

Chemical Oxidative Polymerization of 4-Amino-3-Hydroxynaphthalene-1-Sulfonic Acid and its Salts

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Abstract. New functional homopolymeric, semiconducting materials soluble in polar solvents, were synthesized by chemical oxidative polymerization of 4-amino-3-hydroxynaphthalene-1sulfonic acid (AHNSA) and its salts, using ammonium peroxydisulfate as an oxidant, in water at room temperature. Polymerization products obtained from AHNSA, AHNSA hydrochloride, AHNSA mono-sodium salt and AHNSA di-sodium salt were characterized by elemental analysis, gel-permeation chromatography (GPC), infrared spectroscopy (IR) and conductivity measurements. Polymers of AHNSA salts have increased weight-average molecular weights and polydispersity index values, compared to AHNSA polymer. Molecular weights approach a maximum value of ~25200 for polymers of AHNSA salts. Elemental analysis data of polymeric samples show a decrease of the S/C ratio for all polymeric materials in comparison with the monomer, indicating considerable elimination of sulfonic acid group from the macromolecular structure during the polymerization process. New substitution patterns shown by IR spectroscopic analysis combined with MNDO-PM3 semi-empirical quantum mechanical calculations revealed N-C coupling reactions as dominant, where C belongs to unsubstituted AHNSA ring. Coupling mode N-C1 is also important. Naphthoquinonoid and benzenoid structures were observed by IR spectroscopy. Influence of pH on the AHNSA oxidative chemical polymerization mechanism was examined.

Introduction

Polymers of 1-aminonaphthalene and its derivatives have received increasing attention in the last decade. They have been proposed as materials for corrosion protection [1], pH sensors [2], or electrochromic devices [3]. The particularity of 4-amino-3-hydroxynaphthalene-1-sulfonic acid as a monomer stems from the presence of three functional groups $-NH_2$, -OH and $-SO_3H$, and the fact that *para*-position and both *ortho*-positions to amino group are blocked for known polymerization pathways of aromatic amines. To our best knowledge, there is no report relating to the chemical oxidative preparation of AHNSA homopolymer. Copolymer of AHNSA and aniline was studied [4]. Recently, we have performed electropolymerization of AHNSA-Na salt in aqueous solution [5]. The aim of the present work was to investigate the possibility of AHNSA homopolymer preparation in aqueous solution by standard chemical oxidative polymerization mechanism, as well as on molecular-weight distribution, vibrational spectroscopic characteristics, conductivity and solubility of obtained novel polymeric materials. Particular attention was paid to the determination of

preferential coupling reactions between AHNSA monomer units, especially to the ratio of amine versus phenol oxidative polymerization route.

Experimental

The monomer, 4-amino-3-hydroxynaphthalene-1-sulfonic acid (AHNSA) (Lachema, p.a.), and the oxidant, ammonium peroxydisulfate (Centrohem, p.a.) were used without further purification. Chemical polymerization of AHNSA and its salts was performed in water at room temperature, using the oxidant/monomer molar ratio of 1.25 in all polymerization procedures. The sample polyAHNSA was synthesized by addition of the oxidant solution (2.85 g, 12.5 mmol of (NH₄)₂S₂O₈ dissolved in 25 ml of distilled water) to the monomer suspension (2.39 g, 10.0 mmol of AHNSA suspended in 25 ml of distilled water) under stirring (Scheme 1, 2). The sample poly(AHNSA-HCl) 1 was prepared by pouring, under stirring, the oxidant solution (2.85 g, 12.5 mmol of $(NH_4)_2S_2O_8$ dissolved in 25 ml 1M HCl) in the suspension of 2.39 g, 10.0 mmol AHNSA in 25 ml 1M HCl. Preparation of the sample poly(AHNSA-Na), from *in-situ* synthesized AHNSA mono-sodium salt as the monomer 4, was performed by addition of the oxidant solution (2.39 g, 10.5 mmol of $(NH_4)_2S_2O_8$ dissolved in 5 ml distilled water) to the solution containing 2.0 g, 8.4 mmol AHNSA dissolved in 83.6 ml 0.1 M NaOH. Polymer sample poly(AHNSA-Na₂) was prepared using *in-situ* synthesized AHNSA di-sodium salt as the monomer 5, by addition of the oxidant solution (2.85 g, 12.5 mmol of (NH₄)₂S₂O₈ in 30 ml distilled water) to the solution of 2.39 g, 10.0 mmol AHNSA dissolved in 20 ml 1M NaOH. These reaction mixtures were left under stirring at room temperature for 7 days and after this time were filtered. The precipitated black polymer powders were washed with distilled water and dried in vacua for 2 h at 80 °C.



Scheme 1 Acid-base transformations of AHNSA (2), its dipolar zwitter-ion form (3), AHNSA-HCl (1), AHNSA-Na (4) and AHNSA-Na₂ (5).

Molecular weights of polymer samples were assessed by gel permeation chromatography using a 500 x 8 mm Labio GM 1000 column operating with *N*-methyl-2-pyrrolidone and calibrated with polystyrene standards, using toluene as an internal standard. Spectrophotometric detection at a wavelength of 436 nm was carried out. The samples for GPC measurements were prepared by dissolving 10 mg of polymeric sample in 5 ml *N*-methyl-2-pyrrolidone containing 100 mg triethanolamine to deprotonate the sample and improve its solubility. The mobile phase, *N*-methyl-2-pyrrolidone, contained 0.5 % LiBr to prevent aggregation. The flow rate was 1 ml min⁻¹. GPC data were treated by CSW1.7 software and GPC for Win.

For conductivity measurements, polymeric samples were pressed into pellets, 10 mm in diameter and 1 mm thick, under a pressure of 124 MPa using a hydraulic pellet press. The conductivity was measured between stainless pistons, at room temperature, by means of an ac bridge (Waynne Kerr Universal Bridge B 224), at fixed frequency of 1.0 kHz. During the measurement, pressure was maintained at the mentioned value.

The computational method used here to obtain the molecular orbitals, ionization energy, heat of formation, charges and spin density of the species considered is semiempirical MNDO-PM3 model (included in MOPAC package version 7.01) with full geometry optimization, taking into account solvation in water (using COSMO facility). For the molecular structures, we have used the restricted Hartree-Fock method (RHF) and the unrestricted Hartree-Fock (UHF) method for the radical species.

IR spectra of the monomer and synthesized polymers were recorded in the range of $250 - 4000 \text{ cm}^{-1}$ using an IR spectrophotometer Perkin Elmer 983 G. Powdered samples were dispersed in KBr and compressed into pellets.

Results and Discussion

The values of the peak, weight-average and number-average molecular weights, M_p , M_w and M_n , respectively, together with the polydispersity index (M_w/M_n) for prepared AHNSA polymers are summarized in Table 1. All synthesized polymers were found to be polydisperse. The polydispersity index (PDI) have a minimum value of 1.7 for the polyAHNSA, compared to other samples, which have similar polydispersity values of ~2.7. Bimodal molecular weight distribution (MWD) is observed for the polyAHNSA (Fig. 1(a)), containing negligible proportion of low molecular weight parts (dimers to pentamers). Main peaks on MWD of this sample correspond to ~10-mers and ~27-mers, while the number of repeating units in chains approaches a maximum value of ~85. Poly(AHNSA-HCl) has MWD with three distinct main peaks (Fig. 1(b)). The lowest molecular weight peak corresponds to tetramers and pentamers, middle peak to ~14-mers and third peak to the chains with about 35 repeating units. Molecular weight of poly(AHNSA-HCl) approaches a maximum value of ~25200, corresponding to ~100 repeating units. Poly(AHNSA-Na) and poly(AHNSA-Na₂) have mutually very similar MWDs, which are broad with a low molecular weight tail (Fig. 1 (c) and (d)). The highest peak corresponds to the chains containing ~35 repeating units. Molecular weight a maximum value of ~25200.

Table 1 Summary of the peak, weight-average and number-average molecular weights and polydispersity for different AHNSA polymers.

Polymer sample	M _p	M _n	$M_{\rm w}$	M_w / M_n
PolyAHNSA	2490	2750	4670	1.7
Poly(AHNSA-HCl)	8540	2290	6190	2.7
Poly(AHNSA-Na)	9410	2850	7460	2.6
Poly(AHNSA-Na ₂)	9440	2460	7040	2.9

Polymerization of AHNSA salts, which are more water-soluble than AHNSA, is more efficient and leads to polymers with higher M_w and M_p values. Higher polydispersity of poly(AHNSA-salts) compared to polyAHNSA indicates more complex mechanism of salts polymerization.



Fig. 1 Molecular weight distributions of samples: (a) polyAHNSA, (b) poly(AHNSA-HCl), (c) poly(AHNSA-Na) and (d) poly(AHNSA-Na₂), determined by GPC.

Elemental content (wt. %)			t. %)	Polymer sample	Conductivity	Yield
Ν	С	Η	S		$(S cm^{-1})$	(%)
5.85	50.20	3.79	13.40	PolyAHNSA	1.9×10^{-6}	53
4.14	52.48	4.32	6.78	Poly(AHNSA-HCl)	1.3×10^{-5}	31
2.74	54.90	4.09	5.94	Poly(AHNSA-Na)	3.3×10^{-7}	61
3.49	51.14	4.28	7.26	Poly(AHNSA-Na ₂)	4.1×10^{-7}	49
3.35	50.65	4.34	7.02			
	Elem N 5.85 4.14 2.74 3.49 3.35	Elemental con N C 5.85 50.20 4.14 52.48 2.74 54.90 3.49 51.14 3.35 50.65	Elemental content (wNCH5.8550.203.794.1452.484.322.7454.904.093.4951.144.283.3550.654.34	Elemental content (wt. %)NCHS5.8550.203.7913.404.1452.484.326.782.7454.904.095.943.4951.144.287.263.3550.654.347.02	Elemental content (wt. %) Polymer sample N C H S 5.85 50.20 3.79 13.40 PolyAHNSA 4.14 52.48 4.32 6.78 Poly(AHNSA-HCl) 2.74 54.90 4.09 5.94 Poly(AHNSA-Na) 3.49 51.14 4.28 7.26 Poly(AHNSA-Na2)	Polymer sampleConductivityNCHSConductivity 5.85 50.20 3.79 13.40 PolyAHNSA 1.9×10^{-6} 4.14 52.48 4.32 6.78 Poly(AHNSA-HCl) 1.3×10^{-5} 2.74 54.90 4.09 5.94 Poly(AHNSA-Na) 3.3×10^{-7} 3.49 51.14 4.28 7.26 Poly(AHNSA-Na2) 4.1×10^{-7}

Table 2 Elemental composition of polyAHNSA and polymers of AHNSA salts.

Table 3 Conductivity and polymerization yield for polyAHNSA and polymers of AHNSA salts.

By the elemental analysis considerable decrease of the ratio S/C has been found for all polymer materials in comparison with the monomer (Table 2). This observation can be explained by the elimination of AHNSA sulfonic group during the polymerization process. Also, the reduced content ratio N/C is determined for all polymeric samples and compared to AHNSA. This nitrogen elimination is due to hydrolysis of terminal imine bonds and the formation of C=O group.

The electrical conductivity of polymeric products was of the order $10^{-5}-10^{-7}$ S cm⁻¹ (Table 3). Poly(AHNSA-HCl) sample exhibits the highest conductivity. All polymer samples show excellent solubility in dimethylsulfoxide, *N*,*N*-dimethyl-formamide, *N*-methyl-2-pyrrolidone and good solubility in ethanol.



Fig. 2 IR spectra of AHNSA, polyAHNSA, poly(AHNSA-HCl), poly(AHNSA-Na) and poly(AHNSA-Na₂).

In the IR spectra of all polymers (Fig. 2), several new bands are observed in the "substitution pattern" region 965–650 cm⁻¹. Appearance of these new aromatic C-H outof-plane deformation vibration bands [6-8] suggests the formation of a new substitution pattern(s) on naphthalene rings in the process of polymerization. New substitution pattern with three adjacent H is attributable to the bands at 762 and 800 cm⁻¹, while substitution type with one isolated H and two adjacent H corresponds to the bands at 840, 864 and 906 cm^{-1} [6–8]. This means that coupling reactions occurred on the monomer nucleus that was originally without functional groups. The bands at ~1477, 1511, 1527, 1587, 1622 cm⁻¹ are associated with C₆H₄ ring stretching in polymers [6–8].

The new band at ~1511 cm⁻¹ may also originates from C—N—H bending vibration of secondary aromatic amine [9]. It can be seen that the band at 1588 cm⁻¹ is significantly stronger than that at 1527 cm⁻¹ in the poly(AHNSA-HCl) spectrum, by comparison with spectra of other polymers where these two bands have almost equal intensities. The bands at 1588 and 1527 cm⁻¹ can be attributed to the stretching of naphtho-quinonoid and naphtho-benzenoid units, respectively, indicating an increased amount of naphtho-quinonoid units in poly(AHNSA-HCl) comparing with other polymers. In all polymer spectra a new bands at 1635 cm⁻¹ may be assigned to the C=N stretching vibration and is relatively the strongest for poly(AHNSA-HCl) [6–8]. The new band at 1670 cm⁻¹ is due to the C=O group in naphtho-quinonoid units of polymers [6], the feature good correlated with the reduced content of N in all polymers. The relative intensity of the band at 1670 cm⁻¹ is the highest for poly(AHNSA-HCl), which is consistent with its smallest content of N and previous indications about the highest amount of quinonoid units in this sample. The strong band at 1218 cm⁻¹ in the monomer spectrum, corresponding to C—O stretching vibration of phenols, [6] also appears in all polymer spectra, but is blue-shifted from ~1222 and 1215 cm⁻¹ for polyAHNSA

and poly(AHNSA-HCl), respectively, to 1228 and 1229 cm⁻¹ in poly(AHNSA-Na₂) and poly(AHNSA-Na) spectra, respectively. This shift suggests the formation of ether bond showing the aryl-ether C—O—C asymmetric stretch absorbtion at ~1230 cm⁻¹ [6]. The intensity of bands at 700 and 638 cm⁻¹, corresponding to S—O and C—S stretching vibrations related to SO₃⁻ group attached to the aromatic ring [6] significantly decreases in spectra of polymers comparing to monomer, indicating elimination of sulfonic group during polymerization. In the region 3600-2500 cm⁻¹, the bands due to N—H stretching vibrations and O—H stretching in phenol occurred [6,9]. A very broad peak centered at ~3419 cm⁻¹ in poly(AHNSA-Na₂) spectra, is due to N—H stretching vibration of sulfonic of primary amine N—H stretching vibration of secondary amine with possible contribution of primary amine N—H stretch (existing in terminal units). The broad band centered at ~3200 cm⁻¹ is attributable to hydrogen-bonded O—H and N—H stretching, with possible participation of N—H⁺ stretching in NH₄⁺ ion [6,9].



Fig. 3 Ionization energy, E_i , heat of formation, H_f , charge distribution of hydrated AHNSA molecular species and spin density distribution of AHNSA radical species.

Scheme 2 N– C_1 coupling reaction of AHNSA anion and its radical, followed by elimination of sulfonic group.

MNDO-PM3 semiempirical quantum chemical calculations (Fig. 3) show that AHNSA exists mainly as a dipolar zwitterion form in water. Oxidability of AHNSA, expressed by ionization potentials of hydrated AHNSA molecular species, increases with increasing pH. Based on spin density data for AHNSA radical species at different pH it can be concluded that oxidation via phenolic -OH becomes important only at higher pH. However, contrary to the conclusions of other authors oxidative polymerization regarding of aminonaphtholes, it has been found that even in basic aqueous solutions polymerization of AHNSA proceeds mainly through the oxidation of the -NH₂ group. Taking into account charge distribution in AHNSA at different pH, it can be stated that the dominant coupling reaction between formed radical and starting monomer in the whole pH range is N-C where C belongs to unsubstituted naphthalene ring. Coupling reaction N–C₁ is also important leading thus to the sulfonic group elimination (Scheme 2).



IR spectroscopic results combined with MNDO-PM3 quantum chemical calculations reveal that the structure of produced polymeric materials is a mixture of naphtho-iminoquinonoid and naphthobenzenoid forms of $N-C_1$, $N-C_5$, $N-C_6$, $N-C_7$, and $N-C_8$ dimer units (Fig. 4). Chemical

oxidative polymerization course *via* naphthol –OH, yielding poly(naphthalene oxide) structure, is important only for AHNSA-Na₂ salt.



Fig. 4 Proposed macromolecular structure of poly(AHNSA) with main coupling modes and redox forms.

Conclusion

Novel homopolymers of AHNSA and its salts AHNSA-HCl, AHNSA-Na and AHNSA-Na₂, soluble in polar solvents, are obtained by standard chemical oxidative polymerization route. The use of AHNSA salts, instead of AHNSA, leads to the polymeric materials with higher M_w , M_p , and PDI values. The conductivity of AHNSA polymers was in the range 10^{-5} - 10^{-7} S cm⁻¹, poly(AHNSA-HCl) showing the highest value of 1.3×10^{-5} S cm⁻¹. Semiconducting polymers of AHNSA and its salts can be of particular interest for potential applications as antistatic materials. IR spectra and elemental analysis combined with MNDO-PM3 quantum chemical calculations revealed that the polymerization proceeds mainly through the oxidation of the amino group in the studied pH range, accompanied by considerable elimination of sulfonic group. The resulting functional polymers represent polynaphthylamine-like structures with naphtho-iminoquinonoide and benzenoide N–C₁, N–C₅ N–C₆, N–C₇, and N–C₈ dimer units, bearing free –OH and sulfonic groups in the chains.

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