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Synthesis and characterization of novel self doping water soluble polynaphthylamines

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Abstract

The oxidative polymerization of 5-amino-1-naphthyloxy acetic acid, 5-amino-1-naphthyloxydifluro acetic acid and 3-(5-aminonaphthyloxy)-1-propanesulfonic acid was achieved with reasonable yield (30–56%), and modest electrical conductivity (10^{-4}–10^{-5} S/cm). The sodium salts of the polymers are soluble in water and exhibit fluorescence. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Water soluble; Self doping; Polynapthylamines

1. Introduction

Conjugated polymers with benzenoid and heterocyclic units have recently received greater attention as electrically conducting materials. Polyaniline is a unique electroactive polymer because of its good electrical conductivity (10^2 S/cm) and wide range of potential applications [1]. These have been hampered somewhat due to poor solubility of the acid doped material and the evolution of dopant under conditions of elevated temperature and humidity. A strategy to overcome this deficiency involves introducing side chains bearing strong acid functionality on to the polymer chain [2,3]. This resulted in lowering of electrical conductivity (10^{-2}–10^{-8} S/cm) but improved solubility in water. A similar, but relatively unexplored series of polymers are the polynaphthylamines [4–6]. We have reported earlier the synthesis and characterization of water-soluble poly (5-aminonaphthalene-2-sulfonic acid) [7]. The polymer exhibited fluorescence with modest conductivity (10^{-3}–10^{-5} S/cm). In the present investigation we report the synthesis and characterization of poly (5-amino-1-naphthyloxy acetic acid) (**P1**), poly (5-amino-1-naphthyloxydifluroacetic acid (**P2**) and poly 3-(5-aminonaphthyloxy)-1-propanesulphonic acid (**P3**) (Scheme 1). These water-soluble polymers exhibit fluorescence and moderate conductivity after exposure to iodine vapors (10^{-4}–10^{-5} S/cm). The aqueous methanolic solutions of **P1**, **P2** and **P3** were used for casting thin films on to ITO glass.

2. Experimental

5-Amino-1-napthol, chloroacetic acid, sodium chlorodifluroacetate (Aldrich), 1,3 propane sultone (Aldrich) and distilled acetic anhydride were used for the monomer preparation. Sodium persulfate (BDH) was used as received. The electrical conductivity of the polymer was measured on a four-point resistivity probe connected to a Keithley voltmeter and constant-current source. The samples were in the form of compacted disk pellets of ~0.033–0.035 cm in thickness. Conductivities were calculated from the average readings taken on both sides of the pellet. A Waters GPC unit fitted with 410 Refractometer detector and Ultrahydrogel column (500×10 μm) was used for molecular weight analysis against PEG and PEO standards. XPS spectra were collected using a Kratos XSAM 800 Surface Analyzer with non-monochromated 1486.6 eV Al Kα X-ray emission at 10 kV and 20 mA. A pass energy of 20 eV was set with a 2 mm slit width and 1.0 eV resolution. Survey scans were run from 0 to 600 eV with 1.0 eV step size and 100 ms dwell time for three accumulations. Detail scans of C1s, O1s, N1s were run with 0.3 eV steps at 300 ms dwell times, accumulating 20 scans for Carbon & Oxygen and 60 scans for Nitrogen. Chamber pressure was kept at ~10^{-9} Torr.

The polymer was subjected to oxidative thermal degradation on a Dupont Thermal Analyzer with a TGA 2950 Thermogravimetric analyzer. The analysis was carried out from room temperature to 800 °C at a linear heating rate of 10 °/min with a dynamic airflow of 75 cm^3/min. A fine powder of 2.0 mg was used for the analysis.

Thickness of polymer films was measured using an

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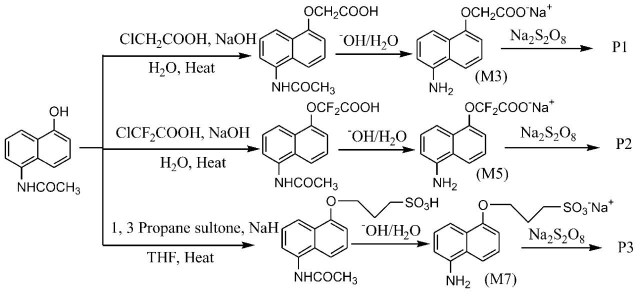

Scheme 1.

Alpha-step 200 fitted with a high power video microscope. The fluorescence experiment was performed on a Perkin Elmer L S 50 B model Luminescence spectrophotometer. An aqueous solution of the polymer (10^{-4} M) and quinine sulfate of similar strength in 0.1 M sulfuric acid (reference solution) was used for the experiment.

*2.1. Preparation of 5-acetylamino-1-naphthol (**M1**)*

5-Amino-1-napthol (10 g, 62.8 mmol) was agitated in a mixture of glacial acetic acid (10 ml) and freshly distilled acetic anhydride (6.5 g, 63.7 mmol) at room temperature for 30 min. The product crystallized out from the reaction mixture and was filtered and washed with plenty of chilled water followed by chilled ethanol. The crude product was recrystallized from hot ethanol to yield 9.4 g (75%) of the title compound. mp 187–188 °C dec. [8].

^{1}H NMR (200 MHz, DMSO-d_6): δ 10.13 (s, 1H, OH), δ 9.78 (s, 1H, –NH), δ 8.01–6.87 (m, 6H, Ar), δ 3.16 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 24.21, 108.85, 113.91, 119.84, 122.58, 124.65, 126.00, 126.84, 129.86, 134.08, 154.04, 169.52. FTIR (KBr): 3439, 3335, 1741, 1664, 1517, 1413, 1365, 1340, 1273, 1222, 1093, 1044, 794 cm^{-1}.

*2.1.1. Preparation of 5-aminoacetyl-1-naphthyloxy acetic acid (**M2**)*

Recrystallized **M1** (10 g, 49.75 mmol) was mixed with monochloroacetic acid (5.87 g, 62.4 mmol) and NaOH (4.58 g, 114 mmol) in water (50 ml) and refluxed for 12 h to provide a clear solution. The reaction mixture was cooled to room temperature and acidified with 1 M HCl to provide a dark brown precipitate. The precipitate was filtered and washed with plenty of water to remove all inorganic salts and dried under high vacuum to yield 10.5 g (81%) of the crude product. This material was dissolved in dilute sodium bicarbonate solution and washed with ether. The aqueous layer was acidified to pH 2.5–3.0 to yield brownish black precipitate. The product was dried under high vacuum to provide 9.2 g (72%) of the title compound, mp 223–224 °C dec.

^{1}H NMR (200 MHz, DMSO-d_6): δ 9.92 (s, 1H, –NH), δ 8.13–6.91 (s, 6H, Ar), δ 4.92 (s, 3H, $-CH_3$), δ 2.20 (s, 2H, $-CH_2$); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 24.21, 65.73, 106.15, 116.15, 119.52, 123.01, 125.60, 126.44, 129.57, 134.19, 154.04, 169.67, 170.68; FTIR (KBr): 3439, 3335, 1741, 1654, 1517, 1413, 1340, 1365, 1273, 1222, 1093, 794 cm^{-1}; λ_{max} (DMSO) 368.5, 445.3, 547.7 nm; Anal. Calcd for $C_{14}H_{12}NO_4Na$: C, 59.78; H, 4.27; N, 4.98. Found: C, 60.86; H, 5.67; N, 4.77.

*2.1.2. Preparation of 5-amino-1-naphthyloxy acetic acid (**M3**)*

Recrystallized **M2** (10 g, 38.61 mmol) was refluxed with sodium hydroxide (3.08 g, 77 mmol) in deionized water (20 ml) for 4 h. The reaction mixture was cooled to room temperature and acidified with 1 M HCl to pH 3 to yield 7.5 g (91%) of the title compound, mp 207 °C dec.

^{1}H NMR (200 MHz, DMSO-d_6): δ 7.66–6.68 (m, 6H, Ar), δ 4.81 (s, 2H, $-CH_2$); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 65.62, 105.68, 109.10, 110.05, 115.80, 124.11, 124.40, 126.69, 144.97, 153.97, 170.83; FTIR (KBr): 3365, 2568, 1587, 1517, 1439, 1273, 1148, 1128, 1078 cm^{-1}; λ_{max} (DMSO): 362.1, 537.1 nm; Anal. Calcd for $C_{12}H_{11}NO_3$ (HCl): C, 56.80; H, 4.33; N, 5.52. Found: C, 56.23; H, 5.19; N, 5.10.

*2.1.3. Preparation of 5-aminoacetyl-1-naphthyloxy difluroacetic acid (**M4**)*

M1 (10 g, 49.75 mmol) was mixed with potassium hydroxide (2.8 g, 49.99 mmol) and sodium chlorodifluoroacetate (14.1 g, 92.48 mmol) in water (50 ml) and refluxed for 12 h. The reaction mixture was cooled to room temperature and acidified with 1 M HCl to yield 5.4 g (36%) of the crude compound. This was dissolved in dilute sodium bicarbonate solution and washed with ether. The aqueous layer was acidified with 1 M HCl to pH 3.0 to yield 4.8 g of the material. This product was recrystallized from hot water to yield 4.2 g (29%) of the title compound, mp 203 °C dec.

^{1}H NMR (200 MHz, DMSO-d_6) δ 10.03 (s, 1H, –NH), δ 8.08–7.45 (m, 6H, Ar), δ 2.21 (s, 1H, $-CH_2$); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 110.67, 110.99, 115.58, 117.22, 121.26, 124.11, 125.09, 128.18, 143.52, 145.96, 161.62 (triplet); λ_{max} (DMSO) 368.5, 414.4, 537.1 nm. FTIR (KBr): 3328, 1749, 1598, 1531, 1399, 1288, 1192, 1063, 787 cm^{-1}; Anal. Calcd for $C_{14}H_{11}NO_4F_2$: C, 56.94; H, 3.72; N, 4.74. Found: C, 57.01; H, 3.66; N, 4.24.

*2.1.4. Preparation of 5-amino-1-naphthyloxy difluoroacetic acid (**M5**)*

M4 was (2.0 g, 6.7 mmol) was refluxed with potassium hydroxide (1 g, 17.8 mmol) for 12 h to provide a clear solution. The reaction mixture was cooled to room temperature and acidified with 1 M HCl. The pH of the reaction mixture was adjusted to 3.0 and cooled to 0–5 °C to yield 1.51 g (88%) of the title compound, mp 225 °C dec.

^{1}H NMR (200 MHz, DMSO-d_6): δ 8.04–6.86 (m, 6H, Ar); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 110.67, 110.99, 115.58, 117.22, 121.26, 124.11, 124.11, 125.09, 128.18, 128.69, 143.52, 145.96, 161.62 (triplet); FTIR (KBr):

3415, 2295, 1730, 1593, 1525, 1433, 1214, 1100, 1063, 787 cm^{-1}; λ_{max} (DMSO): 303.5 nm; Anal. Calcd for $C_{12}H_{10}NO_3F_2Cl$ (HCl): C, 46.94; H, 3.45; N, 4.83. Found: C, 46.52; H, 3.99; N, 4.48.

*2.1.5. Preparation of 3-(5-acetylaminonaphthyloxy)-1-propane sulphonic acid (**M6**)*

Dry 5-acetylamino-1-napthol (5.0 g, 24.8 mmol) was mixed with sodium hydride (0.6 g, 25 mmol) and dry THF (50 ml) and cooled to 10 °C. The reaction mixture was agitated for 30 min. 1,3-Propanesultone (3.83 g, 31.35 mmol) dissolved in dry THF (20 ml) was added dropwise to the reaction mixture which was then refluxed for 12 h to provide a suspension. This suspension was cooled to the room temperature and toluene (50 ml) was added. The reaction was cooled to 5 °C and filtered. The wet cake was washed with toluene (2 × 25 ml) to yield 6.6 g of the sodium salt of the title compound (77.6%). This compound was dissolved in water and 1 M HCl was added to adjust the pH to ~2.0. The reaction mixture was concentrated to obtain a dark brown powder. This dark brown powder was sonicated in methanol and filtered to remove all of the inorganic impurities. The filtrate was concentrated to yield 4.95 g (80%) of the title compound. mp 275–277 °C dec.

^{1}H NMR (DMSO-d_6): δ 9.87 (s, 1H, –NH), δ 6.94–8.02 (m, 6H, Ar), δ 4.24 (t, 2H, $-CH_2$), δ 2.65 (t, 2H, $-CH_2$), δ 2.11–2.16 (m, 5H, $-CH_2$ and $-CH_3$); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 24.21, 26.07, 48.86, 67.84, 105.97, 115.36, 119.23, 122.72, 125.38, 126.44, 126.62, 129.42, 134.23, 154.84, 169.52; FTIR (KBr): 3255, 1592, 1528, 1404, 1361, 1269, 1141, 1021, 982, 914, 861, 773 cm^1; λ_{max} (DMSO): 300.3, 218.1 nm; Anal. Calcd for $C_{15}H_{17}NO_5S$: C, 55.72; H, 5.26; N, 4.33. Found: C, 54.84; H, 4.55; N, 3.47.

*2.1.6. Synthesis of 3-(5-aminonaphthyloxy)-1-propane sulphonic acid (**M7**)*

Sodium 3-(5-acetylaminonaphthyloxy)-1-propane sulphonate (3.0 g, 8.6 mmol) was refluxed with 5 M KOH (20 ml) for 2 h. The reaction mixture was cooled to room temperature and acidified with 1 M HCl and then further cooled to 5 °C for maximum precipitation. The product was filtered and washed with chilled water followed by ethanol. The brown powder was dried under dynamic vacuum for 4 h to yield 1.4 g (60%) of the title compound. mp 333–334 °C.

^{1}H NMR (D_2O): δ 7.59–6.71 (m, 6H, Ar), δ 4.01 (t, 2H, $-CH_2$), δ 3.00 (t, 2H, $-CH_2$), δ 2.13 (dt, 2H, $-CH_2$); ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 24.68, 48.43, 67.22, 97.23, 106.63, 111.98, 113.11, 114.16, 125.16, 125.67, 126.40, 141.99, 154.30; FTIR (KBr): 3476, 2892, 2634, 1612, 1587, 1513, 1476, 1428, 1395, 1332, 1277, 1037, 779, 698, 606, 551, 521 cm^{-1}; λ_{max} (H_2O) 313.1, 22.4 nm; Anal. Calcd for $C_{15}H_{15}NO_4S$ (HCl): C, 50.70; H, 4.39; N, 4.09; S, 10.01. Found: C, 49.15; H, 6.01; N, 4.33; S, 9.65.

*2.1.7. Polymerization of **M3***

M3 (10.0 g, 46.08 mmol) was dissolved in aqueous sodium bicarbonate (0.46 M, 10 ml) and cooled to 5 °C. Ammonium persulfate (12.73 g, 55.7 mmol) dissolved in deionized water (25 ml) was added dropwise over an interval of 30 min. The temperature of the reaction mixture was maintained at 25 °C for 24 h. The reaction mixture was filtered and washed with sufficient water and ethanol to remove all of the oligomeric impurities to yield 7.0 g of the crude polymer. The polymer was dissolved in aqueous sodium bicarbonate and dialyzed using a cellulose acetate membrane with a molecular weight cut off range of 1000 g/mol. Dialysis was continued for several hours with repeated water changes. The sodium salt of the polymer was acidified with 1 M HCl and redialyzed to remove any residual inorganic salts. The water was evaporated to yield 3.2 g (32%) of **P1**.

FTIR (KBr): 3444, 1733, 1584, 1508, 1404, 186, 1106, 757, 618 cm^{-1}; λ_{max} (DMSO): 215, 374.9, 594.7 nm; Anal. Calcd for $C_{12}H_{10}NO_3$; Found: $C_{12}H_{10.02}N_{0.8}$.

*2.1.8. Polymerization of **M5***

M5 (1.5 g, 5.9 mmol) was dissolved in aqueous sodium bicarbonate (0.59 M, 10 ml) and cooled to 5 °C. Sodium persulfate (1.76 g, 7.3 mmol) in water (10 ml) was added over a period of 30 min. The reaction mixture was agitated at room temperature for 12 h and filtered to yield black powder of **P2**. The wet cake was washed several times with water and ethanol to remove all of the oligomeric material. The crude polymer was purified by dialysis in a cellulose acetate bag (molecular weight cut-off of 1000 g/mol). The purified polymer was acidified with 1 M HCl and redialyzed to remove all the inorganic salt. The water was evaporated to yield 0.45 g (30%) of **P2**.

FTIR (KBr): 3380, 1764, 1658, 1529, 1406, 1150, 763 cm^{-1}; λ_{max} (DMSO): 277, 366, 536 nm; Anal. Calcd for $C_{12}H_8N_1O_3$; Found: $C_{12}H_{8.5}N_{0.76}$.

*2.1.9. Polymerization of **M7***

M7 (5.0 g, 17.76 mmol) was dissolved in aqueous sodium bicarbonate (0.89 M, 20 ml) and cooled to 0–5 °C. Sodium persulfate (5.16 g, 21.68 mmol) in deionized water (10 ml) was added dropwise over a period of 30 min. The temperature of the reaction mixture was maintained at 25 °C for 36 h. When the required time had elapsed, the reaction mixture was acidified with 1 M HCl. The reaction mixture was transferred to a cellulose acetate dialysis bag (Molecular weight cut-off of 1000 g/mol) and dialyzed for several hours with repeated changing of the water. The solution was evaporated to yield 2.8 g (56%) of doped **P3**.

FTIR (KBr): 3424, 2922, 1576, 1509, 1447, 1417, 1177, 1037, 787, 739, 602, 521 cm^{-1}; λ_{max} (H_2O): 211, 362, 570.1 nm; Anal. Calcd for $C_{13}H_{15}N_1O_4S_1$; Found: $C_{15.99}H_{19.68}N_1S_{1.02}$.

Table 1
UV–Vis data for **P1**, **P2** and **P3**

Polymers	π–π^* (nm)	Polaron band (nm)
P1	215	594.7
P2	277	536.0
P3	211	570.1

Table 2
GPC peak parameters for **P1**, **P2** and **P3**

Polymers	Peak parameters				
	M_n	M_p	M_w	PD	σ (S/cm)
P1	67,294	78,896	71,841	1.06	2.2×10^{-5}
P2	24,229	28,279	26,689	1.10	4.3×10^{-5}
P3	4813	4774	5164	1.07	2.4×10^{-4}

Table 3
Deconvolution data for the C1s component of **P1**, **P2** and **P3**

Polymers	BE (eV)	Assignments	FWHM	Area (%)
P1	284.9	C–C, C–H	2.1	83.62
	285.9	C–N, C=N	2.1	3.87
	286.5	C–O, C=O	2.1	8.31
	287.9	C–N$^+$	2.1	4.18
P2	285	C–C, C–H	2.3	80.5
	286.7	C–N, C=N	2.2	10.15
	288.2	C–O, C–N$^+$	2.2	9.12
P3	284.98	C–C, C–H	2.1	85.66
	286.5	C–N, C=N	2.1	14.26

Table 4
Surface and bulk stoichiometries of **P1**, **P2** and **P3**

Polymers	Bulk stoichiometry	Surface stoichiometry
P1 ($C_{12}H_9N_1O_3$)	$C_{12}H_{10.02}N_{0.8}$	$C_{19.2}N_1O_{6.4}$
P2 ($C_{12}H_8N_1O_3F_2$)	$C_{12}H_{8.5}N_{0.76}$	$C_{21}N_1O_{5.1}F_{2.3}$
P3 ($C_{13}H_{15}N_1O_4S_1$)	$C_{15.99}H_{19.68}N_1S_{1.02}$	$C_{21}N_1O_{6.1}N_1S_{1.45}$

Table 5
Thermal degradation data for **P1**, **P2** and **P3**

Polymers	Temperature range (%Weight loss)		
P1	45–144 (7.6)	144–374 (20.9)	374–560 (62.5)
P2	41–165 (9.6)	165–363 (19.5)	363–612 (52.3)
P3	41–193 (9.6)	193–362 (24.07)	362–587 (59.89)

Table 6
λ_{max} and quantum yield (φ) of **P1**, **P2** and **P3**

Polymers	Fluorescence λ_{max}	Quantum yield (φ)
P1	398	0.09
P2	387	0.15
P3	405	0.389

3. Results and discussion

Polymerization of **M3**, **M5** and **M7** yielded polymers **P1**, **P2** and **P3**, respectively, with reasonable yield (30–56%) and modest conductivity (10^{-4}–10^{-5} S/cm). **P3** as made and the sodium salt of **P1** and **P2** were soluble in water. The UV–Vis absorption frequencies of the polymers are listed in Table 1.

The π–π^* absorption represents the conjugation present in the polymer chain. The absorption values are shifted towards higher energy presumably due to the twisting of the polymer chain [9]. The polaron bands has also shown hypsochromic shift and the λ_{max} values are comparable with other self doping polymers. The FTIR spectra gave the characteristic absorption bands for the quinoidal (1658–1576 cm^{-1}) and benzenoid (1509–1404 cm^{-1}) stretching frequencies [10]. Molecular weight of the polymers was determined by GPC analysis (Table 2).

XPS spectroscopy was used to identify the different carbon environments present in the polymer. The C1s spectrum was deconvoluted into different components. The details are listed in Table 3.

The components with binding energy 287.9 and 288.2 eV in **P1** and **P2** indicate the presence of charged nitrogen species in the polymer chain [11].

Comparative data for the surface and bulk stoichiometry is listed in Table 4.

The carbon content in the surface stoichiometry was high due to hydrocarbon contamination, which is a common phenomenon in XPS analysis. The high oxygen content could be due to the bonded water or residual oxidant trapped in the polymer matrix.

The thermal stability of the polymers in air were studied (Table 5). The initial loss in mass is due to the evolution of bonded water or organic solvent. The second loss in mass is consistent with the liberation of side chain from the polymer backbone. The third loss in mass is the oxidative thermal degradation of the polymer chain.

The polymers were found to be more stable than HCl doped polyaniline. A plausible reason for this is the electrostatic attraction between the side chain and polaronic nitrogen species in adjacent polymer chains.

Dilute solutions of the polymers (10^{-4} M) were used for fluorescence measurements. Quinine sulfate of similar strength was used as the reference [12] (Table 6).

Aqueous, methanolic solutions of the polymer were used for casting thin films on ITO glass. Films of thickness 40–60 nm were obtained and the formation of the film was confirmed by UV–Vis spectrometry.

4. Conclusions

Novel naphthylamine polymers have been obtained in reasonable yield with modest conductivity. They, or their sodium salts, were soluble in water. All of the polymers exhibited a better thermal stability than polyaniline. The polymers exhibited fluorescence and could be cast as thin films on ITO glass.

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