

Poly(1-aminoanthracene) can also be prepared in high yields by the oxidative polymerization of 1-aminoanthracene with H_2O_2 in the presence of Fe catalyst (nos. 7–10).

Characterization and Properties of the Polymers. Solubility. The prepared powdery PNA and PAA are brown and soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), H_2SO_4, and HCOOH and slightly soluble in $CHCl_3$ and tetrahydrofuran (THF), as shown in Table II.

IR, GPC, and Light Scattering. Figure 1 shows the IR spectra of PNA and PAA. The IR spectrum of PNA

Table II. Solubility of Poly(1-aminonaphthalene) (PNA) and Poly(1-aminoanthracene) (PAA)[a]

	PNA	λ_{max}/nm	PAA	λ_{max}/nm
CH_3OH	i		i	
C_2H_5OH	i		i	
CH_3CN	i		i	
benzene	i		i	
toluene	i		i	
HCl	i		i	
$CHCl_3$	ss		ss	
THF	ss		ss	
H_2SO_4	s		s	
HCOOH	s		s	
DMF	s	295	s	280, 300 330, 345
DMSO	s		s	
NMP	s	295	s	290, 300 330, 345

[a] s, soluble; ss, slightly soluble; i, insoluble. Abbreviations: DMF, dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methylpyrrolidone.

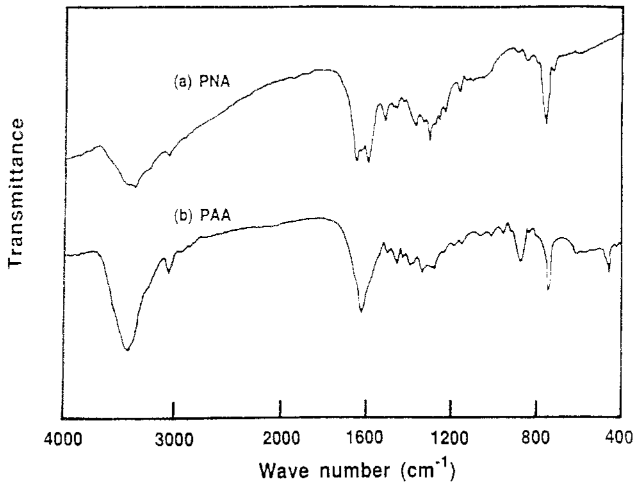


Figure 1. IR spectra of (a) poly(1-aminonaphthalene) (PNA) and (b) poly(1-aminoanthracene) (PAA).

is essentially the same as that of electrochemically polymerized PNA.[21b] Both PNA and PAA give rise to mixed absorption bands assigned to skeletal vibration of the aromatic ring and the quinoid imine group in a region from 1660 to 1580 cm^{-1}. The IR spectrum of polyaniline also exhibits the absorption bands in the same region, and Tang and co-workers have assigned the peak at 1500 cm^{-1} to the benzenoid ring and the absorption at 1600 cm^{-1} to the quinoid ring stretching vibration of polyaniline.[11b]

Since it is known that naphthalene is oxidized chemically by H_2O_2 as well as electrochemically to give oxidized products such as naphthoquinones and phthalic anhydride,[24] a part of the naphthalene rings in PNA may be oxidized to give oxidized units like the 1,4-naphthoquinone-5,8-diyl unit and IR absorptions due to such oxidized units may be included in the absorptions in the region from 1660 to 1580 cm^{-1}. By reduction of PNA with N_2H_4, the absorption pattern in this region becomes simpler, showing a peak at 1610 cm^{-1}, probably due to the reduction of the quinoid imine group to the amine group, as in the case of reduction of the oxidized form of polyaniline with N_2H_4.[6c]

The absorption peaks at 760 and 740 cm^{-1} observed in both the IR spectra of PNA and PAA seem to be assigned to the out-of-plane vibrations for four adjacent H atoms, and those of 840 and 860 cm^{-1} to the two adjacent H atoms.[21]

Table III. Molecular Weight of Poly(1-aminonaphthalene) and Poly(1-aminoanthracene)

polymer[a]	M_n[b]	M_w[b]	M_w/M_n[b]	M_w[c]	ρ_v[c]	$\Delta n/\Delta c$[c,d]/ cm^3 g^{-1}
PNA	4300	6100	1.42	3800	0.33	0.47
PAA	4500	5500	1.23	7000	0.33	0.52

[a] PNA: poly(1-aminonaphthalene). PAA: poly(1-aminoanthracene). [b] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were evaluated by GPC (*vs*, polystyrene, 0.01 M LiBr/DMF). [c] Estimated by light scattering using 632.8 nm of the He–Ne laser at 20 °C in NMP. [d] Refractive index increment.

Acetylation of the NH group of reduced PNA with CH_3COCl carried out in a manner similar to that of polyaniline[25] gives a sample whose IR spectrum shows a very strong absorption band at 1660 cm^{-1}, where the acetylated polyaniline also gives rise to a strong absorption band, although the degree of the acetylation (ca. 15%) of PNA estimated from the peak area of the CH_3CO group in NMR (δ 1.8 ppm) is lower than that (ca. 80%, δ 1.9 ppm) of reduced polyaniline, presumably due to the steric effect of the bulky naphthyl group.

Table III shows molecular weights of PNA and PAA estimated by gel permeation chromatography and light scattering methods. The number-average molecular weights of PNA and PAA were 4.3×10^3 and 4.5×10^3 (GPC, *vs* polystyrene), respectively. Each of the GPC curves of PNA and PAA gives a single peak and reveals a narrow molecular weight distribution ($M_w/M_n = 1.42$ and 1.23 for PNA and PAA, respectively). The weight-average molecular weights (M_w) of PNA and PAA determined by GPC roughly agree with those determined by a light scattering method[23] in NMP. For example, the M_w value of PAA determined from the light scattering method, 7000, roughly agrees with the M_w value ($M_w = 5500$) estimated from GPC.

The light scattering measurement of PNA and PAA also reveals that they have very large degrees of depolarization[23] ($\rho_v = 0.33$) in the NMP solution (the second to last column in Table III). The theoretical limiting value for an ideally linear π-conjugated polymer with a very large polarizability along the polymer chain and negligibly small polarizabilities along the other two perpendicular axes is $^1/_3$,[23,26] and agreement of the observed value with the theoretical value indicates that PNA and PAA essentially take a linear and stiff structure, presumably due to bonding the large aromatic units through a small space of the –NH– or =N– group.

The very large refractive index increment (last column in Table III, $\Delta n/\Delta c = ca.\ 0.5$ cm^3 g^{-1}) supports the presence of a large π-conjugation system. In the case of emeraldine form poly(aniline), $(\text{–NH—}C_6H_4\text{—NH—}C_6H_4\text{–})_l(\text{–N═}C_6H_4\text{═N—}C_6H_4\text{–})_m$, the polymer has a negligibly small ρ_v value ($\rho_v = ca.\ 0.02$) and a relatively lower $\Delta n/\Delta c$ value ($\Delta n/\Delta c = ca.\ 0.2$ cm^3 g^{-1}) compared with those of PNA. Previously, polypyridine having a rigid linear structure was reported to show large ρ_v and a large $\Delta n/\Delta c$ value ($\rho_v = 0.33$, $\Delta n/\Delta c = 0.59$ cm^3 g^{-1}).[26]

NMR, UV–Vis, and Conductivity. Figure 2a exhibits ^1H NMR spectra of PNA in DMSO-d_6. The broad peaks at δ 5.2 and 5.8 ppm disappeared on addition of D_2O due to H–D exchange (Figure 2a) and therefore are assigned to the –NH– hydrogen; similar H–D exchange between the –NH– hydrogen and D_2O also occurs with polyaniline and diphenylamine.[27] The appearance of two signals at δ 5.2 and 5.8 ppm suggests the presence of two kinds of –NH– hydrogen under different magnetic environments. Other signals of a range of δ 6–10 ppm are essentially unchanged by the addition of D_2O and assigned to the aromatic protons, although a broad signal(s) of another

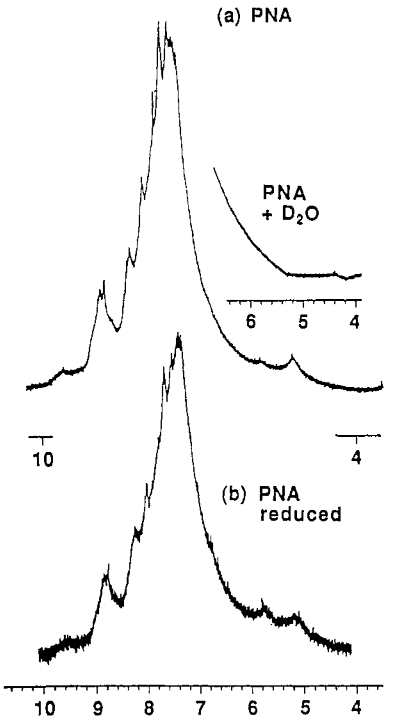


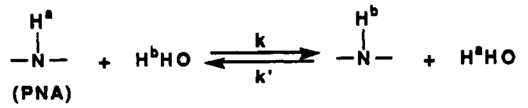
Figure 2. ^1H NMR (500-MHz) spectra of (a) PNA and (b) PNA reduced by N_2H_4. In DMSO-d_6 at 30 °C. The change of the ^1H NMR spectrum of PNA after addition of 15 μL of D_2O to 0.4 mL of DMSO-d_6 is also shown.

kind(s) of NH hydrogen(s) may be hidden under the strong absorption of the aromatic hydrogen. PNA reduced by the treatment with N_2H_4 (*cf.* Experimental Section)

$$\text{PNA} + N_2H_4 \rightarrow \text{PNA reduced} \qquad (3)$$

also gives rise to two peaks at δ 5.1 and 5.8 ppm assignable to -NH- (Figure 2b), which also disappeared by the addition of D_2O to the DMSO-d_6 solution. Although it is difficult to determine the peak area of the -NH- signals due to the strong signals of aromatic hydrogens, the peak area of the -NH- signal at δ 5.8 ppm appears to increase by the reduction with N_2H_4. The reduction of PNA causes a shift of the cluster signals of the aromatic hydrogens to a lower magnetic field by 0.2–0.3 ppm. PAA also gives a peak at δ 5.6 ppm in DMSO-d_6 assignable to the -NH- hydrogen, although such H–D experiments have not been carried out with PAA.

As described above, the NH hydrogen of PAA is exchangeable with the water hydrogen, and the exchange occurs even on the NMR time scale. Although broadening of the NH signals due to the exchange with H_2O in DMSO-d_6 at high temperatures is not obvious because of the broadened NH signals even at 25 °C (Figure 2), broadening of the water–H signal at elevated temperatures is clearly observed, as shown in Figure 3, and this broadening is explained by the exchange between the NH hydrogen and water hydrogen;



$$\underset{\text{(PNA)}}{-\overset{\overset{\displaystyle H^a}{|}}{N}-} + H^bHO \underset{k'}{\overset{k}{\rightleftharpoons}} -\overset{\overset{\displaystyle H^b}{|}}{N}- + H^aHO \qquad (4)$$

the ^1H NMR signal of water in DMSO-d_6 without PNA becomes rather sharper on raising the temperature, presumably due to a decrease in the viscosity of the solution.

The intrinsic half-width of the ^1H NMR signal of water in DMSO-d_6 is estimated as 1.7 Hz, as measured with DMSO-d_6 containing only H_2O as the impurity.[27] The half-widths of the H_2O signal in PNA-containing DMSO-d_6 (Figure 3a) at 90.4, 80.4, 70.5, 60.5, 50.5, and 30.6 °C are 35, 29, 23, 18, 14, and 7.2 Hz, respectively. From the half-width, the lifetime of H^b, τ_b, in water at the respective temperatures are estimated[28] as 0.030, 0.037, 0.047, 0.061, 0.081, and 0.182 s. If the exchange (eq 4) follows the second order equation,

$$R = k[\text{-NH-}][H_2O] \qquad (5)$$

the lifetime of H^b, τ_b, corresponds to a value calculated according to the following equation:

$$\tau_b = 2[H_2O]/R = 2/k[\text{-NH-}] \qquad (6)$$

Application of this equation gives the Arrhenius activation energy of 27 kJ mol^{-1} for the exchange process (k) from the Arrhenius plot shown in Figure 4. The H_2O signal in DMSO-d_6 containing the reduced PNA also shows the broadening of the signal at elevated temperatures (Figure 3b); however, the lifetime τ_b in this system is larger than that in DMSO-d_6 containing nonreduced PNA, as revealed by the sharper signal.

Figure 5 shows the UV–visible spectrum of PNA and PAA recorded in DMF solutions at various concentrations.

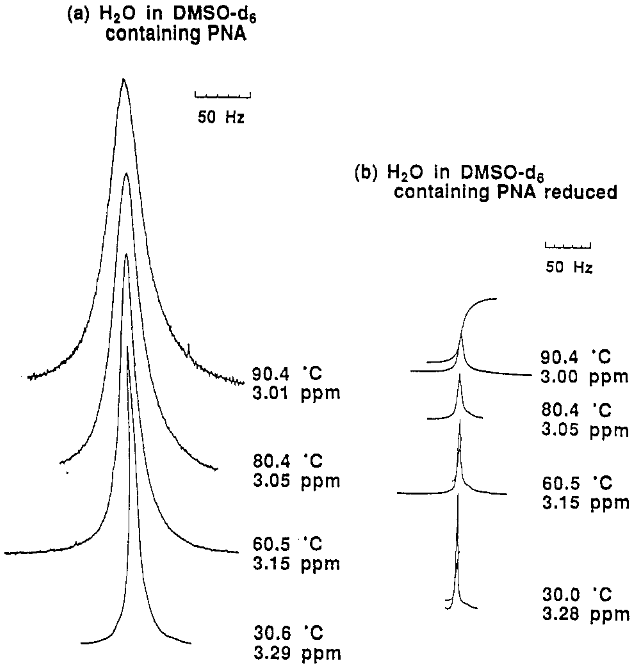


Figure 3. Temperature dependence of the signal of water in DMSO-d_6 containing (a) PNA or (b) PNA reduced. The temperature and the peak position of the signal are given in the figure. Scales in hertz are given for (a) and (b).

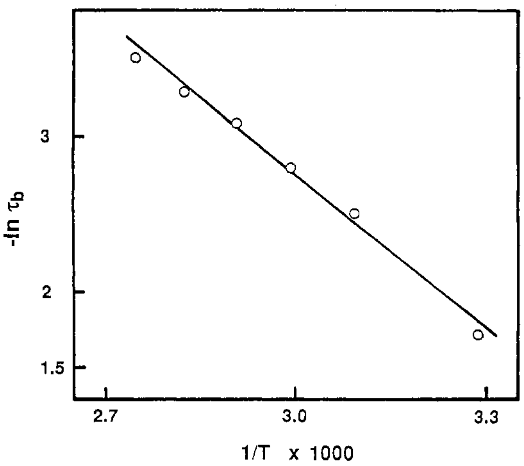


Figure 4. Arrhenius plot of $-\ln \tau_b$.

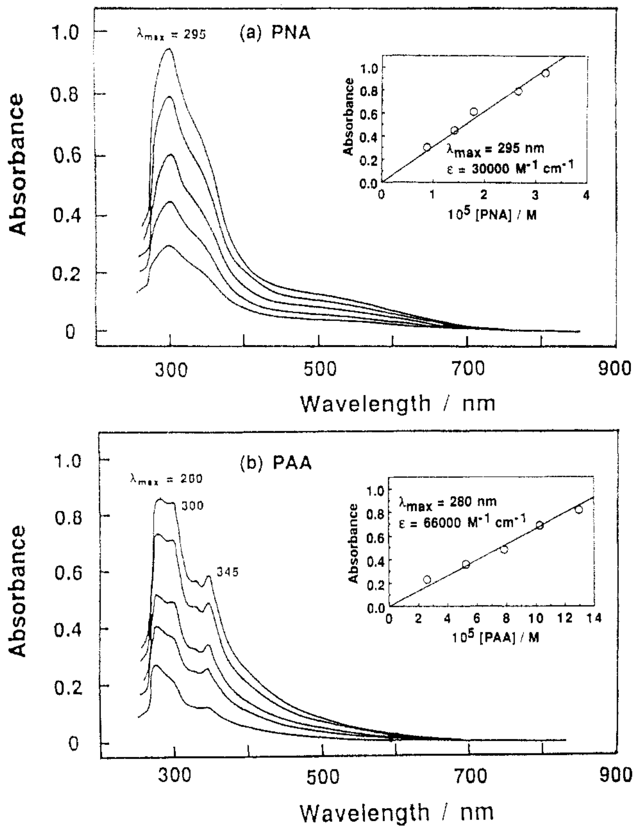


Figure 5. UV-visible spectra of poly(1-aminonaphthalene) (PNA) and poly(1-aminoanthracene) (PAA) at various concentrations: (a) poly(1-aminonaphthalene); (b) poly(1-aminoanthracene). Insets: Change of the absorbance at λ_{max} = 295 nm (a) and λ_{max} = 280 nm (b) at the various concentrations.

PNA shows only one absorption band (λ_{max} = 295 nm) in the UV-visible region. The absorbance at 295 nm at each concentration {molarity calculated on the basis of the sum of the molecular weight of the repeating unit of the oxidized form ($m;n$ = 1:1 in eq 1, $C_{40}H_{26}N_4$)} is 0.3 (0.89 × 10^{-5} M), 0.45 (1.42 × 10^{-5} M), 0.61 (1.78 × 10^{-5} M), 0.79 (2.66 × 10^{-5} M), and 0.95 (3.19 × 10^{-5} M), respectively. The molar absorption coefficient of PNA at 295 nm is determined as about 30 000 M^{-1} cm^{-1} for the molarity calculated on the basis of the molecular weight of ($C_{40}H_{26}N_4$). The tail absorption in the visible region may be due to some impurity or the presence of irregular structure(s) in the polymer chain, and it is considerably weaker for PNA prepared in the presence of CH_3OH (*cf.* Experimental Section). A cast film of PNA prepared in the presence of CH_3OH (no. 2 in Table I) shows a higher transparency in the visible region than a cast film of PNA prepared in the absence of methanol.

Addition of benzoyl peroxide (BPO) to the solution of PNA causes no observable change in its UV–vis spectrum in contrast to an immediate and profound change of the UV–vis spectrum observed on addition of peroxides to the solution of polyaniline. In the case of polyaniline, addition of peroxides like BPO leads to the instant deep change of its UV–visible spectrum due to the abstraction of the N–H hydrogens by the peroxides.[6b,c,29]

PAA shows several absorption bands in the UV region without any distinct absorption band in the visible region, similarly to PNA. The absorbance at 280 nm of PAA is 0.23 (2.61 × 10^{-6} M), 0.36 (5.23 × 10^{-6} M), 0.48 (7.87 × 10^{-6} M), 0.69 (1.03 × 10^{-5} M), and 0.82 (1.30 × 10^{-5} M), respectively, at each molar concentration {molarity calculated on the basis of the sum of the molecular weight of the repeating unit (m:n = 1:1 in eq 2, $C_{56}H_{34}N_4$)} given in parentheses. The molar absorpion coefficient of PAA at 280 nm is determined as about 66 000 M^{-1} cm^{-1}.

Table IV. Electrical Conductivity (σ) of Poly(1-aminonaphthalene) (PNA) and Poly(1-aminoanthracene) (PAA)

	conductivity,[a] S/cm		
	non[b]	HCl[c]	I_2[d]
PNA	1.7 × 10^{-6}	3.8 × 10^{-4}	1.1 × 10^{-3}
PAA	1.6 × 10^{-4}		1.5 × 10^{-3}

[a] Conductivity (σ) was measured with pressed pellets using a two-probe method. [b] Nondoped. [c] HCl doping with 0.2 M HCl solution (aqueous). [d] I_2 doping with I_2 vapors at the vapor pressure of I_2.

The absorption band of PNA reduced by the hydrazine monohydrate shows a similar absorption spectrum; however, the λ_{max} is shifted to a longer wavelength by about 30 nm (λ_{max} = 300–330 nm).

Both the NMP solutions of PNA and PAA show a relatively weak absorption band in the near infrared area (λ_{max} = 1930 and 1580 nm, respectively), which may be due to a coupling of two unidentified vibrations in the IR region. Such an absorption band in the near infrared region is not observed in the NMP solution of PNA reduced by hydrazine monohydrate as well as emeraldine base and leucoemeraldine polyanilines.

Conductivity values are presented in Table IV. PNA and PAA themselves show semiconductivity without doping; the σ values for PNA and PAA are 1.7 × 10^{-6} and 1.6 × 10^{-4} S cm^{-1}, respectively. The electrical conductivity (σ) of PNA is raised to 3.8 × 10^{-4} and 1.1 × 10^{-3} S cm^{-1} by doping with 0.2 M HCl and I_2, respectively.

PNA and PAA have a good thermal stability. The weight loss started at about 300 °C for both polymers, and at 900 °C PNA and PAA show about 72% and 78% residual weights, respectively, under N_2.

Polymerization Mechanism. It is generally accepted that the H_2O_2–Fe redox system generates radical species such as $HO^{\bullet}$ and $HOO^{\bullet}$.[6b,c,19] Therefore, it seems reasonable to assume that the present polymerization proceeds through the hydrogen absorption of the NH_2 group of the aromatic amine $Ar{-}NH_2$ by the radical species and the ensuing attack of the $ArNH^{\bullet}$ radical on another amine to give a coupling species. One of the other plausible mechanisms involves electron transfer from the monomer to the Fe(III) species generated in the redox system to afford a cation radical $ArNH_2^{\bullet+}$, which is expected to undergo coupling with $ArNH_2$.

At the moment, we do not have evidence to support or exclude the two mechanisms shown above. However, that both the present chemical oxidation process and the previously reported electrochemical process[21b] give PNA showing essentially the same IR spectrum suggests that the latter mechanism involving electron transfer as the first step is more plausible, since the electrochemical polymerization is considered to involve the electron transfer from the monomer.

Conclusion

Poly(1-aminonaphthalene) and poly(1-aminoanthracene) have been synthesized by chemical oxidative polymerization using the H_2O_2–Fe catalyst system in high yield. The obtained polymers show good solubility to polar organic solvent and high thermal stability. The large degree of depolarization (ρ_v = 0.33) in NMP indicates that they take a linear and stiff structure in solution. ^1H NMR spectroscopy reveals the presence of the NH hydrogen exchangeable with water in DMSO on the NMR time scale.

They exhibit no observable absorption peak in the visible region and have certain electrical conductivity.

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